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FERROELECTRIC TERPOLYMERS, BASED ON SEMICRYSTALLINE VDF/TRFE/CHLORO-CONTAINING TERMONOMERS: SYNTHESIS, ELECTRICAL PROPERTIES, AND FUNCTIONALIZATION REACTIONS

A Thesis in

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by

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Abstract

In the past decades, many researches have devoted their efforts related to PVDF and VDF/TrFE copolymers to the general goal of reducing the Curie temperature, narrowing the polarization hysteresis loop, and generating a large electromechanical response at ambient temperature. The direct correlation between reduced polar domain size and lower energy barrier, shown in ferroelectric ceramic materials, led to many attempts to alter copolymer morphology. The methods include mechanical deformation, electron irradiation, uniaxial drawing, and crystallization under high pressure or high electric field. By using these physical methods, many shortfalls have been addressed such as the limitation of the processability of the material, the instability of the crystal phase, the extremely high electric field in the strain measurement.

In this thesis, a new chemical method is performs, by incorporating the small amount (~7 mol %) of the chloro-containing termonomers, including chlorotrifluoroethylene (CTFE), 1,1 and 1,2-chloro-fluoroethylene (CFE), 1-chloro-2,2-difluoro ethylene (CDFE), into VDF/TrFE copolymer chains. Along with this study, we also synthesize a functional fluoropolymer that contains the functional group on either one end or both ends, and their diblock or triblock copolymers. The long term objective is to utilize these reactive functional groups to connect fluoropolymer with other materials to further improve the electrical properties of the terpolymers.

A novel polymerization method involves a combination of a low temperature borane/oxygen initiator and a bulk polymerization process. This process allows the thorough mixing of all monomers during the terpolymerization reaction, resulting in the homogeneous distribution of the termonomer units in the polymer chain. A chloro-containing

termonomers, especially CDFE and CTFE, having comparative reactivity ratios with VDF and TrFE, lead to terpolymers with relatively narrow molecular weight and composition distributions. The homogeneous incorporation of the chloro-containing termonomers in the VDF/TrFE copolymer chain is crucial in modifying its polymer chain conformation and crystal structure. With ~7 mol% of the termonomer units, the copolymer alters its crystalline phase from the ferroelectric β phase (all-trans conformation) toward another ferroelectric γ phase $(tttg^+tttg^-$ conformation), without significant reduction of the overall crystallinity. The new ferroelectric γ phase of the terpolymer, with shorter trans-sequence and smaller crystalline domains, reduces the Curie phase transition temperature since it has a much smaller energy barrier for phase transition. The unique combination in this new ferroelectric γ phase, with a small energy barrier and the large unit expansion or contraction during the crystal phase transition, results in high electromechanical response and behaves like a ferroelectric relaxor. The terpolymer shows high dielectric constant, as high as 100, with narrow hysteresis and high field-induced longitudinal strain (up to 4-5% at 150 MV/m) at ambient temperature.

For the functionalization of fluoropolymer, the telechelic VDF/TrFE/chlorocontaining terpolymers having functional (polar and reactive) terminal groups, and triblock copolymers containing a VDF/TrFE/chloro-containing terpolymer and functional polymers was developed. These telechelic and block polymers not only provide interactive properties but also preserve the existing desirable properties due to the undisturbed polymer backbone. Two chemical methods have been studied, including (i) the use of functional borane/oxygen initiators that carry functional groups and exhibit living radical polymerization mechanism, and (ii) the investigation of an improved iodine transfer polymerization (ITP) method to

prepare telechelic fluoropolymers containing two terminal iodine groups. The former method although has some advantages in terms of ease and high purity of the polymer with the desirable reactive functional groups such as acetyl (can be converted to hydroxy group), silane and bromine groups, the polymerization yield is not very high due to the intramolecular interaction between the boron atom and the functional groups. The latter method, the iodine transfer polymerization (ITP), provides a very effective method with high yield, good catalyst efficiency, and well-defined telechelic polymer structure with two reactive terminal iodine functional groups on both chain ends. The chemistry involved an improved iodine transfer polymerization process using the combination of the AIBN imitator and a diiodo-compound chain transfer agent. Both initiation systems also show a living radical polymerization characteristic leading to the well-defined polymer with narrow molecular weight and composition distribution. The living characteristic was demonstrated by the block copolymerization of the terpolymer with the non-fluoropolymer (such as the PMMA homopolymer), or the fluoropolymer (including the PVDF homopolymer and the VDF/TrFE copolymer). The material from the latter case is very useful in terms of the improvement of the mechanical strength of the terpolymer.

Table o	of Co	ntents
---------	-------	--------

List of Tabl	es xii
List of Figu	res xiv
List of syml	polsxxi
Acknowled	gementsxxii
Chapter 1	Introduction1
1.1	Background1
1.2	Definition of Piezo-, Pyro-, and ferroelectricity
1.3	Piezoelectric parameters
	1.3.1 Piezoelectric <i>d</i> constant
	1.3.2 Piezoelectric <i>g</i> constant
	1.3.3 Filed related and charge related electrostrictive coefficient
	1.3.4 Electromechanical coupling factor <i>K</i>
	1.3.5 Acoustic impedance Z
1.4	Conventional piezoelectric polymers: PVDF and its copolymers
	1.4.1 Poly (vinylidene fluoride) PVDF
	1.4.2 Poly(vinylidene fluoride-trifluoroethylene) copolymer14
	1.4.3 Poly(vinylidene fluoride-tetrafluoroethylene) copolymer18
	1.4.4 Other ferroelectric polymers19
1.5	Applications
1.6	Objective and scope of the research
1.7	References
Chapter 2	Functionalization of fluoropolymers42

2.1	Introduction	42
2.2	Homo- and Co-polymerization of fluoropolymers	
2.3	Synthesis of functionalized fluoropolymers	
	2.3.1 Copolymerization of the fluorinated monomer with funct	tional
	comonomers	45
	2.3.2 Functionalization of fluoropolymers by functional initiat	ors47
	2.3.3 Funtionalization of fluoropolymers by iodine transfer	
	polymerization	
2.4	Applications of functional fluoropolymers	51
2.5	Research objective in functional fluoropolymers	53
2.6	References	55
Chapter 3	New family of ferroelectric terpolymers based on VDF/TrFE/c	chloro-
Chapter 3 containing	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization	e hloro- 58
Chapter 3 containing 3.1	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction	2 hloro- 58 58
Chapter 3 containing 3.1 3.2	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental	e hloro-
Chapter 3 containing 3.1 3.2	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals	2 hloro- 58
Chapter 3 containing 3.1 3.2	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer	e hloro-
Chapter 3 containing 3.1 3.2	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer 3.2.3 Polymer characterization	2 hloro-
Chapter 3 containing 3.1 3.2 3.3	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer 3.2.3 Polymer characterization Results and discussion	2 hloro-
Chapter 3 containing 3.1 3.2 3.3	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer 3.2.3 Polymer characterization Results and discussion 3.3.1 Synthesis of terpolymers	2 hloro-
Chapter 3 containing 3.1 3.2 3.3	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer 3.2.3 Polymer characterization Results and discussion	:hloro-
Chapter 3 containing 3.1 3.2 3.3	New family of ferroelectric terpolymers based on VDF/TrFE/c termonomers: synthesis and characterization Introduction Experimental 3.2.1 Chemicals 3.2.2 Polymerization of terpolymer 3.2.3 Polymer characterization 3.3.1 Synthesis of terpolymers 3.3.2 Thermal properties 3.3.3 Molecular and crystal structure	 hloro-

3.5	Referen	nces	95
Chapter 4	New far	nily of ferroelectric terpolymers based on VDF/TrFE/chloro-	
containing	termono	mer: Mechanical and electrical properties	97
4.1	Backgro	und	97
4.2	Experim	nental	98
	4.2.1	Materials	98
	4.2.2	Instrumentation	98
4.3	Results	and discussions	99
	4.3.1	Mechanical properties	99
	4.3.2	Electrical properties	101
4.4	Conclus	ion	125
4.5	Referen	ces	.126
Chapter 5	Functio	nal fluoropolymers: synthesis and characterization	. 127
5.1	Backgro	und	127
5.2	Experim	nental	129
	5.2.1	Materials	.129
	5.2.2	Synthesis of the functional Borane initiator	.130
	5.2.3	Synthesis of the functional low temperature initiators	.130
	5.2.4	Polymerization initiated b functional borane initiator	131
	5.2.5	Polymerization initiated by functional low temperature initiator .	131
	5.2.6	Polymerization initiated by hydrogen peroxide	132
	5.2.7	Polymerization initiated by AIBN/diiodide system	132
	500	Synthesis of block construmen containing D(VDE/UED) and MMA	133

Chapter 6	Conclus	ion and suggestion for future work176
5.5	Reference	ce175
5.4	Conclus	ion174
	5.3.4	Electrical properties of functional fluoropolymers171
		groups by AIBN/diio-compound157
	5.3.3	Synthesis of telechelic fluoropolymers having two terminal iodine
		Initiator147
	5.3.2	Synthesis of telechelic fluoropolymers by functional peroxide
		initiator129
	5.3.1	Synthesis of functional fluoropolymers by functional borane
5.3	Results a	and discussions129
	5.2.10	Characterization of polymer initiated by functional initiators134
		terpolymer and PVDF homopolymer134
	5.2.9	Synthesis of block copolymer containing P(VDF/TrFE/CTFE)

List of Tables

1.1	Typical physical, piezoelectric, and pyroelectric properties of various materials9
2.1	Commercial products of the copolymerization of the fluorinated monomers and non-
	fluorinated monomers
2.2	e and Q values of fluorinated monomer (from ref 5)
2.3	e and Q values of non-fluorinated monomer (from ref 5)
2.4	Functional fluorinated and non-fluorinated comonomers 46
3.1	A summary of VDF/TrFE/CTFE terpolymers produced by
	borane/oxygen initiator71
3.2	Summary of the VDF/TrFE/BrTFE terpolymers (B series) with different termonomer
	concentrations compared with the VDF/TrFE/CTFE (A series) 44
3.3	A summary of the VDF/TrFE/CTFE terpolymers with various VDF/TrFE mole
	fraction and with the CTFE content that shift the Curie temperature to about room
	temperature
3.4	Comparison of the % crystallinity of VDF/TrFE/CTFE terpolymers from WAXD,
	crystallized at different temperatures
3.5	Summarized of the lmella thickness at ambient temperature of the VDF/TrFE/CTFE
	terpolymers crystallized at their optimum conditions compared with the VDF/trFE
	copolymers
4.1	summary of mechanical testing of VDF/TrFE/CTFE terpolymers in the order of
	ascending VDF content
4.2	A summary of electric properties of terpolymers that consist of VDF/TrFE and
	several termonomers

4.3	Summary of the field induced strain of several terpolymers containing
	VDF, TrFE and chloro-fluoromonomer including CTFE, CDFE, VC and CFE
	at different field
5.1	Summary of the copolymers prepared by using the functional borane initiators140
5.2	Summary of the P(VDF/HFP-b-MMA) diblock polymers prepared by controlling the polymerization time of the MMA
5.3	Summary of the polymerization results by three low temperature peroxide
	initiators
5.4	Summary of the VDF/HFP copolymers (A) and the VDF/TrFE/CTFE terpolymers (B)
	prepared by the H ₂ O ₂ initiator
5.5	Summary of the VDF/TrFE/CTFE terpolymers initiated by AIBN/ α , ω -
	diiodoperfluorobutane160
5.6	Summary of the VDF/TrFE/CTFE -b-VDF copolymers165
5.7	Summary of the triblock copolymers having a P(VDF/TrFE/CTFE) center block and
	two P(VDF/TrFE) end blocks (Set 1) or two P(VDF/TrFE/CTFE) end blocks
	(Set 2)
5.8	Summary of the thermal and the electrical properties of the telechelic
	VDF/TrFE/CTFE terpolymers prepared by various initiator systems

List of Figures

1.1	(Left) Schematic depiction of the two most common chain conformations in PVDF :
	(a) tg+tg and (b) all-trans. (Right). Unit cells of (a) α -phase, (b) δ -phase, and (c) β -
	phase of PVDF in projection parallel to the chain axis
1.2	The D-E hysteresis loops of PVDF at various electric fields
1.3	The thermal transition temperatures in VDF/TrFE copolymers
1.4	All-trans conformation of odd-numbered and even-numbered nylons. Arrows
	indicates the dipole direction
3.1	The incorporated comonomer content in the polymer chain vs. the comonomer feed
	raio in the copolymerization reaction with VDF
3.2	Kelen and Tüdõs plot for VDF/CDFE copolymer
3.3	(a) Intrinsic viscosity of VDF/TrFE/CTFE terpolymer vs monomer conversion and
	(b) GPC curves of three VDF/TrFE/CTFE terpolymers prepared by borane/oxygen
	initiator at various polymerization reaction times: (a) 4, (b) 7, and (c) 10 h 68
3.4	¹ H NMR of typical terpolymer (a) VDF/TrFE/CTFE terpolymer (b)
	VDF/TrFE/CDFE terpolymer (c) VDF/TrFE/CFE terpolymer and (d) VDF/TrFE/VC
	terpolymer
3.5	DSC comparison of VDF/TrFE with various terpolymers of similar ter-monomer
	contents (a) 55/45 copolymer, (b) 53.8/38.8/7.4 (sample F-2), (c) 62.4/29.8/7.8
	(sample D-2), (d) 58.3/34.7/7.0 (sample C-2), (e) 62.5/30.9/6.6 (sample B-3), (f)
	59.3/32.9/7.8 (sample A-3), and (g) 63.1/29.9/7.0 (sample G-4) 72
3.6	DSC curve of the VDF/TrFE/BrTFE (a) sample B-1, (b) sample B-2, and (c) sample
	B-3

- 3.9 DSC comparison of VDF/TrFE/CFE terpolymers with various CFE contents and the VDF/TrFE (55/45) copolymer (a) 55/45 VDF/TrFE copolymer, (b) 65.3/31.4/3.3 (sample E-1), (c) 65.5/30.8/3.7 (sample E-2) and (d) 63.9/30.1/6.0 (sample E-3) ... 78

3.14	FTIR spectra of VDF/TrFE/CDFE terpolymers of different CDFE contents
	comparing with VDF/TrFE copolymer (a) 55/45 VDF/TrFE copolymer, (b)
	63.6/31.4/5.0 (sample B-1), (c) 64.5/30.2/5.3(sample B-2) and 62.5/30.9/6.6 (sample
	B-3)
3.15	FTIR spectra of temperature dependence of 59.3/32.9/7.8 VDF/TrFE/CTFE
	terpolymer (sample 8) (a) heating cycle and (b) cooling cycle
3.16	FTIR spectra of temperature dependence of 63.6/31.4/5.0 VDF/TrFE/CDFE
	terpolymer (sample B-1)
3.17	Typical WAXD spectra of VDF/TrFE/CTFE terpolymer films, (a) 55.6/36.1/8.3, (b)
	72.2/17.8/10/0, and (c) 61.4/25.3/13.3
3.18	Crystalline fraction as a function of temperature of the 66.0/22.5/11.5
	VDF/TrFE/CTFE terpolymer (sample A-7) crystallized at different crystallization
	temperatures (after Dr. Edward Balizer)
3.19	Temperature dependence of lattice spacing of the 66.0/22.5/11.5 VDF/TrFE/CTFE
	terpolymer crystallized at different crystallization temperatures (after Dr. Edward
3 20	Balizer)
5.20	7) crystallized at different crystallization temperatures as a function of temperature
	(after Dr. Edward Balizer)
4.1	Shows mechanical three testing curves of VDF/TrFE/CTFE (60.0/32.5/7.5)
	terpolymer
4.2	The comparison of polarization hysteresis loops between two VDF/TrFE/CTFE
	terpolymers (sample) and VDF/TrFE (55/45 mole ratios) copolymer103
4.3	The dependence of the coercive field (Ec) on the CTFE ter monomer units
	incorporated in VDF/TrFE copolymer chain103

4.4	Comparison of the polarization hysteresis loop of VDF/TrFE/CDFE with different	ıt
	termonomer concentrations	105
4.5	The comparison of the polarization hysteresis loops of VDF/TrFE and several	
	termonomers including CTFE, CDFE, 1,1-CFE and VC	105
4.6	The temperature dependence of polarization hysteresis loop of 57.3/31.2/11.5	
	VDF/TrFE/CTFE terpolymer (sample A-4)	107
4.7	The comparison of polarization hysteresis loop of VDF/TrFE/CTFE terpolymer	
	(sample) with different post treatments, without annealing,	
	annealing and stretching	108
4.8	The comparison of several polarization hysteresis loops of VDF/TrFE/CTFE	
	terpolymers with different VDF content	109
4.9	Plots of the polarization (maximun) and the coercieve field as a function of the V	DF
	concentration in VDF/TrFE/CTFE terpolymers	110
4.10	Typical dielectric constant cuves of the terpolymers that consist of about 7 mol%	
	termonomers including CTFE, CDFE, VC, and CFE during heating (open symbol	ls)
	and cooling cycle (filled symbols), (a) 59.3/32.9/7.8 VDF/TrFE/CTFE, (b)	
	62.5/30.9/6.6 VDF/TrFE/CDFE, (c) 58.3/34.7/7.0 VDF/TrFE/VC and (d)	
	VDF/TrFE/1,2-CFE1	11
4.11	Shows the dependence of the dielectric constant and the Curie temperature on the	;
	frequency1	13
4.12	A typical dielectric relaxation of the terpolymers, (a) VDF/TrFE/CTFE and (b)	
	VDF/TrFE/CDFE terpolymers1	14

- 4.13 Comparison of the dielectri constant at 1 kHz of terpolymers that compose of 60/40 VDF/TrFE and 7mol% terpolymers including CTFE, CDFE, 1,2-CFE and VC .. 115

- 4.22 Electrostrictive relation between strain and polarization square measured at electric field from 0-100 MV/m of the VDF/TrFE/CTFE terpolymers (66.0/22.5/11.5) ...125
- 5.1 11 B NMR spectra of several functional borane initiators (a) B(CH₂CH₂CH₂

	$SiCl(CH_3)_2)_3$, (b) $B(CH_2CH(CH_3)CH_2Cl)_3$, (c) $B(CH_2CH_2CH_2CH_2OAc)_3$, and (d) the
	partially oxidized B(CH ₂ CH ₂ CH ₂ SiCl(CH ₃) ₂)138
5.2	Two typical ¹ H NMR spectra of the polymer produced by functional borane initiators
	(a) VDF/TrFE/CTFE terpolymer produced by B(CH ₂ CH ₂ CH ₂ SiCl(CH ₃) ₂) ₃ initiator, and
	(b) VDF/HFP copolymer produced by B(CH ₂ CH(CH ₃)CH ₂ Cl) ₃ initiator139
5.3	Shows plots of monomer conversion vs. average weight of the VDF/HFP copolymer
	initiated by the $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$ and the $B(CH_2CH(CH_3)CH_2Cl)_3$,
	respectively
5.4	¹ H NMR spectra of three polymer fractions (a) the PMMA homopolymer fraction, (b)
	the P(VDF/HFP-b-MMA) diblock copolymer fraction, and (c) the unblocked
	P(VDF/HFP) fraction
5.5	GPC curves of (a) P(VDF/HFP-b-MMA) fraction and (b) PVDF homopolymer
	fraction
5.6	¹ H NMR spectra of P(VDF/HFP-b-MMA) block copolymers with different
	polymerization time (a) 2 h, (b) 5 h, and (c) 12 h, during MMA polymerization146
5.7	Infrared spectra of polymers synthesized by the functional initiator (Br-
	CH ₂ CH ₂ OC(=O)O-) ₂ , and (CH ₂ =CHOC(=O)O-) ₂ .149
5.8	¹ HNMR spectra of polymers initiated by different catalysts (a) by the (Br-CH ₂ CH ₂ -
	$OC(O)O_2$ sample (A-2), and (b) by the $(CH_2=CHCH_2OC(O)O_2)$ sample B-1150
5.9	¹ HNMR spectra of the VDF/HFP copolymers initiated by various [H ₂ O ₂]/[monomer]
	initiator concentrations, (a) = 30% , (b) = 20% , (c) = 10% and (d) = 5% 152
5.10	Infrared spectra of VDF/HFP copolymers (A-1, A-3, and A-4 in Table 5.4) initiated
	by hydrogen peroxide at various concentrations153
5.11	¹ HNMR spectra of several VDF/TrFE/CTFE terpolymers (B-2, B-3, and B-4) with
	different initiator concentrations (a) $[H_2O_2]/[monomer] = 5\%$, (b) 2%, and
	(c) 0.4%
5.12	The relationship of the number average molecular weight and the monomer
	conversion

5.13	¹⁹ F NMR spectra of several VDF/TrFE/CTFE terpolymers with different chain
	transfer agent concentrations (a) 0.8×10^{-3} mol, (b) 2.2×10^{-3} mol and (c) 4.4×10^{-3}
	mol162
5.14	¹ H NMR spectra of VDF/TrFE/CTFE terpolymers initiated by AIBN/I(CF ₂) ₂ I with
	$I(CF_2)_2I$ concentrations (a) 0.8 x 10 ⁻³ mol, (b) 2.2 x 10 ⁻³ mol and (c) 4.4 x 10 ⁻³
	mol163
5.15	Comparison of DSC curves of (a) VDF/TrFE/CTFE terpolymer (the starting polymer)
	and three triblock copolymers of PVDF-b-P(VDF/TrFE/CTFE)-b-PVDF prepared
	with different reaction times, (b) 5 h., (c) 10 h., (d) 24 h., and (e) PVDF
	homopolymer165
5.16	DSC curve comparison among two P(VDF/TrFE)-b-P(VDF/TrFE/CTFE)-b-
	P(VDF/TrFE) triblock copolymers including (b) 1/1 and (c) 2/1 mole ratios between
	P(VDF/TrFE/CTFE) and P(VDF/TrFE) blocks and the corresponding (a) VDF/TrFE
	(55/45) copolymer and (d) VDF/TrFE/CTFE terpolymer168
5.17	DSC comparison of two solution blended samples including (b) $1/1$ and (c) $2/1$ mole
	ratios between P(VDF/TrFE/CTFE) terpolymer and P(VDF/TrFE) copolymer and the
	corresponding (a) VDF/TrFE (55/45) copolymer and (d) VDF/TrFE/CTFE
	terpolymer168
5.18	GPC curve comparison of the triblock copolymers (a) center block, (b) 1 st block, (c)
	3 rd block, and (d) 4 th block169
5.19	GPC curve comparison of the VDF/TrFE/CTFE terpolymer (a) before block, and (b)
	after block170
5.20	DSC comparison of two VDF/TrFE/CTFE terpolymers (a) before and (b) after chain
	extension170
5.21	Dielectric constant of the telechelic VDF/TrFE/CTFE terpolymers prepared by (a)
	functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo
	compounds172
5.22	Polarization loops of the telechelic VDF/TrFE/CTFE terpolymers prepared by (a)
	functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo
	compounds173

xix

Lists of symbols

Х	Strain
D	Dielectric displacement
Е	Electric field
d, g, e	Piezoelectric coefficients
Х	Stress
S	Elastic compliance
8	Relative permittivity, dielectric constant
E ₀	Vacuum permittivity
M, Q	Electrostrictive coefficient
E _c	Coercive field
DK	Dielectric constant
Р	Dielectric polarization
Pr	Remanent polarization
Ps	Spontaneous polarization
P _{max}	Maximum polarization
k	Electromechanical coupling factor
Ζ	Acoustic impedance
ρ	Density
c	Elastic stiffness
Tc	Curie temperature
Tg	Glass transition temperature
T _m	Melting temperature
ΔH	Heat of fusion
r_1, r_2	Relative reactivity ratio
η	Intrinsic viscosity
M _n	mole average molecular weight
M_{w}	Weight average molecular weight
PDI	Polydispersity

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Chapter 1

Introduction

1.1 Background

The development of ferroelectric, piezoelectric, and magnetostrictive materials with high performance for such applications as electromechanical transducers, actuators, and sensors has generated a great deal of interest among scientists in recent decades. However, many traditional electroactive materials (piezoceramic and magnetostrictive materials) have been found to suffer from low strain response (<1%),¹ despite their high dielectric constant, low hysteresis, and fast speed. Developing new ferroelectric, piezoelectric, and magnetostrictive materials with high strain, high elastic density, and high electromechanical coupling has been a scientific and technological challenge.² Recently, polymeric materials have received more extensive attention as new ferroelectric or piezoelectric materials than current ceramic-based materials. Polymeric materials could offer many unique features, such as large strain without structure fatigue, light weight, low cost, great mechanical strength, easy processability into thin and flexible films of various shapes and sizes, and most importantly, flexible architecture design via molecular tailoring.³

In 1969, Kawai demonstrated the significant increase of piezoelectricity in poly(vinylidene fluoride),⁴ while pyroelectricity^{5,6} and ferroelectricity were reported in 1971. Since then, tremendous interest in the new field of ferroelectric polymers has occurred. The exploration of the chemistry, physics, and technology of poly(vinylidene fluoride) led to the search for other classes of novel ferroelectric polymers, such as its copolymers, odd-numbered polyimides, cyanopolymers, polyureas, polythioureas, biopolymers (including

polypeptides), and ferroelectric liquid crystal polymers. Some significant progress, both in new materials and better understanding in structure-property relationships, have been reported in last decade.

Despite many potential advantages, the overall development of ferroelectric polymers has been very slow. Most polymers have the disadvantages of low electric field sensitivity in terms of their dielectric constant, piezoelectric coefficient, and electromechanical coupling coefficient, which limit their use in electro-active applications. The most studied ferroelectric polymers are polyvinylidene difluoride (PVDF) and poly(vinylidene difluoride-cotrifluoroethylene) (VDF/TrFE) copolymers, due to strong dipole in C-F bonds. In PVDF case, the polymer chains are usually crystallized into a (non-polar) α -phase, it is necessary that polymer film be subjected to electrical poling to change to the desirable (ferroelectric) β phase. On the other hand, some VDF/TrFE copolymers spontaneously form ferroelectric phase. Unfortunately, the Curie temperature (Tc) of the copolymers, in which the ferroelectric phase changes to paraelectric phase and creates electro-mechanical response, is well-above ambient temperature, the lowest Tc is about 65°C in the composition VDF/TrFE=55/45 mole ratio. Due to the high Tc phase transition temperature, the electric responses are very low at ambient temperature.

It is both a scientific challenge and technological importance to design a new ferroelectric polymer that has a unique combination of properties, including high dielectric constant, large and fast electromechanical response at ambient temperature, good processability, and good mechanical properties. As will be discussed later in Chapter 3 and 5, we have prepared a new family of fluoropolymers, including fluoro-terpolymers, functional fluoropolymers, and block fluoropolymers, which show a very interesting combination of

physical properties. The study involves the development of new polymer chemistry to prepare fluoropolymers with high purities and well-controlled molecular structures, as well as understanding their structure-property relationships.

1.2 Definition of Piezo-, Pyro-, and Ferroelectrics

It is well established that electrical properties such as piezoelectricity and pyroelectricity can only exist in materials lacking a center of symmetry. In fact, among the 32 classes of the crystal point symmetry group, only 20 can exhibit the piezoelectric and 10 for pyroelectric effect.⁷ A piezoelectric material is one that develops electric polarization only when mechanical stress is applied. Pyroelectric material possesses permanent polarity (spontaneous polarization), which not only responds to stress but also to temperature change. Pyroelectric crystals whose spontaneous polarization can be reversed by an external electric field are called ferroelectrics.

1.3 Piezoelectric parameters

1.3.1 Piezoelectric d constant

The magnitude of the induced strain x by the external field E or the dielectric displacement D by the stress X, is represented in terms of the piezoelectric d constant (an important parameter for acoustic applications)

$$x = dE \tag{1a}$$

$$D = dX \tag{1b}$$

The effect in Eq. (1b) is the direct piezoelectric where the induced charge is proportional to the mechanical stress, whereas the effect in Eq. (1a) is the conversely

piezoelectric effect. Extension of equation (1a) and (1b) with the linear elastic (hook's law) and dielectric equation, and writing in matrix notation form yields equation (2a) and (2b),

$$x_i = s_{ij}^E X_j + d_{mi} E_m$$
(2a)

$$D_m = d_{mi}X_i + \varepsilon_o \varepsilon_{mk}^X E_k \tag{2b}$$

Where s_{ij}^{E} is the elastic compliance, ε_{ik}^{X} is the dielectric constant, and i, j = 1,2,..6; m, k, = 1,2,3. The superscripts refer to the conditions under which these quantities are measured. That is, compliance is measured under constant electric field, and permittivity is measured under constant stress. ε_0 is the vacuum dielectric permittivity (=8.85×10⁻¹² F/m).

1.3.2 Piezoelectric g constant

The induced electric field E is related to an external stress X through the piezoelectric voltage constant g, which is an important parameter for sensor applications;

$$E = gX \tag{3}$$

Taking into account of D = dX, we obtained

$$g = \frac{d}{\varepsilon \varepsilon_0} \tag{4}$$

1.3.3 Field related and charge related electrostrictive coefficient

Generally, there are two phenomenologies used to describe the electric field induced strain: the electrostrictive and piezoelectric effects. The piezoelectric effect is a primary electromechanical coupling effect in which the strain is proportional to electric field (equation 1), whereas the electrostrictive effect is a secondary effect in which the strain is proportional to the square of electric field (this effect exists in any polymers). Electrostriction can be expressed as

$$x = ME^2 \tag{5}$$

$$x = QP^2 \tag{6}$$

Where $P = \varepsilon \varepsilon_0 E$ in the paraelectric phase, and $P = P_s + \varepsilon \varepsilon_0 E$ in the ferroelectric phase. The electric field related electrostrictive coefficient M and charge related electrostrictive coefficient Q are related to each other through $M = Q \varepsilon_0^2 \varepsilon^2$.

For isotropic polymer,

$$x_{33} = Q_{33}P^2$$
 and $x_{31} = Q_{31}P^2$ (7)

Where the two numbers in the subscripts refer to the electric field direction and the measured polarization direction, respectively. Therefore, x_{33} and x_{31} are strains parallel to and perpendicular to the polarization direction, known as longitudinal and transverse strains, respectively. For isotropic polymer, both experimental and theoretical data show that Q_{11} <0 and Q_{13} >0 and M_{33} <0 and M_{13} >0, hence the polymer will contract along the polarization direction as the polarization increases. In other words, the polymer will contract along the thickness direction and will expand along the film direction when an electric field is applied across the thickness.

It should be noted that most polymers exhibit non-linear dielectric behavior and deviate from Eq. (5) at high field, in which the field-induced strain will be saturated.

1.3.4 Electromechanical coupling factor k

The electromechanical coupling factor k is related to the conversion rate between electrical energy and mechanical energy; k^2 is the ratio of stored mechanical energy to input electrical energy, or the ratio of stored electrical energy to input mechanical energy.

When an electric field E is applied to piezoelectric material, k^2 can be calculated as

$$k^2 = d^2 / \varepsilon \varepsilon_0 s \tag{9}$$

There are many electromechanical coupling factors corresponding to the direction of the applied electric field and to the mechanical strain (or stress) direction. For instance, in cases where a polymer actuator is made with the electric field along the 3-direction, the mechanical coupling factor is longitudinal to the electromechanical coupling factor k_t , which can be related to the Eq. (9) as

$$k_t^2 = d_{33}^2 / \mathcal{E}_{33}^X \mathcal{E}_0 S_{33}^E \tag{10}$$

1.3.5 Acoustic impedance Z

The acoustic impedance Z is a parameter used for evaluating the acoustic energy transfer between two materials. It is defined as Z^2 = pressure/volume velocity. In solid material,

$$Z = \sqrt{\rho.c} \tag{11}$$

Where ρ is the density and c is the elastic stiffness of the material.

Polymer Piezoelectric/ferroelectrics fall into four classes: optical active polymers, poled polar polymers, ferroelectric polymers, and ceramic/polymer composites. The poling procedure involves the application of an external field to a ferroelectric to induce a cooperative alignment of constituent dipoles. Most polymers in the first group are biological materials, such as derivatives of cellulose, proteins, and synthetic polypeptides. The origin of piezoelectricity in these polymers is attributed to the internal rotation of the dipoles of asymmetric carbon atoms, which gives rise to the optical activity. The second class of piezoelectric polymers includes polyvinyl chloride (PVC), polyvinyl fluoride (PVF), polyacrylonitriles (PAN), odd numbered nylons, and copolymer of vinylidene cyanide. The piezoelectricity in these polymers is caused by the orientation of the dipoles in the polymer

chains, which are frozen during the poling process, whereas the piezoelectricity in the third class (ferroelectric polymers) originates from the orientation of spontaneous polarization of the polar domains. Polymers in this third group consist of copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) or tetrafluoroethylene (TFE), briefly reviewed in Section 1.4. Recently, other polymers were proved to show ferroelectric behavior such as copolymers of vinylidene cyanide, odd numbered nylons, and polyureas, in which piezoelectricity arises from the functional polar groups in the polymer molecules. In the fourth class (polymer/ceramic composites), the piezoelectric activity comes from the intrinsic piezoelectricity of ceramics. Physical properties of these composites can be controlled by the choice of the ferroelectric ceramics and the polymer matrix. They have a combination of high piezoelectric activity from the ferroelectric ceramics, and flexibility from the polymer matrix.

Table 1 compares the piezoelectric properties of the ferroelectric ceramics and polymers. The piezoelectric strain constant d_{31} of polymers is relatively low compared to that of ceramics. However, the piezoelectric voltage constant g_{31} is larger. In addition, polymers have a high electromechanical coupling factor and low acoustic impedance, which permit their use in ultrasonic transducer applications and medical instrumentation. The combination of these properties with their flexibility, lightweight, toughness, and availability in large area sheets has led to tremendous growth in the research on novel ferroelectric polymers.

	Density	Modulas	Piezoelectric constants			Pyroelectric	Dielectric	Coupling	Acoustic
Materials ^a	ρ	C_{11}	d_{31}	<i>e</i> ₃₁	<i>831</i>	constant	constant	factor	Impedance
	(g/cm^3)	(GN/m^2)	(pC/N)	(pC/N)	(mV-m/N)	$(\mu C/K-m^2)$	$(\boldsymbol{\varepsilon}_{r})$	<i>k</i> ₃₁	(Gg/m^2-s)
PVDF	1.78	1-3	20	6.0	174	30-40	10-15	0.1	2-3
P(VDF/TrFE)	≈1.9	1.2	15-30	2-3	100-160	30-40	15-30	0.2	
PVF	1.4	1	1			10			
PVC	1.5	4	1			1-3	3		
Nylon-11	1.1	1.5	3	6.2		3	4	0.1-0.15	
Nylon11/PVDF		2.3	41	109			13.8		
Laminate film									
P(VDCN/VAc)	1.2	4.5	6	2.7	169		4.5	0.06	
PTUFB						3.0	20-30		
PVDF/PZT	5.3	3.0	20	6.0	19		120	0.07	
Rubber/PZT	5.6	0.04	35	1.4	72		55	0.01	
POM/PZT	4.5	2.0	17	3.4	20		95	0.08	
Quartz	2.65	77.2	2	15.4	50		4.5	0.09	
PZT	7.5	83.3	110	920	10		1200	0.31	

 TABLE 1.1
 Typical physical, piezoelectric, and pyroelectric properties of various materials.

^a PVDF, poly(vinylidene fluoride); P(VDF/TrFE), poly(vinylidene fluoride-co-trifluoroethylene); PVF, polyvinyl fluoride; PVC, polyvinyl chloride; P(VDCN/Vac), poly(vinylidene cyanide-co-vinyl acetate); PTUFB, polyurea-formaldehyde; PZT, lead zirconate titanate.

1.4 Conventional Piezoelectric polymers: poly(vinlyidene fluoride) and its copolymers

1.4.1 Poly(vinylidene fluoride)

1.4.1.1 Synthesis

Poly(vinylidene fluoride) is commercially produced by free radical polymerization of 1,1-difluoroethylene (CH₂=CF₂) at high temperature (50-150°C) and high pressure (10-300 atm). The most common polymerization process is emulsion or suspension using water as a reaction medium. The catalysts used in these processes are either inorganic (persulfate) or organic peroxides. Since the monomer units of PVDF have a directionality (CH₂ denoted as "head" and CF₂ as "tail"), typically 5% of the monomer units enter the growing chain with a reverse orientation, leading to head-to-head and tail-to-tail defects. These defects cause a reduction of the average dipoles by 6-10%. Polymers with defect concentrations ranging from 0.2% to 23.5% have been synthesized, and the effect of defects on crystal structure has been studied.⁸⁻¹¹

1.4.1.2 Molecular and crystal structure

PVDF (-CH₂-CF₂-) has a chemical structure between those of PE (-CH₂CH₂-), and PTFE (-CF₂CF₂-). Unlike PTFE, which has a helical conformation due to the steric hindrance of the fluorine atom, or PE, which takes the most stable conformation (*all-trans* conformation due to low rotational barrier), PVDF can take several conformations. The three known conformations are tg^+tg^- , *all-trans*, and $tttg^+tttg^-$.¹²⁻¹⁴ The first two conformations are the most common and important ones, and are schematically drawn in Figure 1.



Figure 1.1 (Left). Schematic depiction of the two most common chain conformations in PVDF : (a) tg⁺tg and (b) *all-trans*. (Right). Unit cells of (a) α -phase, (b) δ -phase, and (c) β -phase of PVDF in projection parallel to the chain axis.

The C-F bond is a polar bond (dipole moment, μ = 6.4 x 10⁻³⁰ C-m), and contributes to the polar conformation. The *all-trans* conformation has the highest dipole moment (μ =7.0 x 10⁻³⁰ C-m/repeat) due to the alignment of all dipoles in the same direction. The $tg^+tg^$ conformation is also polar, but the net dipoles that are perpendicular and parallel to the chain are approximately the same, giving rise to lower net dipole.

The packing of these polar chains in crystal adopts several distinct morphologies in PVDF. The four known ones are the α , β , γ , and δ phases, which can easily be transformed into one another.¹⁵ The most common one is the α phase, which may be obtained by crystallization from the melt. As depicted in Figure 1.1, the unit cell of the α phase consists of two tg^+tg^- chain conformations whose dipole components normal to the chain are antiparallel

and neutral to each other. Thus the α phase is a nonpolar phase. The polar analog δ phase can be obtained by poling under a high electric field.¹⁶⁻¹⁸ The lattice dimensions of these two phases are essentially the same: a = 4.96 Å, b = 9.64 Å, and c = 4.96 Å.

The β -phase is the most highly polar and important phase, and is typically prepared by stretching polymer film at room temperature or by crystallization from the melt under high pressure¹⁹ or epitaxial technique.¹⁵ The unit cell of the β phase contains two *all-trans* chain conformations in orthorhombic symmetry with the lattice a = 8.58 Å, b = 4.91 Å, and c = 2.55 Å.^{20,21} The dipole components normal to the chain (b-axis) are parallel. Thus, this β phase is a polar phase that possesses spontaneous polarization and exhibits piezoelectricity as well as pyroelectricity.

The γ phase contains two $tttg^+tttg^-$ chain conformations that are packed in a polar fashion. It has unit cell dimensions of a = 4.96 Å, b = 9.58 Å, and c = 9.23 Å. This phase may be obtained by the crystallization of a molten sample at high temperature or solution cast from dimethylacetamide (DMA) or dimethylformamide (DMF).²²⁻²³

1.4.1.3 Morphology of PVDF

The crystallization of PVDF from the melt results in spherulitic morphologies in which the lamella stacks have a periodicity of about 10 nm and have no net dipoles. A number of papers have reported on the morphology of melt solidified PVDF.²⁴⁻²⁶ There are two types of spherulites grown from the melt at high temperature (up to 60°C). The most common is a spherulite from the nonpolar phase (α form), which is larger and has high birefringence and tightly spaced concentric bonding. The second type is smaller and has less birefringence, and comes from the γ phase.²⁷ The morphology of PVDF has recently been

investigated as a function of head-to-head defects²⁸ and crystallization temperature²⁹ for a wide range of temperatures.

1.4.1.4 Ferroelectricity and related properties of PVDF

Although β and δ phases are known to be polar since the components of their dipoles are arranged in the same direction, the β phase has stronger pyroelectric and piezoelectric coefficients than the other phase. Therefore, to obtain a useful PVDF as a transducer material, polymer film must be oriented and polarized. The orientation or stretching can be performed between the glass temperature (T_g) and melting temperature (T_m) by stretching polymer film to several times its original length. Poling can be accomplished either at room temperature with a high electric field³⁰ or at high temperature with a low field. For conventional thermal poling, polymer film is stretched, annealed, electroded on both surfaces, and subjected to an electric field of about 0.5 MV/cm at high temperature (80-100°C), followed by cooling in the presence of the applied field. Other methods of poling include corona discharge, plasma, and poling during orientation.

For many years, there was debate over the origins of the piezoelectric and pyroelectric properties in PVDF.^{31,32} The arguments seem to have reached the conclusion that the properties primarily arise from the dipole orientation, rather than from trapped space charge.³³ The discovery of the enhancement of piezoelectric activity in PVDF in 1969, by Kawai,⁴ led to the revelation of other properties, such as pyroelectricity^{5,6} and ferroelectricity properties. Although there is no obvious evidence of the Curie transition in PVDF, the existence of polarization loops, together with polarization reversal and the switching phenomena, is generally accepted as proof of ferroelectricity in PVDF. Figure 1.2 shows the D-E hysteresis loops at various temperatures.



Figure 1.2 The D-E hysteresis loops of PVDF at various temperatures.

Even at -100° C a square-shape hysteresis loop is clearly observed with a remanent polarization P_r about 60 mC/m², which does not change with temperature. However, the coercive field E_c , which is the electric field used for neutralizing polarization in material, is temperature-dependent. The value is about 50 MV/m at room temperature and remains almost constant above the glass transition temperature (-50° C), but increases sharply at lower temperatures.

The remanent polarization P_r , which is the polarization resulting from the removal of the field, is dependent on the crystallinity. For PVDF, the calculated macroscopic polarization for 100% alignment of all dipoles is 130 mC/m², and the measured polarization of 60 mC/m², is consistent with about 50% crystallinity and perfect alignment. The direction of P_r can be reversed by subsequent application of the field in the opposite direction. This phenomenon, called ferroelectric switching, has been investigated extensively to elucidate the mechanism of polarization reversal.³⁴⁻³⁶ Although the PVDF exhibits strong piezoelectric and pyroelectric properties, it is necessary that polymer film be subjected to mechanical stretching and electrical poling to get the polar β phase. Such procedures include, for example, subjecting ferroelectric polymer to mechanical deformation,³⁷ electron irradiation,³⁸ uniaxial drawing,³⁹ crystallization under high pressure,⁴⁰ and crystallization under high electric field.⁴¹ It is tempting to speculate about how much improvement of the dielectric, piezoelectric, and pyroelectric properties may yet be achieved by modification of the chemical structure of the polymer. Some improvement has been achieved by synthesizing copolymers of vinylidene fluoride with trifluoroethylene (TrFE), tetrafluoroethylene (TFE), or vinyl fluoride (VF), and indeed, some of these copolymers exhibit even higher piezoelectric and pyroelectric properties that will be discussed in the next section.

1.4.2 Poly(vinylidene fluoride-trifluoroethylene) (VDF/TrFE) copolymer

P(VDF/TrFE) is the most studied copolymer. Lando, et al.^{42,43} and Yagi, et al.^{44,45} initially studied the properties and structure of this copolymer. The randomly distributed VDF and TrFE units form the co-crystalline phase in the whole composition range of the copolymers. The greater proportion of bulky trifluorine atoms in the PVDF prevents the molecular chains from accommodating the tg^+tg^- conformation. Therefore, copolymers crystallize at room temperature into a ferroelectric phase with the extended planar zigzag (*all-trans*) conformation,⁴⁶ whose crystalline phase is similar to the β phase of PVDF homopolymer.

1.4.2.1 Ferroelectric-paraelectric phase transition

Probably the solid evidence for the ferroelectricity in this copolymer is the existence of the ferroelectric to paraelectric (F-P) phase transition or Curie temperature Tc. The Curie temperature of synthetic polymer was discovered in 1980.^{47,48} At this temperature, the dielectric constant shows a maximum value, the polarization and piezoelectric constants go down to zero,⁴⁹ and the Young's modulus and elastic constant decrease.^{50,51} The phase transition of copolymers has been found to be affected by several factors, especially the VDF content. As shown in Figure 1.3, copolymers with VDF content below 82 mol% exhibit a phase transition below the melting.^{52,53}



Figure 1.3 The thermal transition temperatures in VDF/TrFE copolymers.

The lowest Curie temperature of the copolymer is about 60°C, and this phase temperature increases linearly with the increasing of VDF content,⁵⁴ which allows an extrapolation of the Curie transition temperature of PVDF homopolymer to about 215°C, Other widely studied factors that affect the Curie transition are hydrostatic pressure, tensile stress, external electric field, annealing temperature and time, mechanical drawing, poling, irradiation, solution history, thermal history, and crystallization conditions.

1.4.2.2 Crystal structures

A number of experimental techniques such as differential scanning calorimetry (DSC), dielectric constant, ferroelectric measurement, and X-ray diffraction have been employed to investigate structural change during the phase transition.^{55,56} It is not clear whether the double peak at the ferroelectric transition of 70/30 VDF/TrFE copolymer⁵⁷⁻⁵⁹ is associated with the formation of different sizes of ferroelectric domains⁶⁰ or the two-step phase transformation. Tashiro suggested the existence of two types of ferroelectric phases: a low-temperature phase *LT* consisting of a parallel arrangement of dipoles in planar zigzag (*all-trans*) chain (as seen in the β phase of PVDF homopolymer) and the cooled phase *CT* consists of long *trans* segments connected by irregular *gauche* linkages along the chain axis (depending on the VDF content⁶¹ of the copolymer as well as the sample preparation conditions).⁶²

The transition behavior of copolymer changes with variations in the VDF content in copolymers.⁶²⁻⁶⁴ For instance, in a copolymer with a VDF content of 70-80 mol%, the first-ordered transition between the *LT* and *HT* phases at high temperature has been observed, whereas the second-ordered transition between the *CT* and *HT* phases occurred in copolymer with a VDF content of <50 mol%. The 50-60 mole% VDF samples show more complicated transitional behavior. The *trans* zigzag chains transfer once to the irregular *trans* form of the *LT* phase, which easily changes to the random *gauche* conformation. Recently, the phase transition from the *LT* to *CT* phases has been confirmed.⁶¹

During the transition from ferroelectric to paraelectric phase, the structural change in the crystal lattice and the domain size are clearly demonstrated.^{65,66} The phase transition occurs through the *trans-gauche* conformational change, where *all-trans* molecular chains
change their conformation to a disordered sequence of conformation isomers (tg^+ , tg^- , tt), resulting in the non-polar unit cell structure of hexagonal packing, which has unit cell dimensions of a = 9.96 Å, b = 4.96 Å, and c = 4.64 Å.^{67,68}

Interestingly, during the phase transition, there is a large strain change associated with the phase transformation. For 65/35 mol% VDF/TrFE copolymers, respective lattice strain as high as 10% and 7% in the crystalline phase along (001 reflection) and perpendicular (200, 110 reflections) to the polymer chain has been detected during the phase transition.⁶⁹ Therefore, for a high crystalline (>50% crystallinity) copolymer, these strains can be transformed to macroscopic strains, indeed, a thermal strain of more than 6% in 65/35 copolymer has been observed.⁷⁰ More importantly, for a ferroelectric polymer, the phase transformation can be controlled by an external electric field, hence the high field-induced-strain can be achieved by exploring the lattice strain at the phase transition.

1.4.2.3 Ferroelectricity and related properties

The copolymers were demonstrated to possess ferroelectricity over a wide composition range.^{71,72} The piezoelectric^{73,74} and pyroelectric⁷⁵ properties of these copolymers have also been reported. Since the electrical properties originated from the crystal units, the chain orientation by drawing, crystallization by annealing, and CF₂ dipole orientation by poling are important for achieving high piezoelectric and pyroelectric constants. The dipole orientation can result in a change of chain conformation, chain packing, crystallinity and crystal size.⁷⁶ Recently, the structural and crystal changes of the copolymers have been reported as functions of poling conditions⁷⁷ and high-pressure crystallization.⁷⁸ The polarization reversal of copolymers strongly depends on their thermal and mechanical treatment. The polarization reversal of quenched copolymer proceeds over several decades, if

annealed above the Curie temperature (Tc), whereas it is completed within one decade, if annealed below T_c .⁷⁹

The phase transition T_C of all VDF/TrFE copolymers occurs at high temperatures (>60° C) and the transition is relatively sharp. In addition, the early experimental results showed a large hysteresis at the phase transition, which is not desirable for practical applications. Therefore, many attempts have been devoted to achieving the general goal of broadening and reducing the phase transition to room temperature and to minimizing or eliminating the hysteresis.^{80,81} Zhang, et al. found that by systematic study of the irradiation conditions of copolymer, high electromechanical response could be achieved.^{82,83} The longitudinal strain S_3 measured at room temperature, and 1 Hz frequency reaches -4% at 150 MV/m. The irradiation significantly reduces the hysteresis in the polarization loop. However, the polarization is also significantly reduced, and the sample becomes completely insoluble in common solvent because of a severe crosslinking side reaction during the high-energy irradiation.

The increase in hardness of the copolymer due to crosslinking was also revealed in the electromechanical response. A very high field was required to get high strain response. It appears that the irradiation process produces many undesirable side reactions that increase the amorphous phase content and diminish the processability of the sample.

1.4.3 Poly(vinylidene fluoride-tetrafluoroethylene) (VDF/TFE) copolymer

The second mostly studied copolymer is the VDF/TFE random copolymer, which can be viewed as a PVDF polymer containing an increase amount of head-to-head and tail-to-tail defects. The steric hindrance created by the TFE unit effectively stabilizes the *trans* conformer of the VDF chain. As the content of the TFE units increases, the *trans* conformation is stabilized overwhelmingly, and the generation of the *gauche* bonds is suppressed. The copolymers of VDF/TFE with at least 7% are crystallized into the β form. The Curie transition was clearly observed in 18-23 mol% TFE. The crystal structure and phase transition behavior of copolymers have been studied by X-ray, IR, and Raman spectroscopies.⁸⁴

The piezoelectric and pyroelectric studies of the VDF/TFE copolymers showed highly inhomogeneous polarization across the thickness of the copolymer films.^{85,86} Ferroelectric studies revealed a hysteresis loop, but no Curie transition in the temperature dependent dielectric curve.⁸⁷ However, there was some evidence showing that the Curie transition occurs in the vicinity of the melting temperature.^{88,89}

1.4.4 Other ferroelectric polymers

1.4.4.1 Ferroelectric nylon

A. Polymeric and crystal structure

The discoveries of piezoelectric and pyroelectric properties in PVDF polymer led to the search for other classes of novel ferroelectric polymeric materials. Recently, oddnumbered nylons have emerged as a new class of ferroelectric polymer similar to PVDF.⁹⁰ These materials have attracted much interest in the past two decades because of the stability of their electroactive properties at relatively high temperatures,⁹¹⁻⁹² and with relatively high electromechanical coupling coefficient.⁹³

Polyamides, commonly known as nylons, have molecular repeated units of $(-HN(CH_2)_xCO-)$. Generally, nylons are named after the number of carbon in the repeating unit of the polymer backbone. For example, if x=5, the corresponding nylon is identified as nylon 5. The nylons with odd numbers of carbon atoms are called "odd nylon", whereas the

nylons with even number of carbon atoms are known as "even nylon". There are other categories of polyamides having molecular repeating units of [-HN(CH2)_xNHOC(CH2)_yCO-] that are termed odd-odd nylons, if the number of carbon atoms in the repeating units (X and Y) are both odd numbers. Nylons are prepared by melt polymerization solution and interfacial polymerization, ring-opening polymerization, and anionic polymerization. The morphology and degree of crystallinity of the nylons depend on the basic structure of their chemical linkages. Strong interactions between the amides group of neighboring chains account for the unique physical properties of nylons, such as toughness, stiffness, high melting points, and low coefficient of friction.

Odd nylons and odd-odd nylons are important classes of ferroelectric polymers. Nylons crystallize in *all-trans* conformation and are packed so as to maximize the hydrogen bonds between the adjacent amine and carbonyl groups, as seen in Figure 1.4.



Figure 1.4 *All-trans* conformation of odd-numbered and even-numbered nylons. Arrows indicate the dipole direction.

The dipoles of odd nylons are aligned in the same direction, and give rise to large dipole moment and spontaneous polarization in the unit cell of the crystalline phase, whereas the dipole components of even nylons cancel each other out. The density of NH···C=O dipoles per unit volume of nylon is larger for lower numbered nylons, thus nylon-5 is expected to possess a larger dipole moment (i.e. remnant polarization) than nylon-7, nylon-9, and nylon-11. Indeed, the experimental results show that the remnant polarization of nylon-5 is ~135 mC/m².⁹⁴ Odd-numbered nylon shows polymorphs. Nylon-11 shows at least five different crystal structures - triclinic α form I, monoclinic form II, and pseudo-hexagonal γ form III, δ' phase and γ' phase^{. 95-97} The α form nylon-11 is polar in nature, with dipoles that are hydrogen-bonded and aligned in the same direction, whereas the γ form is non-polar and has amide groups that lay in the plane perpendicular to the chain axis. The crystal phase transformation of nylon-11 occurs between a triclinic α form and a pseudo-hexagonal γ form at high temperature $(>90^{\circ} \text{ C})$ through the randomization of the hydrogen bonding. Polymorphs of nylon-9, nylon-5,7, and nylon-7,7 have also been prepared.^{98,99} The α form seems to be the most common polymorph in many odd-numbered nylons.

B. Ferroelectricity and related properties

Nylons exhibit very interesting dielectric behavior in that the dielectric constant changes significantly with alterations in temperature and frequency.¹⁰⁰ The dielectric constants of poled and annealed nylons are relatively low (about 2.5-3) at various frequencies below 0°C, and increase rapidly above the glass transition. The peak position, magnitude of dielectric constant, and relaxation process in nylon change with poling conditions and the presence of absorbed water.^{101,102} Several journal articles have focused on the high frequency properties that are of interest for ultrasonic transducers.^{103,104}

The pyroelectricity and piezoelectricity of the α phase and γ phase of nylon-11 films with variation of poling conditions have been reported.¹⁰⁵ It has been found that the γ phase nylon films showed much higher piezoelectric response than α phase films under the same poling conditions. This characteristic difference was interpreted by the breaking and reforming of hydrogen under a high electric field. The γ phase has a more regular arrangement of dipoles and has stronger hydrogen bonding, thus it is more strongly influenced by an applied electric field. However, it is found that a mixture of the α phase and γ phase, rather than the pure α phase or γ phase, has the highest piezoelectric constants. The piezoelectricity and pyroelectricity of odd nylons were also affected by the anisotropy, absorbed water, orientation, and annealing temperature.

Ferroelectric properties of nylons have been investigated by several research groups.¹⁰⁶⁻¹⁰⁸ The polarization reversal was found to be complete in a few tens of milliseconds under 140 MV/m at 20°C. This fast polarization reversal and the rectangular D-E hysteresis loop are evidence of the dipoles' origin. The effect of annealing on the ferroelectric behavior of nylon-11 and nylon-7 has been investigated.¹⁰⁹ The remnant polarization decreases with an increasing annealing temperature and disappears at an annealing temperature of 185°C, whereas the coercive field increases as annealing temperature increases, indicating the rearrangement of the hydrogen bonding structure. The mechanism of ferroelectricity of poled nylon-11 is related to the hydrogen bond breaking, followed by the reorientation of the amide groups toward the electric field's direction and the re-forming of hydrogen bonds in a new direction.¹¹⁰ The orientation is retained in the glassy state below T_g even after the electric field is removed. The ferroelectricity has also been

observed in polyamides containing m-xylylenediamine, aliphatic dicarboxylic acids, and fluorinated odd-odd nylons.¹¹¹

Ferroelectricity in aliphatic odd nylons has been reported in the past few years.¹¹² Unlike nylons with ring systems in which the ferroelectric nature arises from the orientation of the amide dipoles in the amorphous region, the ferroelectric polarization of aliphatic odd nylons originates from the crystalline phases.¹¹³ A slightly higher density of amide dipoles contributes to a larger value for the remnant polarization, as seen in other nylon systems. A new class of ferroelectric and piezoelectric polymer, nylon-11/PVDF laminated films prepared by a co-melt-pressing method, has also been reported.¹¹⁴ The laminated films exhibit a typical ferroelectric hysteresis loop with high remnant polarization (higher than that observed in PVDF homopolymers or nylon-11 under the same measurement conditions). The film's piezoelectric stress constant ($d_{31} = 41$ pC/N) and piezoelectric strain constant ($e_{31} =$ 109 mC/m²) are significantly higher than those of PVDF and nylon-11. Another new class of ferroelectric polyamides is the ferroelectric polyamide blends. The D-E hysteresis curves were observed in all blends of nylon 6I/6T copolymers (6 = hexamethylenediamine, I = isoththalic acid, T = terephthalic acid) and m-xylylenediamine-6 (MXD6).^{115,116} It was concluded that the intermolecular exchange of hydrogen bonding in the amide groups is responsible for the ferroelectricity.

1.4.4.2 Cyanopolymers

Cyanopolymers discussed here include polyacrylonitriles (PAN), poly(vinyl cyanide), and cyanocopolymers. The cyano group (C–CN) has a unique feature of large dipole moment (3.5D) and the ability to form complexes with transition metals. The polymerization can occur through free radical and ionic polymerization leading to nonstereoregular (atactic) cyano groups in the polymer structure. Thus, cyanopolymers have no clear melting temperature because of their high cohesive force and low thermal stability. It has been accepted that the strong interaction and repulsion of the cyano groups force polymer chains to adopt a helical conformation. However, the *all-trans* conformation is more stable.^{117,118}

The ferroelectricity of poled and annealed PAN has been studied by X-ray and IR spectroscopy.¹¹⁹ It is believed that the ferroelectricity of PAN is related to the dipole orientation and kinking of the chain above the glass transition temperature. The piezoelectric and pyroelectric properties of PAN were initially studied by Ueda and Carr,¹²⁰ and were proved by Von Berlepsch¹²¹ using copolymer with methylacrylate. The D-E hysteresis loop of a stretched film of this copolymer has been measured at 68° C, which is below the glass transition temperature.¹²² The copolymer showed very low remnant polarization and high coercive field at low temperature. However, an alternating copolymer of PAN, poly(allycyanide[35%] /acrylonitrile[65%]), showed very high remnant polarization, i.e. 200-700 mC/m² at 105° C.¹²³

Another alternating copolymer that received much attention as an amorphous copolymer is the vinylidene cyanide/vinyl acetate copolymer. The dipole moment of the repeating unit is 4.5 D in *trans* conformation, thus contributing to a large piezoelectric constant after poling.¹²⁴ The piezoelectricity (d_{31}) of drawn and poled films is comparable to that of the PVDF in the temperature range of 20-100°C. Interestingly, this copolymer shows a very large dielectric strength of more than 100, one of the largest values among polymers. It is concluded that the large dielectric relaxation strength originated from the cooperative motion of 10 or more CN dipoles.¹²⁵ The exceptionally high dielectric peaks occur near the glass transition temperature, similar to a ferroelectric transition.^{126,127} The most unique

feature of this copolymer is its low density, which results in low acoustic impedance, close to those levels seen in water and the human body. It makes this copolymer very useful in medical applications.

1.4.4.3 Polyureas and polythioureas

Polyureas and polythioureas are in the class of amino resins, and are thermosetting polymers. They are usually synthesized by condensation polymerization, and their products are mostly in the form of powder. The preparation of thin films from them was not possible due to their insolubility until a technique of vapor deposition polymerization was developed.^{128,129} The synthesis and characterization of different kinds of thin film polyurea have been reported elsewhere.^{130,131} A typical polymerization consists of vapor deposition of monomers onto the surface of a substrate in a vacuum chamber. The monomers will diffuse on the surface and react with each other to form urea bonds between an amino (NH₂) group and isocyanate (CNO) group. The urea bond (NHCONH) has dipole moment of 4.9 D and is responsible for high piezoelectric and pyroelectric properties.

The dielectric constants of aromatic polyureas [P(4,4'-diphenylmethane diisocyanate (MDI)/4,4'-diamino diphenylmethane (MDA)] have been reported.^{130,131} The dielectric constant of MDA-rich films of poled and annealed P(MDA/MDI) are relatively constant up to 200°C, whereas the MDI-rich films have a low dielectric constant but show good stability up to 200°C. The dielectric constants of the balanced stoichiometric films increase with higher temperatures above 100°C. Pyroelectric and piezoelectric constants are also large for the balanced composition films. This is due to the fact that a crosslinked network structure does not form in a balanced film the way it does in unbalanced films. The high molecular weight molecules are oriented or crystallized in a local region under a high poling field and

form a semicrystalline structure, thus stabilized residual polarization is produced and gives rise to high piezoelectric and pyroelectric constants.

The pyroelectric and piezoelectric properties of aliphatic polyureas display similar features those seen in nylons, i.e. there is no observation of these activities, if the number of carbon atoms between the urea bonds is even. This is because alternating urea bond dipoles arrange in antiparallel direction, and the dipole moments are cancelled out. Strong hydrogen bonds are possible in cases where the parallel orientation of dipoles in a planar zigzag chain gives rise to high glass transition and high melting temperatures. Dielectric peaks above 125°C have been observed in poly(heptamethylene/nanomethyleneurea).¹³² The relatively large dielectric constant is believed to be related to the crystal transition from the mobile dipole to the rigid dipole state, corresponding to the different hydrogen bonding states. The value of remnant polarization obtained from D-E hysteresis of the same sample is as high as 200-440 mC/m² at 90°C, which may be attributed to the effect of the ionic currents of impurities. The remnant polarization disappears above 110°C, which suggests the rearrangement of the hydrogen bonding at this temperature.

Polythioureas are known as pyroelectric, pyroelectric, and ferroelectric polymers. Their chemical structure is $H_2N-CS-NH_2$. Ferroelectric thiourea polymers have been prepared by condensation reaction of thiourea and formaldehyde under different conditions.^{133,134} Thiourea [SC(NH₂)₂] has a large dipole moment of 5.4 D. Ferroelectricity in polythioureas was initially studied in 1978. The sharp dielectric constant of thiourea-formaldehyde (PTUBFB) observed at 145°C is as high as 320. In past decade, an odd number aliphatic polythiourea, polythiourea-9, has been synthesized.¹³⁵ The odd number of carbon was chosen to ensure a polar chain and polar packing. Large dielectric relaxation as well as a

large dielectric constant was observed in the glass transition region. According to the theoretical data derived by Meakins et al.,¹³⁶ the dielectric relaxation and dielectric loss increase with increments in the hydrogen bonding. As a result, the hydrogen-bonded thiourea dipoles in the intermolecular chains are easily rotated under an electric field above glass transition. The ferroelectric transition in thiourea is essentially due to both crystalline domains and "incommensurate-phase", which are due to both hydrogen bonding and dipole interactions.¹³⁷ The D-E hysteresis was first observed in drawn polythiourea-9 above Tg.¹³⁸ The remnant polarization is very small. This may be due to the fact that only a small amount of chains can form hydrogen bonding. Therefore, the remnant polarization stabilized by hydrogen bonding is small.

1.4.4.4 Polyurethane

Polyurethanes have emerged as nonlinear optic, ferroelectric, and piezoelectric materials,^{139,140} in which molecular structures can be tailored for each specific application. Polyurethanes have the chemical structure of $[-(CH_2)_xOC(O)NH(CH_2)_yNHCO(O) -]$. The dipole moment of the urethane group is 2.8 D. Polyurethanes are usually composed of a polyester or polyether soft segment and a diisocyanate-based hard segment. From the view point of the chemical structure of the hard segments, polyurethanes can be classified into urethane polymers (PU), which are formed by extending a diisocyanate with low molecular weight diols, and urethane-urea polymers (PUU), which are formed by extending a diisocyanate undergo microphase separation due to the immisibility of the hard and soft segments. The hard segment domain acts as the physical crosslink as well as the filler particles for the soft segment matrix. The

driving force of the domain formation is the strong intermolecular interaction of the hydrogen bondings between the hard-hard segments and the urea/urethane linkages.

Both temperature dependence and the pressure-temperature effects on the dielectric constant and relaxation processes of aliphatic polyurethanes have been studied.¹⁴¹ It was revealed that the relaxation times for both the I-process, associated with the molecular motion in hard segments, and the α process, associated with the glass transition temperature, increase with pressure, and that these shifts are much more pronounced for the I-process.¹⁴² Dielectric properties of polyurethanes were also studied as a function of drawing and poling effects.¹⁴³

The ferroelectricity in polyurethanes was originated from the crystal region by controlling the hydrogen bondings. In 1999, there was a report on the origin of the ferroelectricity that suggested systems in which ferroelectricity derives from the amorphous region above the glass transition temperature.¹⁴⁴ The electrostrictive responses, which are proportional to the square of the electric field, have been investigated in the polyurethane.¹⁴⁵ The field induced strain was found to be very sensitive to the processing conditions and the thickness of the specimen. The increase of the strain response as the sample thickness was reduced, is suggested to be caused by a non-uniform electric field across the thickness direction. It is known that in non-piezoelectric materials, the field induced strain can be caused by the electrostrictive and also the Maxwell stress effects.¹⁴⁶ The experimental results showed that the Maxwell stress significantly contributed to the strain response at temperatures higher than the glass transition temperature, and that the electrostrictive coefficient is much higher than those of other materials.¹⁴⁷

1.5 Applications

Since 1970, many kinds of piezoelectric devices have been developed from organic polymer materials and widely used in industrial settings as well as in medical instruments. These device applications can be grouped into sensors, medical instrumentation, robotics, low or audio frequency transducers, ultrasonic and underwater transducers, electroacoustic transducers, electromechanical transducers, actuators, pyroelectric devices, and optical devices. The pyroelectric, biomedical, robotic applications and the optical devices will not be discussed here. The conclusive reviews can be found in ref. 148 and 149.

The first commercial application of piezoelectric polymer film was in audio transducers (tweeters) and loudspeakers.^{150,151} The merits of ferroelectric polymers for piezoelectric devices over ferroelectric ceramics is their light weight, toughness, flexibility, and ability to be fabricated into large sheets. In addition to these traits, they have high piezoelectric g constant and much lower acoustic impedance (this property is proportional to the product of density and stiffness) than ferroelectric ceramics. Therefore, they are suitable for acoustic applications in such media as air, water, and human tissue. Such applications include audio transducers (headphones, microphones, and loudspeakers), underwater acoustic hydrophones, where the bimorph structure of polymer/ceramics was used, and biomedical transducers (sensors and probes, imaging systems, and acoustic sources). Other merits of polymer piezoelectrics are their thin film-forming ability and scissor usable. This led to very promising applications, such as ultrasonic transducers or paperlike speakers for the thin TVs, decorations, and interiors (which was commercialized by Mitsui Petrochemical in late 1980s). The main disadvantages of polymer piezoelectrics are their relatively low piezoelectric *d* constant and relatively poor dimensional stability.

Devices based on the conversion of a mechanical input (stress or strain) to an electrical output signal are often used as sensors to detect displacement, stress, vibration, and sound. Typical sensors are hydrophones, blood pulse counters, blood pressure meters, pressure sensors, acceleration sensors, shock sensors, vibration sensors, touch sensors, microphones, antinoise sensors, and keyboards. Reverse devices, in which the input is an electrical signal and the output is a mechanical signal, include position controls, acoustic systems, and actuators.

1.6 Objective and scope of this research

As mentioned earlier in section 1.4.2, the VDF/TrFE copolymer is the most widely studied ferroelectric polymer because of its unique piezoelectric and pyroelectric properties. Unfortunately, the Curie temperature (Tc) of the copolymers, in which the ferroelectric phase changes to paraelectric phase and creates electromechanical response, are well-above ambient temperature, the lowest Tc is about 65° C in the composition VDF/TrFE=55/45 mole ratio. Due to the high Tc phase transition temperature, the response of the dipoles to the electric field is very low at ambient temperature. The slow response to the electric field is also revealed in a large polarization hysteresis loop, due to the high-energy barrier of switching the dipole at ambient temperature. Our initial speculation of the slow switching of the dipoles under electric field may be due to large ferroelectric domain size. In earlier works, physical treatments, namely, mechanical drawing or electrical poling, were used to modify crystal structure. However these physical treatments do not provide stable structure. Although controlled electron radiation improves electrical properties, it brings many drawbacks, as discussed above.

To address these problems, we have adopted a new chemical strategy of altering crystalline domains and creating relaxor ferroelectric behavior of VDF/TrFE copolymer, with the objective of achieving a processable polymer with controllable phase transition temperature, high dielectric constant, and fast and large electromechanical response at ambient temperature. The research approach was to homogeneously incorporate a small amount of bulky termonomer units such as chlorofluoroethylene (CTFE), vinyl chloride (VC), 1,1-chlorofluoroethylene (1,1-CFE), 1,2- chlorofluoroethylene (1,2-CFE), 1-chloro-2,2-difluoroethylene (CDFE), as the crystalline defects into a VDF/TrFE copolymer chain. Ideally, the incorporated termonomers result in a reduced polar domain size without changing the overall crystallinity. The smaller polar domains reduce the energy barrier needed in the phase transition, and therefore reduce the Curie transition temperature and its activation energy. The research involves the development of a new living radical initiator (based on the oxidation adducts of borane) to prepare the terpolymers containing VDF, TrFE, and bulky ter-monomer, with good purity, completely soluble and melt processable, high molecular weight, narrow molecular weight and composition distributions.

Our research was also extended to functional ferroelectric fluoropolymers and block copolymer structures, with the objective of further improving electric and mechanical properties of the terpolymers. Despite significant progress, the relatively low mechanical modulus and high electric voltage for electromechanical response in the terpolymers post significant limitation in this technology for a wide range of applications-for example, in biological systems in which high modulus and low voltage are essential. To address these shortfalls, we further modified the fluoropolymer by preparing new families of functional ferroelectric fluoropolymers and block ferroelectric copolymers. In addition to the general information on ferroelectric materials discussed in Chapter 1, Chapter 2 will provide the prior knowledge in the functionalization of fluoropolymers. Our experimental results are discussed in the remaining chapters. Chapter 3 focuses on new polymer chemistry, based on the oxidation adducts of boranes and bulk reaction process, to prepare fluoro-terpolymers, containing VDF, TrFE, and bulky ter-monomers. Their structure characterization is discussed in detail. The mechanical and electric properties of the terpolymers are presented in Chapter 4, while Chapter 5 shows our results in the preparation of functional ferroelectric fluoropolymers and block ferroelectric copolymers, with some of their physical properties. The final Chapter summarizes our experimental results and provides some suggestions for future research.

1.7 References

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Chapter 2

Functionalization of fluoropolymers

2.1 Introduction

Fluoropolymers (PTFE, PVDF, etc) exhibit many unique properties, including thermal stability, chemical inertness, low water absorptivity, excellent weatherability, good resistance to oxidation, and very interesting surface properties. Therefore, fluoropolymers are commonly used in many high-end applications, including aerospace, textile finishing, and microelectronics. However, the fluoropolymers have some drawbacks, for instance, poor melt processability, poor solubility in common organic solvent, and resistance in chemical modification and crosslinking reactions. One solution to improve processability was by performing a copolymerization of fluorinated monomer with non-fluorinated monomer, which has led to various commercial products, including TFE/ethylene, TFE/propylene, and CTFE/ethylene copolymers. Table 2.1 lists some of the major commercial fluoro-copolymers.

monomer	Trade name	Producer
CTFE/E	HALAR®	Ausimont
TFE/E	TEFZEL®	Dupont
HFIB/VDF	CM1	Allied
TFE/propene	AFLAS [®]	Asahi Glass Co.
CTFE/vinyl ether	LUMIFLON®	Asahi Glass Co.
CTFE/2-allyoxyethanol/vinyl	FLUOROBASE[®]	Ausimont
acetate		
CTFE/2-ally oxyethanol		Elf Atochem

 Table 2.1
 Commercial products containing fluorinated and non-fluorinated monomers

TFE : Tetrafluoroethylene, VDF : Vinylidene fluoride, CTFE : Chloro trifluoroethylene, HFIB : Hexafluoro isobutene

In the past decades, the attention has been shifted to the further improvement of some properties of fluoropolymers, such as adhesion, curability, hydrofilicity, and other surface properties.¹⁻⁴ Many research activities have been focusing on the preparation of functional fluoropolymers containing some specific functional groups. As will be discussed in Chapter 5, many research approaches, including functional comonomers, have been investigated. This chapter briefly summarizes the chemistry used in the preparation of fluoropolymers, with special focus on their functionalization chemistry.

2.2 Homo- and Co-polymerization of fluoro-monomers

In general, the preparation of fluoropolymers requires special reaction conditions. Fluorinated monomers, such as vinyl fluoride (VF), vinylidene fluoride (VDF), and tetrafluoroethylene (TFE), usually exhibit very low reactivity compared to other ethylenically unsaturated monomers, due to lack of resonance and electron deficiency in the double bond. The conventional free radical solution polymerization that is used for polymerization of vinyl monomers, including vinyl chloride (VC) and vinyl bromide (VBr), gives low yield. In the past decades, two processes have been developed for the polymerization of fluorinated monomer, including suspension and emulsion processes in aqueous solution. Many catalyst systems have been employed including the inorganic peroxides, such as potassium, sodium or ammonium persulfate, and organic peroxides, including dibenzoyl peroxide, diacetyl peroxides or di-tert-butylperoxide. Both initiators were found to have some disadvantages. The inorganic peroxy initiators produce polymer with less processability and somewhat thermal instability, while organic peroxide initiators require extreme conditions in polymerization, such as high pressure, high temperature, and long reaction time to achieve reasonable yield.

Random copolymerization between the fluorinated monomer and non-fluorinated monomer is usually very difficult, which can be understood by the qualitative Q-e scheme (Q and e being attributed to the resonance and inductive effects of the monomer, respectively). The Q and e values could be explained in terms of monomer reactivity where e associated with the ease of the monomer to polymerize and Q associated with the stability of the monomer radical. Tables 2.2 and 2.3 list the Q and e values of selective fluorinated monomers and non-fluorinated comonomers, respectively.

Table 2.2e and Q values of fluorinated monomer (from ref 5)				
Monomer	е	Q		
CH ₂ =CHCF ₃	0.42	0.130		
CHF=CH ₂	0.72	0.008		
$CF_2=CH_2$	0.5	0.015		
CF ₃ CF=CHF	2.1	0.002		
CF ₂ =CHF	1.15	0.009		
CF ₂ =CFCH ₂ OH	1.52	0.011		
CF ₂ =CFC ₃ H ₆ OH	1.04	0.008		
CF ₂ =CFC ₃ H ₆ OAc	1.14	0.060		
CF ₂ =CFCl	1.56	0.026		
$CF_2 = CFCO_2CH_3$	1.2	0.048		
$CF_2 = CFO - Rf - CO_2R$	1.08	0.006		
$CF_2 = CFCF_3$	4.09	0.047		
$CF_2=CF_2$	1.22	0.049		
$CF_2 = CF - CF = CF_2$	0.58	0.820		

Table 2.3 *e* and *Q* values of non-fluorinated monomer (from ref 5)

Monomer	е	Q
CH ₂ =CHOC ₄ H ₉	-1.64	0.014
CH ₂ =CH-CH ₂ OCOCH ₃	-1.13	0.028
N-vinyl pyrrolidone	-1.62	0.088
$CH_2 = CHCH_2Si(OC_2H_5)_3$	-0.94	0.024
Vinyl acetate	-0.22	0.026
Vinyl chloride	+0.20	0.044
Butadiene	-1.05	2.390
Styrene	-0.80	1.000
N-Phenyl maleimide	+3.24	2.810
Maleic anhydride	+3.69	0.860
Ethylene	+0.05	0.016
Propene	-0.78	0.002
Isobutene	-0.96	0.033

All fluorinated monomers have high positive e values but low Q values. On the other hand, non-fluorinated monomers exhibit negative e values and low Q values, except styrene and butadiene. It is well known that the ideal copolymerization occurs between two monomers having similar Q and e values, for example, styrene-butadiene and vinylacetatevinyl chloride. The tendency toward alternation is greatest for monomers having the same Qvalues with high e values of opposite sign. The failure in the copolymerization between styrene and fluorinated monomer is clearly due to considerable differences between the two Q values. Several reported copolymerization reactions⁶ between fluorinated monomers and non-fluorinated monomers, such as ethylene, vinyl ether, and N-vinyl pyrroridone, showed a strong tendency of forming alternative copolymer structures. The reactivity ratios of these copolymers were tabulated by Greenley⁷ via the Kelen and Tudos equation.

2.3 Synthesis of functional fluoropolymer

In general, there are two research approaches to achieve the functionalization of fluoropolymers, namely (i) copolymerization of fluorinated monomer with functional monomers to form functional fluoro-copolymers,⁶⁻⁸ and (ii) the control polymerization process by using functional initiators ⁹⁻¹¹ or chain transfer agents to prepare telechelic fluoropolymers containing two terminal functional groups.

2.3.1 Copolymerization of fluorinated monomer with functional comonomers

Theoretically, the most effective way to obtain the functional fluoropolymers is by copolymerization of the fluorinated monomers with functional comonomers. However, the numerous attempts made so far, have received very little success. In the past few years, several new functional monomers have been synthesized and studied, including nonfluorinated and fluorinated comonomers, which are listed in Table 2.4.

Name	Chemical formula	References
AOE : 2-allyoxyethanol	CH2=CHCH2-O-CH2CH2OH	18
AOPD:3-allyoxy-1,2-propanediol	CH2=CHCH2-O-CH2CHOH-CH2OH	18
AGE: Ally glycidyl ether	CH ₂ =CHCH ₂ -O-CH ₂ CHCH ₂ O	18
TMPAE: Trimethylolpropane monoallyl	CH2=CHCH2-O-CH2-C(CH2OH)2-	18
ether	CH_2CH_3	
HEA: 2-hydroxyethyl acrylate	CH2=CH-CO-O-CH2-CH2OH	18
NMA: N-methylolacrylamide	CH ₂ =CH-CO-NH-CH ₂ OH	18
AAG: Acrylamidoglycolic acid	CH2=CH-CO-NH-CH(OH)COOH	18
MAGMAE: Methyl acrylamido	CH ₂ =CH-CO-NH-	18
(methoxy)acetate	CH(OCH ₃)COOCH ₃	
2,2,3,4,4-pentafluoro-3-ene-butylnol	CF ₂ =CFCF ₂ CH ₂ OH	15
3,3,4,4,5,6,6-heptafluoro-5-ene-hexanol	$CF_2 = CF(CF_2)_2 CH_2 CH_2 OH$	15
Perfluorovinyl alcohol	$CF_2 = CF(CH_2)_mOH, m = 1-3$	15, 19
2,2,3,4,4-pentafluoro-3-ene-butyric acid	CF ₂ =CFCF ₂ COOH	15
1,1,2-trifluorovinyloxirane	CF ₂ =CFCH ₂ CHCH ₂ O	15
-		
Methyl perfluoroacrylate	CF ₂ =CFCOOCH ₃	27
4,5,5-trifluoro-4-ene-pentylacetate	CF ₂ =CF(CH ₂) ₃ OAc	28
4,5,5-trifluoro-4-ene-pentylthioacetate	CF ₂ =CF(CH ₂) ₃ SAc	29
Perfluorovinyl ether ester	CF ₂ =CFO-R _f -COOR,	30
Perfluorovinyl ether sulfonyl fluoride	CF ₂ =CFO-R _f -SOOF	31
perfluorobutadiene	$CF_2 = CFCF = CF_2$	32

 Table 2.4
 Functional fluorinated and non-fluorinated comonomers

Among these comonomers, perfluorovinyl functional monomers¹⁵, i.e. $CF_2=CF(CF_2)_n(CH_2)_mX$, where n = 0-10, m = 1-4, and X = -OH, -COOH or epoxy group, developed by the Daikin Company, are the most interesting comonomers in copolymerization reactions with both fluorinated or non-fluorinated monomers.¹²⁻¹⁴ Recently, some trifluorovinyl functional monomers, i.e. $(CF_2=CF(CH_2)_mX)$, where m = 1-3 and X = -OH, OCOCH₃, -COOH, SO₃H, epoxy, and thiol functional groups, have also been synthesized via telomerization reaction.¹⁶⁻¹⁷

The copolymerization reactions of fluoro-monomers and functional comonomers were investigated under various reaction conditions, including bulk, solution, suspension, and emulsion, using thermal and redox free radical initiators. Tournut¹⁸ summarized the copolymerization results of VDF and non-fluorinated functional comonomers containing at least one functional group. In general, the introduction of the non-fluorinated functional comonomers significantly degrades the properties of the final products. To preserve the desirable fluoropolymer properties during the functionalization reaction, the fluorinated functional comonomers, which have a CF₂=CF- vinyl group that transforms into the perfluorinated polymer backbone after polymerization, is necessary.

Perfluorovinyl comonomers¹⁹ are generally very expensive chemicals, however, they are also the most effective monomers in the copolymerization reactions to achieve good incorporation and high copolymer molecular weight. On the other hand, the trifluorovinyl functional comonomers give low yields and low molecular weight copolymers, which are due to the existing allylic hydrogen atoms in the comonomers. As well-known in free radical polymerization, allylic hydrogen facilitates chain transfer reaction, therefore, reducing the polymer molecular weight and catalyst activity.

2.3.2 Functionalization of fluoropolymers by functional initiators

The radical polymerization of fluoro-monomers using functional initiator carrying functional group(s) was pioneered, by Rice and Sandberg⁹⁻¹⁰ in the 3M Company. They reported the preparation of low molecular weight telechelic VDF/HFP elastomers containing two ester terminal groups by using diester peroxide initiator, as illustrated below in scheme 2.1.

Scheme 2.1

The average functionality of the resulting telechelic VDF/HFP elastomer was not reported. However, it is logical to predict some difficulties in achieving a perfect telechelic structure with the functionality of 2 in each polymer chain, which requires all the propagating radicals involving radical coupling reaction in the termination step.

Recently, a similar strategy was used by Ameduri et al.¹¹ to prepare telechelic VDF/HFP elastomer containing two hydroxy terminal groups, which involves hydrogen peroxide initiator. Several advantages of using hydrogen peroxide initiator include cost effective, high reactivity, and directly forming hydroxy terminal groups. However, many side reactions are also occurring in this polymerization, and the final product contains not only hydroxy terminal groups but also carboxylic acid terminal groups, as well as some unsaturated terminal groups. To improve the hydroxy content, hydroxy fluoroelastomers would require an additional step: the reduction of carboxylic acid into hydroxy end groups using a strong reducer such as LiAlH₄, which sometimes generate more unsaturated double bond and cause the decoloration of the product.

2.3.3 Functionalization of fluoropolymers by Iodine Transfer Polymerization (ITP)

In general, the chemical methods employed to prepare telechelic polymers with two terminal reactive functional groups are very limited, especially in the vinyl polymer cases. Most of the commercial telechelic polymers, such as aliphatic polyesters with two terminal acid or alcohol groups and polyethylene oxide or polypropylene oxide with two terminal alcohol groups, are prepared by polycondensation and ring opening polymerization with suitable initiators, respectively. As discussed above, the preparation of telechelic vinyl polymers usually requires difunctional initiators.

In the late 1970's, Oka et.al.²⁰⁻²¹ disclosed an interesting iodine transfer polymerization (ITP) method (illustrated in Scheme2.2) to prepare telechelic fluoropolymers containing two terminal iodine groups. The chemistry is based on the combination of a reversible addition-fragmentation chain transfer (RAFT) process and an α,ω diiodoperfluoroalkane (I-R_F-I) chain transfer agent, where R_F includes CF₂CF₂, CF₂CF₂CF₂CF₂, CF₂CFCl, and CF₂CF(CF₃). The α,ω -diiodoperfluoroalkane chain transfer agents are usually prepared by two methods, including telomerizations of small diiodoperfluoroalkane molecules and direct organic synthesis. While the direct organic synthesis leads to well-defined diiodo-compounds, telomerizations of diiodoperfluoroalkane molecules usually results in a mixture of α,ω -diiodoperfluoroalkanes with relatively higher molecular weight. The latter process has been commercially scaled up by the Daikin Corp.

In general, CF₂-I bond exhibiting low dissociation energy can be easily cleaved in the presence of various initiators, such as organic peroxides, hydrogen peroxide, diazo compounds, triethyl borane, alkyl phosphines, and various metals. Interestingly, the thermal decomposition temperature of CF₂-I bond is very sensitive to the molecular weight. For I-C₄F₈-I or higher TFE adducts, they are stable up to 260°C for at least 3 days. In contrast, I-C₂F₄-I starts to degrade at about 180°C, whereas I-CF₂-I decomposes below 90°C, and I-CF₂CFCl-I undergoes cleavage at 40°C or at room temperature under sunlight.



Scheme 2.2

As shown in Scheme 2.2, the presence of I-R_F-I chain transfer agent is crucial to achieve reversible addition-fragmentation chain transfer (RAFT) pseudo-living process. The living characteristics are usually demonstrated by the increase of molecular weight with conversion of monomer and relatively narrow molecular weight distribution (Mw/Mn <2). The active CF₂-I groups are always located at both ends of the polymer chain and maintain similar reactivity regardless of the growing polymer's molecular weight. This reaction process has led to an important commercial product, i.e. diiodo-terminated VDF/HFP elastomers with the trade name Dai-E1[®], a high performance fluoroelastomer produced by

the Daikin Company. This telechelic VDF/HFP elastomer is found to be easily cured using organic peroxide and a coagent to give excellent physical properties. Similar RAFT pseudo living process has also been recently applied to styrene and methyl methacrylate (called "degenerative transfer")²²⁻²³ and synthesis of block and graft copolymers.

2.4 Applications of functional fluoropolymers

As mentioned above, fluoropolymers exhibit many unique and desirable physical properties, including high thermal and chemical stability, excellent weatherability, low flammability, low dielectric constant, and low surface energy. The improvement of their key deficiencies in processability, adhesion, and compatibility is crucial to achieve the new polymeric material with a complete package of physical properties for high-end applications.

$$\begin{array}{c|c} - [(CF_2 - CF_2)_n (CF_2 - CF)]_{\overline{x}} & - [(CF_2 - CF_2)_n (CF_2 - CF)]_{\overline{x}} \\ (a) & OCF_2 CFCF_3 & (b) & OCF_2 CF_2 SO_3 H \end{array}$$

Figure 2.1 Molecular structure of Nafion from (a) DuPont and (b) Dow Chemical Company.

So far, only a few functional perfluoro copolymers are commercially available due to the chemical difficulties and cost. The best known functional copolymer may be the Nafion produced by the DuPont and the Dow Chemical company, which is a copolymer of TFE with perfluorinated vinyl ether with a terminal sulfonic acid group (shown in Figure 2.1). These sulfonated PTFE copolymers are commonly used in high performance fuel cells as the proton transport membranes. Under strong oxidative conditions, Nafion exhibits long durability with high proton exchange capacity.

Most of the telechelic fluoro-molecules used in the industry are small perfluorotelechelics that serve as the relevant monomers in the polycondensation and ringopening reactions, which lead to well-architectured fluoropolymer structures. For instance, fluorinated diols are forerunners for the synthesis of high performance polyurethanes, polyesters, and polyethers, while fluorinated diacids are precursors for specialty polyesters and polyamides. Fluorinated diamines are also used as the precursors of preparing high-end polurethanes, polyamides, polyimides and polyureas. Specific applications of these high value added materials are, for example, the fluorinated polyurethane, which exhibits antithrombogenic properties and durability for use in an artificial heart pump;²⁴ the fluoroaromatic diisocyanates is also a useful material for liquid oxygen container and novel adhesive.²⁵ The fluorinated epoxy resins have found interesting applications as hydrophobic and oleophobic coatings.²⁶ The fluorinated polyimides exhibit very interesting properties such as high thermal, chemical and dimensional stability, low moisture uptake, dielectric constant, and coefficients of thermal expansion, good mechanical properties, which are of special importance in electronic space and automotive applications. Fluorosilicones exhibit very good properties at low and high temperatures. They are quite thermostable (up to 380° C), which is 180°C better than the commercially available Silastic[®] produced by the Dow Corning Company.

On the other hand, the telechilc iodo-terminated VDF/HFP elastomer (Dai-E1[®]) is a liquid rubber at room temperature. The two terminal iodine groups provide readily curable sites via heating or radiation to form 3-D network that has excellent heat oil, solvent,
chemical and ozone resistance, and high mechanical strength and low compression set. It is a very useful sealing material employed in O-rings, gaskets, tubes, valves and bellows, linings, protective gloves and shoes. In addition, this iodo-terminated telechelic also provides new route to prepare segmental polymers (block or graft copolymers), which comprises two or more different polymer segments.

2.5 Research objective in functional fluoropolymers

It is evident that the functionalization of fluoropolymers is the most effective way for broadening fluoropolymer applications and enhancing product performances. Technically, these are difficult areas for fluoropolymers, which are known to be inadequate for applications where adhesion, compatibility, wetability, printability, or reactivity (i.e., functional chemical groups) are required. In other words, the lack of chemical functionality has been the major stumbling block prohibiting the applications of fluoropolymers in coating, polymer blends, and composites. If the aforementioned problems could be overcome, it would phenomenally expand the available market for fluoropolymers.

In my immediate research objective of developing high performance electro-active polymers, functionalization of fluoropolymers becomes a crucial step for further improving their electrical properties. As will be discussed in Chapter 4, our new family of fluoro terpolymers (including VDFTrFE/CDFE and VDF/TrFE/CTFE terpolymers) exhibits improved electrical properties, such as high dielectric constant, fast and large electromechanical response at ambient temperature, comparing with those of the VDF/TrFE copolymers. However, there are two concerns for some applications, including the required high voltage for achieving large strain due to the relatively low dielectric constant (< 100) and the insufficient modulus for moving some payloads. To reduce high voltage, two

possible approaches are either by reducing space between the electrodes or increasing the dielectric constant of the material. The former one could be done by connecting fluoro terpolymer with conducting polymer, and the latter one could be achieved by introducing high dielectric constant materials. Both approaches require some reactive functional groups in the terpolymer. In addition, the reactive functional groups in the terpolymers could be used as the crosslinking sites for forming 3-D network and improving mechanic strength.

Unfortunately, the existing chemical methods in the functionalization of fluoropolymers (both "chain end" and "in chain" functionalization routes, discussed above) are very limited in scope, and only very few methods and few functional fluoropolymers have shown commercial value. In the "chain end" functionalization approach, the iodine transfer polymerization (ITP process) has shown many advantages over other processes in the preparation of commercial liquid fluoro-elastomers. This ITP process produces the telechelic iodine terminated fluoropolymers with high molecular weight and narrow molecular weight distribution. However, to ensure the functionality of two in each polymer chain and the high yield of telechelic polymers, the reaction has to be operated under extremely low initiator concentration and very long polymerization time, respectively;²⁰⁻²¹ even though, it is not guaranteed that every polymer chain contains two terminal iodine groups. Therefore, it is very interesting to further explore other reaction conditions that can effectively produce pure fluorinated polymer containing iodine groups at the chain ends. As will be discussed in Chapter 5, we have discovered a new initiator system by the combination of AIBN initiator and mono- or di-iodo compounds as the chain transfer agent, which prepares pure telechelic fluoropolymers with two terminal iodine groups in a broad range of reaction conditions.

On the other hand, the known "in chain" functionalization approach is limited by the suitable functional comonomers that can be effectively incorporated into the fluoropolymers, due to low comonomer reactivity, side reactions, and the prohibited cost of functional comonomers. It is very interesting to explore our boron-based initiators that show good reactivity for a broad range of fluoro-monomers, which may be due to some special interactions between acid B element in the initiator and F elements in the monomer. In addition, the borane-mediated polymerization also exhibits good stability at the propagating sites, which may minimize some undesirable side reactions. Therefore, we may be able to expand the pool of functional comonomers to some common functional monomers.

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Chapter 3

New Family of Ferroelectric Terpolymers based on VDF/TrFE/Chloro-fluoromonomers; Synthesis and Characterization

3.1 Introduction

Ferroelectric polymers that generate mechanical actuation have attracted a great deal of attention due to their many desirable properties, such as flexibility, light weight, high mechanical strength, ease of processability in large area films, and ability to be molded into a desirable configuration. Despite these advantages, most ferroelectric polymers have the disadvantages of low electric field sensitivity, in terms of their dielectric constant, piezoelectric coefficient, electromechanical coupling coefficient, and field induced strain, which limit their applications.

In the past two decades, most research activities in ferroelectric polymers have been focused on ferroelectric fluorocarbon polymers, especially semicrystalline VDF/TrFE copolymers. Many research efforts have been devoted to the general goal of reducing the energy barrier for ferroelectric-paraelectric (Curie) phase transition, and generating large electric-induced mechanical response at ambient temperature. Although the VDF/TrFE copolymer exhibits a high piezoelectric constant ($d_{31} = 15-30 \text{ pC/N}$)¹, the response of the dipoles to the electric field is very low at ambient temperature. The slow response to the electric field is also revealed in a large polarization hysteresis loop (in the frequency range of 1-10 Hz.)², due to the high-energy barrier of switching the dipole direction at ambient temperature. The direct correlation between the reduced polar domain size and lower energy

barrier, shown in ferroelectric ceramic materials,³⁻⁴ led to many attempts to alter the copolymer morphology by creating non-equilibrium states that produced some improved electric responses. The methods include mechanical deformation,⁵ electron-irradiation,⁶ uniaxial drawing,⁷ crystallization under high pressure,⁸ and crystallization under high electric field.⁹

Zhang et al.¹⁰⁻¹¹ recently improved the electron-irradiation process with a systematic study of the radiation conditions, such as dosage, temperature, inert atmosphere, and stretching sample. Some irradiated VDF/TrFE copolymers showed an exceptionally high electrostrictive response (~4%) at ambient temperature and behaved like a relaxor ferroelectric. The polarization hysteresis loop became very slim at room temperature compared to that of the sample before irradiation. However, the polarization was also significantly reduced and the sample became completely insoluble because of the severe crosslinking side reaction during the high-energy radiation. The increase in the hardness of the copolymer sample, due to crosslinking, was also revealed in its electric response. A very high electric field was required (150 MV/m) for the irradiated sample to get a high strain response. It appears that the radiation process not only reduces the polar crystalline domain size, it also produces many undesirable side reactions that increase the amorphous phase and diminish the processability of the sample.

In our laboratory, we have adopted a new chemical strategy for altering the crystalline domains and creating a relaxor ferroelectric behavior of the VDF/TrFE copolymer. The objective is to achieve a processable polymer with controllable phase transition temperature, high dielectric constant, and fast and large electromechanical response at ambient temperature. The chemistry involves homogeneous incorporation of a small amount of bulky chloro-fluoromonomer units into polymer chain. The resulting terpolymers are completely soluble and melt processable, and exhibit high dielectric constant and high electrostrictive response at ambient temperature.

This chapter concentrates on the synthesis of the terpolymers and establishes the correlation between the changes of molecular structure, such as polymer chain conformation, crystallinity and the incorporated termonomer units. To gain a better understanding on the structure-property relationship, a systematical study was performed to synthesize and examine a broad range of the terpolymers containing various bulky termonomers. It was expected that a certain content of slightly bulky groups (in termonomer units) homogeneously distributed along the polymer chain would reduce both the Curie temperature and the activation energy for the phase transition without significant reduction of the overall crystallinity.

3.2 Experimental

3.2.1 Chemicals

Vinylidene Fluoride (VDF) was obtained from the PCR, Inc, Pittsburgh, Pennsylvania. Trifluoroethylene was purchased from the Halocarbon Company, while vinyl chloride (VC), chlorotrifluoroethylene (CTFE), chlorodifluoroethylene (CDFE), and 1,1- and 1,2-chlorofluoroethylene (CFE) were received from the Aldrich Chemical Company. All monomer gases were purified by the freeze-thaw process before they were used. Triethylborane and tributylborane were obtained from the Aldrich Chemical Company, and were used as received. All solvents used in the polymerization studies of the borane initiator were dried and distilled over calcium hydride before they were used.

3.2.2 Polymerization of the terpolymer

In a typical example, 0.05 g of tributylborane initiator was added to a 75-ml autoclave under argon atmosphere. The reactor was then cooled from outside by liquid nitrogen and 16.7 g of VDF, 7.6 g of TrFE, and 1.7 g of CTFE was condensed into the reactor. After introducing a known amount of oxygen (1:0.5 of boron: oxygen), the reactor was warmed to ambient temperature. The bulk polymerization took place at this temperature for 5 hours before vacuum-distilling the unreacted monomers. The resulting terpolymer (6.5 g) was recovered, washed with methanol, and dried. The combination of chlorine analysis and ¹H NMR spectra indicate that the mole ratio of VDF/TrFE/CTFE = 72.2/17.8/10.0 (sample 1 in Table 1). In the case of the trichloroacetyl peroxide system, a known amount of peroxide solution was injected into the reactor that was previously cooled down to the liquid nitrogen temperature. The solvent was then vacuum evaporated to dryness at -30°C. After that, the monomer and comonomer were condensed into the reactor using the same vacuum distillation technique. The reactor was then rapidly warmed up to 0°C, and was held in the ice-water bath for a certain reaction time. The conversion of the polymer was controlled at less than 30% conversion to ensure the constant mole ratio between comonomers.

3.2.3 Polymer characterization

The composition of the terpolymer was determined using the combination of ¹H NMR and elemental analysis provided by the Galbraith Laboratories, Inc. In the ¹HNMR measurement, typically about 128 scans were recorded using about 20 % polymer solution in either d⁷-dimetylsulfoxide or d⁶-acetone, with a sweep width of 30 kHz. Chemical shifts are referenced to an external standard, trimethylsilane (TMS). The infrared spectrum was obtained using the Bio-Rad FTIR-60 spectrometer. A Polymer film was prepared by solution casting from tetrahydrofurane (THF) containing 0.5-1 wt% of polymer. Intrinsic viscosity of terpolymer was measured using the Cannon Ubbelohde viscometer at 25°C in dimethylacetamide solution. The molecular weight and molecular weight distribution of terpolymers were measured by GPC on waters 710B delivery system with 410 refractive index detector and calibrated with monodisperse polystyrene. The solvent was tetrahydrofuran. The melting temperature and heats of fusion were determined by the Perkin-Elmer DSC-7 at the scanning rate of 20°C, and were taken from the second heating cycle. Indium was used to calibrate the melting point and heats of fusion. The commercial copolymers, P(VDF/TrFE) 55/45 and 70/30, were also evaluated in comparison with the synthesized terpolymers.

3.3 Results and Discussions

This section of the chapter discusses the synthesis and the characterization of a family of ferroelectric terpolymers composed of VDF, TrFE, and a chloro-containing termonomers (illustrated in Scheme 3.1) as the crystalline defects into a VDF/TrFE copolymer chain. The chloro-containing termonomers includes chlorotrifluoroethylene (CTFE), 1,1-chlorofluoroethylene (1,1-CFE), 1,2-chlorofluoroethylene (1,2-CFE), 1-chloro, 2,2-difluoroethylene (CDFE), and vinyl chloride (VC). In addition to the above termonomers, a larger size termonomer, hexafluoropropene (HFP) and a smaller size termonomer, vinyl fluorides (VF) are also prepared for comparison.



Scheme 3.1

As discussed, the slightly bulky chlorine atoms (radii of F and Cl are 1.19 and 1.67 Å, respectively) homogeneously located along the VDF/TrFE polymer chain introduce the kinks (with gauche conformation) into the otherwise planar zigzag *all-trans* conformation. As a result, they spontaneously alter the crystalline phase from the ferroelectric β phase (*all-trans* conformation) toward another ferroelectric γ phase ($tttg^+tttg^-$ conformation) without significant reduction of overall crystallinity. The shortened *trans* sequence in the polymer chain significantly reduces the activation energy of the Curie transition, and the terpolymers show high dielectric constant, strong ferroelectricity, and large electromechanical response at ambient temperature.

3.3.1 Synthesis of terpolymers

Prior to our research, some reports had discussed the terpolymerization involving VDF, TrFE and a small amount of termonomers, such as hexafluoropropene (HFP), Chlorotrifluoroethylene (CTFE) and tetrafluoroethylene (TFE) by conventional free radical polymerization processes. The terpolymerization was traditionally carried out in the emulsion or suspension process (heterogeneous reaction condition and water is usually used as reaction medium) using inorganic or organic peroxides as initiator at elevated temperatures.¹³⁻¹⁵

Because of the poor solubility and low diffusion coefficient of fluoro-monomers in water, usually polymerization requires high pressure (10-300 atm.). In the terpolymerization reaction where each monomer gases have different diffusion rate and different comonomer reactivity ratios, it is inevitable to produce terpolymer with inhomogeneous molecular structure and having a broad composition distribution. Indeed, several reports of VDF/TrFE/CTFE terpolymers,¹⁶⁻¹⁷ prepared at elevated temperatures by the conventional process showed a low dielectric constant (about 20 at ambient temperature) over a wide range of temperatures. The dielectric constant is very low compared to that of the terpolymers (50-90) produced by bulk process using the borane/oxygen system (discussed later in Chapter 4). This low dielectric constant implied the inhomogeneity of the terpolymer structure and a broad terpolymer composition distribution. To minimize this inhomogeneity problem of the terpolymer, our idea is to conduct the polymerization in the condensed liquid phase (with homogeneous monomer mixing) at low temperature. Thus, we adopted the bulk (homogeneous) polymerization process, in which all three monomers were condensed into the liquid phase and well-mixed with a low-temperature initiator, an oxidation adduct of trialkylborane and oxygen.¹⁸⁻¹⁹ The homogeneous solution was expected to provide better reaction conditions to achieve an uniform terpolymer structure. As anticipated, the homogeneous distributed termonomer units are crucial to regulate the polymer chain conformation and crystalline phases. Scheme 3.2 illustrates the possible reaction mechanism.



Scheme 3.2

Upon exposure to a controlled quantity of oxygen, the alkylborane (I) is autooxidized at the linear alkyl group to produce ethylperoxyborane (II). The peroxyborane (II) behaves very difference from the regular benzoyl peroxides and consequently decomposed to alkoxy radical (C-O*) and a borinate radical (B-O*) (III) that is relatively stable due to the back donating of the electron density to the empty p-orbital of the boron. In the presence of fluoromonomers, the homolytical cleavage of the peroxide occurs even at very low temperature (-30 °C). The alkoxy radical is very reactive and initiates the radical polymerization at ambient temperature. On the other hand, the borinate radical forms a weak and reversible bond with the growing chain end, which assures the "stable" radical polymerization. During the propagation reaction, a coordination intermediate (IV) may form due to the B-F acid-base complex between the active site and the incoming monomer. Such an interaction may facilitate the insertion of all fluoro-monomers at the active site. It is interesting to note that this chemistry produces fewer impurities, boric acid and butanol, that can be easily removed by methanol washing.

To understand the reactivity ratio of each fluoro-monomer in the bulk process, a series of the copolymerization reactions between the VDF and the various fluoro-monomers were prepared using the tributylborane/oxygen initiator at ambient temperature. Figure 3.1 shows plots of the fluoro-monomer incorporation in the copolymer vs. the comonomer feed ratio. All reactions were terminated at low polymer conversion (<10%) to ensure a constant monomer feed ratio during the polymerization. In general, the fluoro-monomer containing chlorine atom shows high reactivity, especially the CFE with a small molecular size. On the other hand, HFP with no chlorine atom exhibits poor incorporation. Two most interesting CDFE and CTFE monomers showed comparable reactivity with the VDF and a comonomer incorporation ratio that is close to the comonomer feed ratio. Therefore, the copolymers of the VDF and the CDFE or CTFE are further investigated in terms of the reactivity ratio. Figure 3.2 shows the Kelen and Tüdõs plot of the VDF and CDFE copolymer. By calculation, according to this method, the reactivity ratio of the VDF (r_1) is 1.28 and the reactivity ratio of the CDFE (r_2) is 0.44. Conversely, the reported reactivity ratios of the VDF and the TrFE copolymer are 0.7 (r_1) and 0.5 (r_2) respectively. The combination of the homogeneous monomer feed and the close reactivity ratios among the fluoromonomer imply that the terpolymer with a narrow composition and molecular weight distribution can be achieved by this bulk process using the borane/oxygen initiator.



Figure 3.1 The incorporated comonomer content in the polymer chain vs. the comonomer feed ratio in the copolymerization reaction with VDF.



Figure 3.2 Kelen and Tüdős plot for VDF/CDFE copolymer

The other unique properties of the borane intiator, other than produce fewer impurities (boric and butanol) that can be easily removed by methanol washing, is the long-life propagation site. A weak and reversible bond of the borinated radical at the growing chain regulates the insertion of the incoming monomer in a prefered head-to-tail sequence. No chain transfer and termination reactions are expected during the propagation process, which will lead to a linear polymer structure with relatively narrow molecular weight and composition distribution $M_w/M_n \sim 2.5$. Figure 3.3 (a) and (b) show an increase of the intrinsic viscosity with the conversion of the monomer and the GPC curves of a series of the VDF/TrFE/CTFE terpolymers that increase molecular weight with polymerization reaction time, respectively.



Figure 3.3 (a) Plot of the intrinsic viscosity of VDF/TrFE/CTFE terpolymer vs. monomer conversion



Figure 3.3 (b) GPC curves of three VDF/TrFE/CTFE terpolymers prepared by borane/oxygen initiator at various polymerization reaction times: (a) 4, (b) 7, and (c) 10 h.

The composition of the terpolymer was determined by the combination of the ¹H NMR and elemental analysis. Figure 3.4 shows the typical ¹H NMR of several terpolymers. Two major chemical shifts were observed at 2.8-3.2 ppm (-CH₂-CF₂) and 5.3-5.7 (-CHF-CF₂). Their subscribed intensity ratio and the number of protons each unit represents determine the VDF/TrFE ratio in the terpolymer. The small peaks at chemical shift around 4.8-5.2 ppm represent the proton on the same carbon with chlorine atom of the termonomers (CHCl-CF₂, CFH-CHCl, CH₂-CHCl). On the other hand, the chlorine elemental analysis also provides the concentration of the termonomers. The detailed experimental results are summarized in Table 3.1. All terpolymers are high molecular weight (>20,000) polymers, which are completely soluble in common organic solvents and are melt processable at T>150°C. Despite having relatively high concentrations of termonomer units, all of the terpolymers are still semicrystalline thermoplastics with melting temperature >100°C and a crystallinity about 40-50 %.



Figure 3.4 ¹H NMR of the typical terpolymers (a) VDF/TrFE/CDFE, (b) VDF/TrFE/CFE, and (c) VDF/TrFE/VC terpolymers.

	C	ompositio	on (mol%)	Melti	ng temp	Curie temp		
Run no.	VDF	TrFE	Termonomer	Tm(°C)	$\Delta Hm(J/g)$	T <i>c</i> (°C)	$\Delta Hc(J/g)$	
	55.0	45.0	0.0	150.0	25.4	64.0	10.0	
A 1	60.0	26.0	CTEE/A O	140.0	25.7	12 0	65	
A-1	58.0	25.1	CTFE/4.0	140.9	23.7	43.0	0.5	
A-2	50.0	22.0	CIFE/0.9	120.0	21.0	33.3 24.9	1.0	
A-3	59.5 57.2	52.9 21.2	CIFE//.8	125.1	20.3	24.8	1.4 Nama	
A-4	57.5	31.2 42.6	CIFE/11.5		14.8	none	None	
A-3	53.2	42.6	CIFE/4.2	111.1	14.8	none	None	
A-6	64.9	26.1	CTFE/9.0	119.4	19.7	23.7	2.7	
A-7	66.0	22.5	CTFE/11.5	117.2	21.6	25.2	2.5	
A-8	68.8	21.7	CTFE/9.5	109.6	20.8	28.5	1.5	
A-9	72.2	17.8	CTFE/10	107.8	17.8	25.0	0.4	
B-1	63.6	31.4	CDFE/5.0	135.8	24.5	36.9	6.9	
B-2	64.5	30.2	CDFE/5.3	128.7	26.0	31.6	5.5	
B-3	62.5	30.9	CDFE/6.6	126.0	24.0	24.2	3.9	
B-4	69.0	21.2	CDFE/9.8	111.0	20.4	17.9	1.5	
B-5	72.1	21.3	CDFE/6.6	123.7	23.4	24.0	2.5	
B-6	73.2	21.6	CDFE/5.2	131.7	24.6	31.8	2.8	
B-7	77.7	16.2	CDFE/6.1	126.2	126.2 24.0 35.5		3.4	
C-1	55.1	33.1	VC/11.8	103.0	18.2	14.0	2.1	
C-2	58.3	34.7	VC/7.0	132.8	25.3	27.7	4.5	
D-1	60.1	20.3	1 1-CEE/10 6	115 1	51 2/15 1		18	
D-1 D-2	62 A	29.5	1,1-CFE/7 8	138.5	18 5	25.2	1.0	
D-2 D-3	63.4	30.4	1,1-CFE/6.2	141.8	27.5	37.3	8.6	
						10 -		
E-I	65.3	31.4	1,2-CFE/3.3	147.7	24.4	49.5	8.2	
E-2	65.5	30.8	1,2-CFE/3.7	142.2	25.3	30.8	5.0	
E-3	63.9	30.1	1,2-CFE/6.0	138.0	25.0	25.0	4.0	
F-1	66.7	30.5	VF/2.8	161.1	29.9	81.1	16.4	
F-2	53.8	38.8	VF/7.4	171.2	27.9	103.3	9.0	
G-1	52.6	46.6	HFP/0.8	139.3	23.2	49.5	9.3	
G-2	54.3	43.8	HFP/1.8	128.3	18.0	40.6	4.1	
G-3	55.2	42.4	HFP/2.5	120.5	15.6	35.6	2.6	
G-4	63.1	29.9	HFP/7.0	96.3	6.8	28.5	3.3	

 Table 3.1
 A summary of VDF/TrFE/CTFE terpolymers produced by borane/oxygen initiator

3.3.2 Thermal properties

Figure 3.5 shows the DSC curves of several terpolymers containing similar VDF and TrFE contents and about 7 mol % of various termonomers, and a reference VDF/TrFE (55/45 mole ratio) copolymer that has the lowest Curie temperature. The detailed DSC data are summarized in Table 3.1. The smaller fluoroethylene (VF) termonomer fails to reduce the Curie temperature. In fact, both the melting and the Curie temperatures increase with the addition of the VF units. On the other hand, the large HFP units destroy most of the crystallinity, and the VDF/TrFE/HFP terpolymer (>7 mol % HFP) becomes an amorphous elastomer.



Figure 3.5 DSC comparison of VDF/TrFE with various terpolymers of similar termonomer contents (a) 55/45 copolymer, (b) 53.8/38.8/7.4 (sample F-2), (c) 62.4/29.8/7.8 (sample D-2), (d) 58.3/34.7/7.0 (sample C-2), (e) 62.5/30.9/6.6 (sample B-3), (f) 59.3/32.9/7.8 (sample A-3), and (g) 63.1/29.9/7.0 (sample G-4)

The suitable termonomers seem to be the vinyl chloride (VC), chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE) and chlorotrifluoroethylene (CTFE) containing a slightly larger size of the chlorine atom. The terpolymer with about 7 mol % of the randomly distributed chlorine atoms in the polymer chain clearly reduces both the melting and the Curie temperatures and diminishes the activation energy for the phase transition. Despite changing the crystalline phase (discussed in Section 3.3.3), the incorporated chlorine atoms (up to 7 mol %) did not significantly reduce the overall crystallinity. However, each termonomer seems to have some slight difference in serving as the crystalline defect. With less termonomer units of CDFE (~6.6 mol%) and 1,2-CFE (~6.0 mol%), a similar result of lowering the melting and the Curie temperatures, as seen in 7.8 mol% CTFE, was achieved. The reason for this fine alternation is not yet understood. Nonetheless, overall results show that the chloro-containing termonomers are very effective in reducing the Curie temperature to ambient temperature without destroying the overall crystallinity.

It is significant to further investigate the size effects of the termonomer, especially to answer a fundamental question: Is the chlorine atom unique and the only bulky group suitable in the termonomer application?. The next larger size atom is the bromine (radii of Cl and Br are 1.67 and 1.95 Å, respectively). Several VDF/TrFE/BrTFE terpolymers (BrTFE : bromotrifluoroethylene) were, therefore, synthesized and compared with the corresponding VDF/TrFE/CTFE terpolymers. It is logical to predict that the larger size bromine may have larger effects on the crystallinity and the melting temperature of the terpolymer. One major concern is that the larger size bromine atoms may dramatically reduce the overall crystallinity that is crucial to the electric properties. Table 3.2 summarizes the thermal properties of two comparative sets of VDF/TrFE/BrTFE and VDF/TrFE/CTFE terpolymers. With similar

termonomer contents, the Curie temperatures shift to about the same level. However, the Δ Hc (activation energy for phase transition) is higher in the bromine cases, indicating higher energy needed for the conformational change (associated with phase transition) in the bromo-containing terpolymers. The overall crystallinity, based on the Δ H_m (heat of fusion), seems very comparative in each pair. However, the Tm is very different, and the bromo-containing terpolymer shows significant lower Tm than the corresponding chloro-containing terpolymer. The larger size bromine atom may reduce the crystal size, but not the overall crystallinity. One thing to note is the inhomogeneity of the VDF/TrFE/BrTFE terpolymers due to the relatively high reactivity of BrTFE termonomer. Figure 3.6 shows the DSC spectra of VDF/TrFE/BrTFE terpolymers with broad Curie transitions, indicating several modes of the phase transition.



Figure 3.6 DSC spectra of VDF/TrFE/BrTFE (a) sample B-1, (b) sample B-2, and (c) sample B-3

Table 3.2Summary of the VDF/TrFE/BrTFE terpolymers (B series) with different termonomer concentrations compared with theVDF/TrFE/CTFE terpolymers (A series).

Run	Polymer	CTFE/	Monomer conversion (%)		Conversion	Melting temp.		Curie temp.		
no.	composition	BTFE	VDF	TrFE	CTFE/	(%)	Tm	ΔH	Tc	ΔHc
		(mol)			BTFE		(°C)	(°C)	(°C)	(°C)
A-1	60/36/4	0.006	28.1	17.6	22.6	21.8	140.9	25.7	43.8	6.5
A-2	58/35.1/6.9	0.011	31.5	24.7	19.1	26.6	126.6	21.0	33.5	1.6
A-3	59.3/32.9/7.8	0.015	18.2	13.1	10.4	15.0	125.1	20.3	24.8	1.4
A-4	57.3/31.2/11.5	0.020	12.6	8.6	8.0	10.0	111.1	14.8	-	-
B-1	67.8/28.6/3.6	0.006	41.6	22.0	42.4	30.8	126.0	27.5	42.6	10.7
B-2	66.2/27.9/5.9	0.012	37.8	20.0	30.6	23.6	114.1	22.3	31.6	7.1
B-3	67.7/25.4/6.9	0.017	46.8	22.0	28.0	31.5	108.4	19.1	29.8	4.6

To understand the effect of the termonomer concentration on the thermal transition temperatures, the DSC thermograms of the VDF/TrFE/CTFE terpolymers with different CTFE concentrations were compared. Figure 3.7 shows the DSC curves of four VDF/TrFE/CTFE terpolymers with similar VDF/TrFE ratio (samples A1-4) compared with that of a reference VDF/TrFE (55/45 mole ratio) copolymer.



Figure 3.7 DSC comparison of the VDF/TrFE/CTFE terpolymers with different CTFE concentrations and 55/45 VDF/TrFE copolymer. (a) 55/45 VDF/TrFE copolymer, (b) 60.0/36.0/4.0 (sample A-1), (c) 60.0/31.5/6.9 (sample A-2), (d) 59.3/32.9/7.8 (sample A-3), and (e) 57.3/31.2/11.5 (sample A-4).

The relatively sharp melting and Curie phase transition imply a relatively uniform molecular structure. With the increase of the CTFE units, the Curie temperatures of the terpolymers gradually shift toward ambient temperature and the intensity becomes smaller and broader. Whereas the Curie temperature in 3.7(e) almost disappears, this indicates a very small energy barrier for the phase transition. The results are consistent with the electrical response of the terpolymer under electric field (discussed in Chapter 4).

Similar results were also observed in other terpolymer systems. Figure 3.8 and Figure 3.9 show the DSC curves of VDF/TrFE/1,2-CFE and VDF/TrFE/CDFE terpolymers with different termonomer concentrations, respectively. Both sets of DSC curves are also compared with that of the VDF/TrFE (55/45) copolymer. Similar to the VDF/TrFE/CTFE cases, both the melting and Curie temperatures systematically decrease as the termonomer content increases. The activation energy for the phase transition almost completely disappears while the termonomer content reaches > 6 mol%.

Figure 3.10 shows plots of the melting and the Curie temperatures of the VDF/TrFE/CTFE terpolymers vs. the CTFE concentrations. It is clear that as the termonomer content increases the melting and the Curie temperature decreases linearly. Despite the high mole fraction of the CTFE units (about 13 mole %), which reduce the Curie temperature to about 0°C, the melting temperature is still higher than 100°C.



Figure 3.8 DSC comparison of VDF/TrFE/CDFE terpolymers with various CDFE contents and the VDF/TrFE (55/45) copolymer (a) 55/45 VDF/TrFE copolymer, (b) 62.7/33.6/3.6 (not include in Table 3.1), (c) 63.6/31.4/5.0 (sample B-1) and (d) 62.5/30.9/6.6 (sample B-2).



Figure 3.9 DSC comparison of VDF/TrFE/CFE terpolymers with various CFE contents and the VDF/TrFE (55/45) copolymer (a) 55/45 VDF/TrFE copolymer, (b) 65.3/31.4/3.3 (sample E-1), (c) 65.5/30.8/3.7 (sample E-2) and (d) 63.9/30.1/6.0 (sample E-3).



Figure 3.10 Melting temperature (upper line) and Curie temperature (lower line) vs. mole fraction of CTFE in VDF/TrFE/CTFE terpolymer with similar mole ratio of VDF and TrFE (60/40 mol %)

Table 3.3 summarizes the VDF/TrFE/CTFE terpolymers having the Curie temperature at about room temperature and various VDF and TrFE contents. Figure 3.11 compares the melting and the Curie temperatures of these terpolymers versus the VDF content. It is very interesting to see a broad composition range of VDF/TrFE/CTFE terpolymers exhibiting ferroelectric relaxors with the phase transition at ambient temperature and very low energy for phase transition. In general, the terpolymer with the higher VDF content requires higher concentration of the CTFE termonomers. The ideal terpolymer may be the one with 60 mol% VDF and 7.8 mol% CTFE, which shows high melting temperature (T_m) and high crystallinity (ΔH_m).

	Composition (mol%)			Meltir	ng temp	Curi	Curie temp	
Run no.	VDF	TrFE	Termonomer	<i>Tm</i> (°C)	$\Delta Hm(J/g)$	Tc(°C)	$\Delta Hc(J/g)$	
1	0.0	100.0	-	180.0		-	-	
2	53.2	42.6	CTFE/4.2	111.1	14.8	none	none	
3	55.6	36.1	CTFE/8.3	124.6	21.2	none	none	
4	59.3	32.9	CTFE/7.8	125.1	20.3	24.8	1.4	
5	64.9	26.1	CTFE/9.0	119.4	19.7	23.7	2.7	
6	66.0	22.5	CTFE/11.5	117.2	21.6	25.2	2.5	
7	68.8	21.7	CTFE/9.5	109.6	20.8	28.5	1.5	
8	72.2	17.8	CTFE/10	107.8	17.8	25.0	0.4	
9	100.0	0.0	-	168.0	48.0	-	-	

Table 3.3A summary of the VDF/TrFE/CTFE terpolymers comprising various VDF/TrFEmole ratio and the CTFE content that shift the Curie temperature to about room temperature.



Figure 3.11 Melting tepmerature (upper curve) and Curie temperature (lower line) vs. mole fraction of VDF in VDF/TrFE/CTFE with similar CTFE content

3.3.3.1 FTIR

The changes of the chain conformation and the crystalline structure that occur upon introducing the termonomer in the polymer chain are very intriguing. The FTIR is one of the most powerful tools to examine this conformation change. Figure 3.12 compares the infrared spectra of several terpolymers containing similar VDF (~60 mol%) and TrFE contents and about 7 mol% of various termonomers to a reference VDF/TrFE (60/40 mole ratio) copolymer at ambient temperature. In general, two strong absorption bands at 1288 cm⁻¹ and 850 cm⁻¹, intrinsic to the CF₂ vibration and CH₂ rocking modes²⁰⁻²² of the *all-trans* ($t_{m>4}$) conformation in the β phase, significantly reduce their intensities. On the other hand, two weak absorption bands centered at 614 and 505 cm⁻¹ corresponding to the CF₂ vibration band of tg^+tg^- conformation in the α phase and $tttg^+tttg^-$ conformation in the γ phase, respectively, become more visible. It is interesting to note that the most profound change in the VD/TrFE/CFE terpolymer with 7.8 mol% CFE (Figure 3.12e) shows an intense 614 cm⁻¹ band $(tg^+tg^- \text{ conformation})$ and the almost disappearance of all 1288, 850 and 505 cm⁻¹ bands $(t_{m>4} \text{ and } tttg^+tttg^- \text{ conformations})$. This is probably because the VDF/TrFE/CFE needs less termonomer unit to alter the crystalline structure. The 7.8 mol% CFE is far beyond and probably the crystalline structure has been changed from the ferroelectric β phase to nonferroelectric α phase. This means that the CFE probably is the most effective termonomer in altering the chain conformation. The experimental results from the DSC and the FTIR indicated that the termonomer units needed for altering the crystalline structure of the terpolymers are in the ascending order of CTFE~VC > CDFE > CFE.



Figure 3.12 Comparison of the FTIR spectra of VDF/TrFE/ter-monomers with similar composition (a) 60/40 VDF/TrFE copolymer, (b) 58.3/34.7/7.0 VC (sample C-2), (c) 62.5/30.9/6.6 CDFE (sample B-3), (d) 59.3/32.9/7.8 CTFE (sample A-3), and (e) 62.4/29.8/7.8 CFE (sample D-2).

To study how the polymer structure changes with the termonomer concentration, a series of FTIR spectra of terpolymers with about 60 mol% VDF and various different CTFE concentrations were compared. Figure 3.13 shows these FTIR spectra of the terpolymers. With the increase of the CTFE content, the absorption bands (1288 and 850 cm⁻¹) for the *all-trans* conformation gradually decrease and the CF₂ vibration bands (614 and 505 cm⁻¹) for the tg^+tg^- and the $tttg^+tttg^-$ conformations relatively increase in intensity. At about 11.5 mol% of CTFE, the vibration bands for the *all-trans* sequences are almost completely transformed to tg^+tg^- and $tttg^+tttg$ conformations. The general trend was also observed in other terpolymers containing the VC, CFE, and the CDFE terpolymer with about 60 mol% VDF and various CDFE concentrations. The results indicated a similar trend, as the CDFE units

increase, the vibration bands for *all-trans* gradually decrease and the vibration bands of $tg^+tg^$ and $tttg^+tttg$ conformation gradually increase in intensity.



Figure 3.13 FTIR spectra of VDF/TrFE/CTFE terpolymers of different CTFE contents comparing with VDF/TrFE copolymer (a) 55/45 VDF/TrFE copolymer, (b) 60.0/36.0/4.0 (sample A-1), (c) 60.0/31.5/6.9 (sample A-2), 59.3/32.9/7.8 (sample A-3), and (e) 57.3/31.2/11.5 (sample A-4).



Figure 3.14 FTIR spectra of VDF/TrFE/CDFE terpolymers with different CDFE contents comparing with VDF/TrFE copolymer (a) 55/45 VDF/TrFE copolymer, (b) 63.6/31.4/5.0 (sample B-1), (c) 64.5/30.2/5.3 (sample B-2) and (d) 62.5/30.9/6.6 (sample B-3).

The incorporation of the termonomer units seems to create the kinks (with gauche conformation) along the otherwise *all-trans* (zigzag) conformation. The postulated mechanism, upon introducing the termonomer units, is schematically drawn in Scheme 3.3. The introductions of the termonomer units into the copolymer chain (originally possess *all-trans* conformation) create gauche defects, which will shorten the long *trans* sequences of the copolymer. Upon an increase of the termonomer contents, more gauche bonds are created and, at certain termonomer concentration, the long *trans* sequences are completely transformed into the mixture of *tt*, tg^+ and tg^- conformations.



Scheme 3.3

It is very interesting to note that the gradual shift from the *all-trans* conformation (β phase) to the $tttg^+tttg^-$ conformation (γ phase) in the terpolymers coincides with the gradual reduction of the Curie temperature and the activation energy for the phase transition. The correlation implies that the length of the *all-trans* sequence between the two gauche structures plays an important role in the crystalline phase transition. With proper choice of

the termonomer content, we are able to control the Curie phase transition at the application temperature.

Thermal effect on the chain conformation of the terpolymer, especially around the Curie temperature, was also studied. Figure 3.15 shows a series of the infrared spectra of a VDF/TrFE/CTFE terpolymer film (with 7.8 mol% CTFE) annealed at various temperatures. As the annealing temperature increases to near Curie temperature (at about 25°C as determined by the DSC), the *all-trans* conformation bands (1288 and 850 cm⁻¹) gradually decrease in intensity whereas the tg^+tg^- (614 cm⁻¹) and the $tttg^+tttg^-$ (505 cm⁻¹) bands gradually increase in intensity. These slow changes indicate the gradual process of the phase transition in the terpolymer. At about 50°C, the *all-trans* sequences are completely transformed to tg^+ , tg^- , tt sequences. It is interesting to note that the whole spectra pattern is reversible during heating and cooling cycles. The overall results indicate the reversible process of the polymer chain conformation at the Curie temperature, from predominately low temperature mixed β phase and γ phase to high temperature mixed α phase and γ phase. The general trend is also observed in other terpolymers containing the VC, CFE and CDFE termonomer units. Figure 3.16 shows temperature dependence of the *all-trans* and *tttg⁺tttg⁻* conformation bands in infrared spectra of the VDF/TrFE/CDFE terpolymer that has T_c about 40°C. The All trans conformation gradually disappears as the temperature increases from 30°C to 85°C.



Figure 3.15 FTIR spectra of temperature dependence of 59.3/32.9/7.8 VDF/TrFE/CTFE terpolymer (sample A-3) (a) heating cycle and (b) cooling cycle.



Figure 3.16 FTIR spectra of temperature dependence of 63.6/31.4/5.0 VDF/TrFE/CDFE terpolymer (sample B-1).

3.3.3.2 X-rays

The morphological change of the terpolymer can be analyzed via small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD) using synchrotron radiation. The difference in density between the crystalline and the amorphous region gives rise to the scattering at small angle, whose integrated intensity is related to the microstructure parameters (volume fraction of crystalline phase, densities of crystalline and amorphous phase). The SAXS patterns of semi-crystalline also provide a correlation peak. It is usually assumed that the scattering maximum arises from spatial correlation of the lamella. The Bragg spacing thus can be derived, which gives an estimate of the average distance between the crystal lamella, whereas, the proportion of amorphous, ferroelectric and paraelectric phase, lattice parameters, and the coherence length of the crystalline regions can be obtained from the Bragg reflection at wide angle. A degree of crystallinity can be determined from the

WAXD data using curve-fitting program where the diffraction profile was separated into crystalline and amorphous halo. The apparent (bulk) crystallinity was defined as the ratio of the area under the resolved crystalline peak to the total area.

In this thesis, all SAXS data and analysis were measured and provided by Dr. Edward Balizer (Naval Surface Warfare Center, MD). The experiments were performed at the Advanced Polymer Beamline (X27C) in the National Synchrotron light source (NSLS), Brookhaven National Laboratory using terpolymers that were synthesized in our laboratory. The WAXD data were partly provided by Dr. Edward Balizer and partly obtained from our own measurements. Figure 3.17 shows a typical WAXD curve of the VDF/TrFE/CTFE terpolymer films, which has the T_c at about ambient temperature as indicated by the DSC, annealing at 120°C. The WAXD curve shows two unresolved peaks at 20~18.5 Å, which presumably is the (110) and (200) reflections of the ferroelectric phase of the terpolymers.



Figure 3.17 Typical WAXD spectra of VDF/TrFE/CTFE terpolymer films, (a) 55.6/36.1/8.3 (Tc~20°C), (b) 72.2/17.8/10.0 (Tc~25°C), and (c) 61.4/25.3/13.3 (Tc~19°C).
The crystallinity of the VDF/TrFE/CTFE terpolymers, which was obtained from the ratio of the area under the crystalline peak to the total area from the WAXD experiment, was summarized in Table 3.4. Typically, the VDF/TrFE/CTFE terpolymers have a crystallinity in the range of 45-55% depending on the crystallization temperatures. The optimum crystallization temperature at which the terpolymers have the highest crystallinity is about 105-110°C, which is possibly because of the kinetic favor. As the crystallization temperature (Tc) gets close to the equilibrium crystallization temperature (Tm°), the kinetic is less favorable and, therefore, less crystallinity is observed.

Table 3.4Comparison of the % crystallinity of VDF/TrFE/CTFE terpolymers fromWAXD, crystallized at different temperatures (data obtained from Dr. Edward Balizer).

Crystallization	% Crystallinity (WAXD)					
Temperature (°C)	Sample (a)	Sample (b)	Sample (c)			
100	44.9	48.2	44.9			
105	53.3	55.3	56.7			
110	55.8	53.2	42.6			
115	52.1	38.3	38.9			

VDF/TrFE/CTFE terpolymers (a) 59.3/32.9/7.8, (b) 54.4/35.4/10.2, and (c) 66/22.5/11.5

Figure 3.18 shows temperature dependence of the crystallinity of the three VDF/TrFE/CTFE terpolymers, which has the Curie temperature near room temperature (determined by the DSC), crystallized at their optimum conditions. Basically, the % crystallinity of terpolymers are in the range of 45-55% at ambient temperature and slightly decreases as the temperature increases until it reaches near 80°C, where the % crystallinity significantly drops because the crystals start to melt. It is noted that in the 66/22.5/11.5 VDF/TrFE/CTFE terpolymer, the % crystallinity increases as a sample was annealed at the temperature higher than the Curie temperature (T_c).



Figure 3.18 Crystalline fraction of VDF/TrFE/CTFE terpolymers crystallized at their optimum conditions as a function of temperature (a) 59.3/32.9/7.8, (b) 54.4/35.4/10.2, and (c) 66.0/22.5/11.5 (data obtained from Dr. Edward Balizer).

To understand how the termonomer affects the crystalline unit cell, the change of the lattice spacing of the terpolymer was monitored as a function of temperature. At ambient temperature, lattice spacings (d_{110} , d_{200}) of the VDF/TrFE/CTFE terpolymers are in the range of 4.8-4.85Å, which is a little bit larger than that of the VDF/TrFE copolymer (~ 4.5-4.6 Å) of a similar composition. This indicates that the termonomer has some effects on the lattice spacing, possibly that the chlorine atoms are embedded in the unit cells. Figure 3.19 shows temperature dependence of the lattice spacing of one of the VDF/TrFE/CTFE terpolymer region between RT-50°C, the lattice spacing, corresponding to the lattice spacing of the ferroelectric phase, drastically increases as the temperature increases. A steep of a slope primarily

accounts for the phase transition of the terpolymer, which is completed at about 50°C. Unlike the phase transition behavior observed in the 60/40 VDF/TrFE copolymer, which the lattice spacing changes discontinuously at the Curie transition, the solid phase transition (ferroelectric to paraelectric) of the terpolymer occurs continuously. This is probably due to the diffuse ferroelectric phase transition of the terpolymer (broadening of the Curie temperature in the DSC). As a result, the process of the phase transition gradually occurs. As temperature further increases, the lattice spacing corresponding to the lattice spacing of the paraelectric phase linearly increases with the temperature, mostly due to the expansion of the crystal.



Figure 3.19 Temperature dependence of lattice spacing of the 66.0/22.5/11.5 VDF/TrFE/CTFE terpolymer crystallized at its optimum conditions (data obtained from Dr. Edward Balizer).

The lamella thickness is one of the most effective ways to show whether or not the crystalline size of the VDF/TrFE copolymer has been changed after the incorporation of the termonomers. Table 3.5 summarizes the lamellar thickness of the VDF/TrFE/CTFE terpolymers crystallized at their optimum conditions compared with the VDF/TrFE copolymers. Basically, the lamella thickness at ambient temperature of the VDF/TrFE/CTFE terpolymers is smaller than that of the copolymers. This indicates that as we incorporated the termonomer into the VDF/TrFE copolymer chains, it serves as defects and cuts down the sequence of the crystallizable polymer chains resulting in smaller crystalline size. Figure 3.20 shows the temperature dependence of the lamella thickness of one of the VDF/TrFE/CTFE terpolymers, which shows the Curie temperature at about 25°C, as indicated by the DSC, crystallized at its optimum conditions.

Table 3.5 summarizes the lamellar thickness at ambient temperature of the VDF/TrFE/CTFE terpolymers crystallized at their optimum conditions compared with the VDF/TrFE copolymers.

VDF/TrFE/CTFE	Lamella thickness (Å)
composition	
55/45/0	~300 ^a
65/35/0	~325 ^b
54.4/35.4/10.2	210
59.3/32.9/7.8	193
66/22.5/11.5	168

(a) and (b) data obtained from ref 23 and 24, respectively

In the ferroelectric phase (25-50°C), the lamella thickness of the terpolymer slowly increases with the temperature, which may be due to the constrained network of the stacked lamella linked by amorphous chains. The lamella thickness increases sharply in the

temperature region of 60-80°C. The chain mobility is greatly enhanced at higher temperature thus enabling the reorganization of the microstructure.

The lamella thickness keeps increasing as the temperature further increases, the cause of which is uncertain. A possible explanation may be due to the coexisting of the thin lamella crystallites with stacks of thick lamella. Upon heating, thin crystals melt thus the initial microstructure is replaced by one that has similar thickness resulting in an increase of the average lamella thickness. Another explanation may be due to the melting and the recrystallization of the thin lamella into thicker lamella.



Figure 3.20 The change of the lamella thickness of the 66.0/22.5/11.5 VDF/TrFE/CTFE terpolymer (sample A-7), crystallized at its optimum conditions, as a function of temperature (data obtained from Dr. Edward Balizer).

3.4 Conclusions

In this chapter, we demonstrated a novel chemical method, involving a combination of a borane/oxygen low temperature initiator and a bulk process, to prepare a new family of ferroelectric fluoroterpolymers, composed of the VDF, TrFE and a chloro-containing third monomer. Similar reactivity ratios between the VDF, TrFE and the termonomer, especially chlorodifluoroethylene (CDFE) and chlorotrifluoroethylene (CTFE), led to the terpolymer with relatively narrow molecular weight and the composition distribution. The experimental results demonstrated that the homogeneously incorporated chlorine-containing termonomer in the VDF/TrFE copolymer chain with a controlled quantity (~7mol% of termonomer units) alters the crystalline phase from ferroelectric β phase (t_{m>4} conformation) toward ferroelectric γ phase (*tttg*⁺*tttg*⁻ conformation), without significant reduction of the overall crystallinity. The stable ferroelectric γ phase in the terpolymer results in a low Curie phase transition temperature with a low energy barrier. The homogeneous incorporation of a controlled amount of chlorine atoms into the VDF/TrFE copolymer not only changes the polymer structure but also the morphology, for instance the reduction of the thickness of the ferroelectric crystalline domains. During the phase transition, the continuous transformation of the polymer conformation and the crystalline phase are evidenced by the FTIR results, and the expansion of the crystal is evident by the SAXS experiments.

3.5 References

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Chapter 4

New Family of Ferroelectric Terpolymers based on VDF/TrFE/Chloro-fluoromonomers; Mechanical and Electrical properties

4.1 Background

It is generally accepted that the electrical properties of the PVDF and its copolymer originated from the polar crystalline domain. Although the VDF/TrFE copolymer exhibits high piezoelectric and high pyroelectric constant $(d_{31} = 15-30 \text{ pC/N})$,¹ the response of the dipole to the electric field is very low at ambient temperature. The slow response to electric field is also revealed in a large polarization hysteresis loop (in the frequency range of 1-10 Hz),² due to the high energy barrier of the switching of the dipole direction at ambient temperature. The direct correlation between the reduced polar domain size and lower energy barrier, shown in ferroelectric ceramic materials,³⁻⁴ led to many attempts to alter the copolymer morphology. The methods include mechanical deformation,⁵ electron irradiation,⁶⁻⁷ uniaxial drawing,⁸ crystallization under high pressure,⁹ and crystallization under electric field.¹⁰ Although electron irradiation is an effective method to reduce the polar crystalline domain size, this process involves very complicated chemical reactions including crosslinking between the chains, chain session, and/or dehydrofluorination creating the unsaturated chain ends. More importantly, this process is not cost effective. The strain response although high (~4%), high electric field is also needed (~150 MV/m) because of the hardness of the sample. Furthermore, the polymer after irradiation becomes intractable, which limits its fabrication capacity.

In the previous chapter, we reported a new chemical approach to produce the soluble and melt processable polymer by incorporating some chlorine-containing third monomers into the VDF/TrFE copolymer chain. The incorporation of the chlorine atoms homogeneously distributed along the polymer chain not only alters the crystalline structure but also the morphology of the polymer. Consequently, the terpolymer exhibits a stable ferroelectric phase with reduced Curie temperature and small energy barrier for the phase transition. In this chapter, we will evaluate the mechanical and electrical properties of the terpolymers, including polarization, dielectric constant, and strain vs. stress.

4.2 Experimental

4.2.1 Materials

For the electrical measurement including the polarization, dielectric constant and field induced strain, polymer films (20-25 μ m thickness) were prepared either by solution casting on a glass slide from *N*, *N*- dimethylformamide solution containing 8-10% polymer or melt-pressing polymer powder at 200°C. The polymer films ware annealed at 20°C below their melting temperature under vacuum for 5 h. Gold (<1 μ m thickness) was sputtered on both surfaces of the polymer film as two circular electrodes (7.07 mm² in area). For the mechanical property measurements, the polymer film (thickness about 30 μ m) was prepared in the same way and was cut into dog-bone pieces with dimensions of 1.0x4.0 cm.

4.2.2 Instrumentation

The polarization hysteresis loop was performed using the Sawyer Tower circuit at the frequency of 1 Hz and 10 Hz. A high voltage up to several kV was applied to the sample electrodes in forms of triangular waves by a function generator and a high voltage amplifier.

The longitudinal strains of terpolymers were determined by measuring the displacement of the polymer film thickness using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR830). Gold sputtered samples with thickness of about 20-25µm and a diameter of 2.5 mm were used. Electric field, generated by a Trek 609C-6 high voltage DC amplifier, in the range of 20-150 MV/m were applied across the polymer film thickness using an amplified ramp waveform at 1 Hz. Since the strain of the polymer is affected by the stress from the polymer film holder, due to the softness of polymers compared to ceramics, under each electric field, the actual strain was determined by extrapolating the plot of the stress vs. inverse strain to zero stress. The dielectric constant was measured by multifrequency LCR meter (HP4284A impedance analyzer) equipped with a temperature chamber. The heating rate was 2° C/min and the frequency was range from 1 kHz to 1 MHz.

4.3 **Results and discussions**

4.3.1 Mechanical properties

Mechanical testing, including young modulus, strain, and toughness, was performed on an Instron tensile testing apparatus using the average values of six samples. Figure 4.1 shows one typical example of a VDF/TrFE/CTFE terpolymer with 60/32.5/7.5 composition. Table 4.1 summarizes all mechanical data for several VDF/TrFE/CTFE terpolymers. In general, a terpolymer has high strain and high toughness, but the Young modulus is not as high as that of the VDF/TrFE copolymer. Their Young moduli are in the range of 0.1-0.2 Gpa compared to about 1 Gpa in the copolymer, which may be due to the reduced crystal size in the terpolymers.

Sample	Yield strain	Max.stress	Max.Strain	Toughness	Modulus	BRK.	BRK.
no.	(mm/mm)	(Mpa)	(mm/mm)	(Mpa)	(Mpa)	stress	strain (%)
						(Mpa)	
A-1	0.06	20.8 ± 2.6	9.5 ± 0.9	96.0 ± 17	264.8 ± 8.8	20.8 ± 2.5	943.1 ±87
A-2	0.07 ± 0.1	7.4 ± 0.5	0.09 ± 0.01	9.6 ± 2.6	201.5 ±8.6	4.2 ± 0.1	-
A-3	0.07 ± 0.01	24.4 ± 3.0	8.0 ± 0.3	84.4 ± 11.4	210.8 ± 7.8	24.4 ±2.9	794.9 ±59
A-4	0.06 ± 0.01	8.1 ± 0.5	0.07 ± 0.01	10.2 ± 1.8	197.9 ±9.9	4.4 ± 1.1	210.6 ± 84
A-5	0.06 ± 0.01	6.6 ± 0.3	10.1 ± 0.5	42.6 ± 3.3	151.5 ±23.6	6.6 ± 0.3	959.2 ±54
A-6	0.07 ± 0.01	6.9 ± 0.3	9.6 ± 0.6	45.5 ± 3.2	156.2 ±29.0	6.8 ± 0.3	879.6 ±42
A-7	0.05 ± 0.01	4.8 ±0.1	0.08 ± 0.02	14.2 ± 1.2	136.2 ±43.3	2.6 ±0.2	517.6 ±33

 TABLE 4.1
 summaries of mechanical data of VDF/TrFE/CTFE terpolymers

Sample compositions: A-1 53.5/42.8/3.8, A-2 59.9/32.8/7.3, A-3 59.3/32.9/7.8, A-4 64.9/26.1/9.0, A-5 54.4/35.4/10.2, A-6 54.6/35.1/10.3, and A-7 57.3/31.2/11.5.



Figure 4.1 shows mechanical three testing curves of VDF/TrFE/CTFE (60.0/32.5/7.5) terpolymer.

4.3.2 Electrical properties

Electrical properties of terpolymers were evaluated via three measurements including dielectric constant, polarization hysteresis loop and field induced strain. Experimental results are summarized in Table 4.2. In general, the terpolymer with about 7 mol% termonomer content exhibits very slim hysteresis loop with high dielectric constant, and the dielectric peak (the Curie temperature) shows near ambient temperature, which is well below the dielectric peak observed in the 55/45 VDF/TrFE (60°C). The detailed comparison shows some dielectric constant dependence on the termonomer used. The dielectric constant at the peak of >90 was observed in some of the VDF/TrFE/CDFE and VDF/TrFE/CFE terpolymers. Probably because of less destructive dipoles from these termonomers compared to that of the CTFE. In addition, the mechanical stretching of the polymer film, usually very important for increasing the dielectric constant in the VDF/TrFE copolymers, is not necessary in these terpolymers. The effective orientation of dipoles under an electric field may be attributed to the low phase transition energy, which occurs at near ambient temperature.

Sample No.	Composition/ Termonomer	Diel 1 l	ectric kHz	Dielectric 100kHz		Polarization 100Mv/m, 25°C, 10 Hz	
		DK	Peak (°C)	DK	Peak (°C)	Pmax (mC/m ²)	Ec (MV/m)
A-1	60.0/36.0/4.0 CTFE	79.9	52.9	67.1	54.7	85	21.8
A-2	58.0/35.1/6.9 CTFE	69.2	38.5	59.8	40.9	110	55.9
A-3	59.3//32.9/7.8 CTFE	74.4	32.5	63.8	37.9	70	11.5
A-4	57.3/31.2/11.5 CTFE	50.7	25.3	43.3	34.3	45	39.4
A-5	55.6/36.1/8.3 CTFE	52.3	33.8	44.4	39.1	42	7.5
A-6	64.9/26.1/9.0 CTFE	70.8	30.4	58.6	40.3	55	9.0
A-7	72.2/17.8/10 CTFE	61.4	38.7	53.7	41.3	82	19.6
B-1	63.6/31.4/5.0 CDFE	91	40	76	48	80	28.9
B-2	64.5/30.2/5.3 CDFE	82	34	66.6	43	60	19.7
B-3	62.5/30.9/6.6 CDFE	69.3	33	56.3	42	50	11.8
B-4	72.2/21.3/6.5 CDFE	64.3	36.3	56.2	41.0	60	18.9
B-5	73.3/21.6/5.1 CDFE	63.4	50.2	58.5	50.1	85	50.8
B-6	77.6/16.2/6.1 CDFE	60.7	50.5	55.8	50.3	65	42.0
C-1	58.3/34.7/7.0 VC	82.3	35.4	66.5	45.2	55	13.2
D-1	60.1/29.3/10.6/1,1CFE	36.4	26	32.7	44.6	47	57.2
D-2	62.4/29.8/7.8/1,1CFE	39.0	62	37.3	61.8	70	63.1
D-3	76.1/19.9/4.0 /1,1CFE	54.7	55.9	51.7	60.5	100	59.5
E-1	65.3/31.4/3.3/1,2 CFE	91.1	51.0	81.3	50.9	75	45.1
E-2	65.5/30.8/3.7/1,2 CFE	93.4	37.8	77.5	47.2	72	23.5
E-3	63.9/30.1/6.0/1,2 CFE	82.7	30.9	68.3	45.6	58	5.3
F-1	66.7/30.5/2.8 VF	79.5	86.5	71.9	88.9	-	-

Table4.2. Summary of electric properties of terpolymers that consist of VDF/TrFE and several termonomers.

4.3.2.1 Polarization

To understand the effect of the termonomer on the response of the electric field, polarization hysteresis loops of two terpolymers with different termonomer contents were compared. Figure 4.2 compares the polarization hysteresis loops of two VDF/TrFE/CTFE

terpolymers (sample A-1 and A-5), containing 4.0 and 8.3 mol% of CTFE units, with that of the corresponding VDF/TrFE (55/45 mole ratios) copolymer.



Figure 4.2 The comparison of polarization hysteresis loops between two VDF/TrFE/CTFE terpolymers (samples A-1 and A-5) and VDF/TrFE (55/45 mole ratios) copolymer.



Figure 4.3 The dependence of the coercive field (Ec) on the CTFE ter monomer units incorporated in VDF/TrFE copolymer chain.

The hysteresis loops of the terpolymers are far slimmer than that of the copolymer. As the termonomer units increase, the hysteresis loop becomes narrower, and both the coercive field (E_c) and the remanent polarization also become smaller. The reduction of the remanent polarization is probably due to the destructive dipole created by the incorporated termonomer units along the polymer chain. Figure 4.3 shows the plot of the coercive field (E_c) vs. the termonomer content. As the termonomer units increase, the coercive field decreases, having the minimum value at about 8 mol%. Above 8 mol% CTFE units, where the terpolymers are in paraeletric phase at the measurement temperature (25°C), the polarization loop of the terpolymer is supposed to show a double hysteresis. However, the apparent polarization shows one big loop with the round edge. The combination of the fast relaxation time and an additional phase transition of the terpolymer possibly make a big round loop instead of the double hysteresis. The round edge at high electric field is possibly contributed to the loss conduction.

Figure 4.4 shows several polarization hysteresis loops of the VDF/TrFE/CDFE terpolymers with different CDFE concentrations. Similar results to that of the VDF/TrFE/CTFE terpolymer were observed, the coercive fields (E_c), as well as the overall polarization (P_{max}), decrease as the CDFE concentration increases. In general, other terpolymers containing CTFE, CDFE, CFE, and VC units show a similar trend. With the initial increase of the termonomer units (before T_c reaching room temperature), the polarization hysteresis loop becomes narrower, as well as the reduction of coercive field (E_c) and remanent polarization (P_r). Figure 4.5 compares the polarization hysteresis loop of several terpolymers that have similar terpolymer composition (about 7 mol% termonomer content) and different termonomer units, including CTFE, CDFE, CFE, and VC.



Figure 4.4 Comparison of the polarization hysteresis loop of the VDF/TrFE/CDFE with different termonomer concentrations.



Figure 4.5 The comparison of the polarization hysteresis loops of several terpolymers, which consist of about 60/40 VDF/TrFE and about 7% termonomers including CTFE, CDFE, 1,1-CFE and VC.

The coercive fields (E_c) of all terpolymers are in the range of 10-15 MV/m, which are very narrow, compared to that of the corresponding VDF/TrFE (60/40) copolymer (~50 MV/m). The overall maximum polarization of terpolymers are in the range of 50-60 mC/m², which are lower than that of the 60/40 VDF/TrFE copolymer (P_{max} ~80 mC/m²). The reduction of dipoles in the terpolymer is due to the destructive dipoles from the third termonomers and are in the ascending order of CTFE > CDFE > CFE > VC.

It is also very interesting to study the temperature dependence of polarization hysteresis loop of the sample that has the Curie temperature lower than ambient temperature, and to observe the change of the polarization hysteresis loop as the temperature goes down to its Curie temperature. Figure 4.6 shows the temperature dependence of the polarization hysteresis loop of the 57.3/31.2/11.5 VDF/TrFE/CTFE terpolymer, whose Curie temperature could not be observed by the DSC measurement. The hysteresis is very big at ambient temperature for the reason mentioned above. As the sample was cooled down, as expected, the coercive field began to decrease and the hysteresis loop appeared to become slimmer. At 0°C (believed to be the Curie temperature of this sample), the terpolymer has a very slim loop. However, as the temperature goes lower than 0°C, the polarization level starts to decrease. This is probably because the dipoles of the terpolymer are now frozen as the temperature is lower than its glass transition temperature (~-20 °C), therefore, it can not respond to the electric field very well, resulting in the low polarization.



Figure 4.6 The temperature dependence of polarization hysteresis loop of 57.3/31.2/11.5 VDF/TrFE/CTFE terpolymer (sample A-4)

It is significant to study the effects of both the annealing and the stretching processes on the polarization of the terpolymer, especially the ones with high T_c and large polarization hysteresis loop. Figure 4.7 compares the polarization hysteresis loops of 60.0/36.0/4.0 VDF/TrFE/CTFE terpolymer with different processes, without annealing, annealing and stretching. The sample without annealing and without stretching shows a bigger polarization hysteresis loop with lower polarization level, whereas the samples with either annealing or stretching show slimmer loops and higher polarization levels. The lower polarization in the sample without annealing could account for the lower crystallinity. Stretching and annealing processes enhance the crystallinity of the terpolymer and therefore the polarization level increases. The decrease of the coercive field in both the annealing and the stretching samples is probably due to the arrangement of dipoles in similar direction and, therefore, less energy is needed to force the dipoles to align with the electric field . It is concluded that the annealing process is necessary in this terpolymer to enhance the crystallinity, and the streching process also has some effect to the crystalline structure. However, the stretching process is not necessary for the terpolymer with T_c near room temperature due to its reversible ferroelectric phase with good response to the applied electric field.



Figure 4.7 The comparison of polarization hysteresis loop of the VDF/TrFE/CTFE terpolymers (sampleA-1) with different post treatments, without annealing, annealing and stretching.

As mentioned in the previous chapter, the VDF content in the terpolymer affects both the melting and the Curie temperatures. It is curious to know whether or not the polarization hysteresis loop of the terpolymer is also affected by the VDF content. Figure 4.8 compared several polarization hysteresis loop of the VDFTrFE/CTFE terpolymers with different VDF contents. All samples had Curie temperature of about room temperature designated by the DSC measurement. It is well known that the strong dipole in the constituted CF₂ units of the VDF mostly attributed to the polarization of the VDF/TrFE copolymer. As expected, the terpolymers with higher VDF content showed higher polarization, but it aslo increased the coercive field increases. With higher units of the VDF segment in the polymer chain, more energy is needed to arrange the dipoles both within the individual chain and within the crystal, resulting in a bigger hysteresis loop. Figure 4.9 shows plots of the polarization and the coercive field as a function of the VDF content. It is clearly seen that as the VDF content increases, both the polarization and the coercive field increase due to the reason stated above.



Figure 4.8 The comparison of several polarization hysteresis loops of VDF/TrFE/CTFE terpolymers with different VDF content.



Figure 4.9 Plots of the polarization (maximun) and the coercieve field as a function of the VDF concentration in VDF/TrFE/CTFE terpolymers.

4.3.2.2 Dielectric constant

As mentioned before, in the polarization hysteresis loop experiment the terpolymers containing ~7 mol% termonomers showed very slim hysteresis loops, the small hysteresis during heating and cooling cycles was also observed in the dielectric constant measurement. Figure 4.10(a)-(d) shows the dielectric curves of terpolymers composed of about 7 mol% termonomers including CTFE, CDFE, VC, and CFE, respectively. In general, the dielectric constant hysteresis, during heating and cooling of these samples, are very small with very high dielectric constant in the range of about 70-90. The dielectric constant peaks show frequency dependence as can be seen from Figure 4.11. As the frequency increases, the dielectric constant decreases whereas the Curie temperature increases. At high frequency, dipoles can not keep up with the change of the electric field, compensated energy input is, therefore, necessary. As a result, the Curie temperature shifts to higher temperature, which is a common feature of the ferroelectric relaxor.



Figure 4.10 Typical dielectric constant cuves of the terpolymers that consist of about 7 mol% termonomers including CTFE, CDFE, VC, and CFE during heating (open symbols) and cooling cycle (filled symbols), (a) 59.3/32.9/7.8 VDF/TrFE/CTFE, (b) 62.5/30.9/6.6 VDF/TrFE/CDFE, (c) 58.3/34.7/7.0 VDF/TrFE/VC and (d) VDF/TrFE/1,2-CFE.



Figure 4.10 (con't) Typical dielectric constant cuves of the terpolymers that consist of about 7 mol% termonomers including CTFE, CDFE, VC, and CFE during heating (open symbols) and cooling cycle (filled symbols), (a) 59.3/32.9/7.8 VDF/TrFE/CTFE, (b) 62.5/30.9/6.6 VDF/TrFE/CDFE, (c) 58.3/34.7/7.0 VDF/TrFE/VC and (d) VDF/TrFE/1,2-CFE.



Figure 4.11 The dependence of the dielectric constant and the Curie temperature on the frequency.

Figure 4.12(a)-(b) shows typical dielectric relaxation of the terpolymers, 59.3/32.9/7.8 VDF/TrFE/CTFE and 62.5/30.9/6.6 VDF/TrFE/CDFE, respectively. Generally, the relaxation process of the terpolymer consists of two relaxations, designated as α -and β -processes in the order of descending temperature. The α -process at about 25°C is attributed to the phase transition in the terpolymer from the ferroelectric phase to the paraelectric phase. At high frequency, the relaxation in this process is almost disappeared due to the fact that the dipoles are incapable of keeping up with the frequency. The β -process near -20°C is associated with the glass transition of the non-crystalline phase. The relaxation peaks are frequency dependence. As the frequency increases, the relaxation peak shifts toward higher temperature. Energy from heat is needed as a compensation for the dipoles to align with the electric field at high frequency.



Figure 4.12 A typical dielectric relaxation of the terpolymers, (a) VDF/TrFE/CTFE and (b) VDF/TrFE/CDFE.

To study how the termonomer affects the dielectric constant of the terpolymers, we compared the dielectric constant of several terpolymers containing about 60 mol% VDF and about 7 mol% termonomer units, including CTFE, CDFE, CFE, and VC. Figure 4.13 compared the dielectric constant peaks at 1 kHz of these terpolymers. All terpolymers shows very high dielectric constant. Although only a few mole percent of termonomer units are presented in the terpolymer structure, the possitive dipoles contributions from the CFE, CDFE, and VC units (compared to almost no net dipoles in the CTFE unit) are reflected in the slightly higher dielectric constants.



Figure 4.13 Comparison of the dielectri constant at 1 kHz of terpolymers that are composed of the 60/40 VDF/TrFE and 7mol% terpolymers including CTFE, CDFE, 1,2-CFE and VC.



Figure 4.14 Shows the dependence of the dielectric constant on the termonomer concentration of (a) VDF/TrFE/CTFE and (b) VDF/TrFE/CDFE terpolymer, respectively.

As evidenced by the DSC and the FTIR results shown in the previous Chapter, the polymer conformation, the melting temperature, and the Curie temperature are all dependent on the termonomer concentration. It is curious to know whether or not the dielectric constant depends on the termonomer concentration. Figure 4.14 (a) and (b) compare the dielectric constants of the VDF/TrFE/CTFE and VDF/TrFE/CDFE terpolymers, which consist of a similar VDF content and various TrFE/termonomer ratios. As the termonomer concentration increases, the dielectric constant decreases and becomes broader and more diffuses due to the increase of destructive dipoles, as reason mentioned above. Figure 4.15 shows plots of the dielectric constant and the Curie temperature as a function of mol% CTFE. The dielectric constant and the Curie temperature depend on the termonomer concentrations. All values decrease as the destructive dipoles from the third termonomer increase.



Figure 4.15 plots of the dielectric constant and the Curie temperature vs. the termonomer concentration of 59.3/32.9/7.8 VDF/TrFE/CTFE terpolymer.

4.3.2.3 Field-induced strain

One of the most effective ways to measure the piezoelectricity or the electrostrictive in the polymer is by measuring the field-induced strain. Piezoelectricity refers to changes in the electrical polarization in response to a mechanical stress. By applying external force either mechanical (pressure) or electrical (applied field), mechanical strain is produced and hence causes the material to deform due to the electrostatic or repulsion between the dipoles and the external field. One of the most desirable properties of the electroactive polymer is to possess large mechanical deformation at low electric field. Ceramics are known to have small hysteresis and fast speed, but one drawback is their low strain deformation (<0.1%). On the other hand, the irradiated VDF/TrFE copolymer shows promising longitudinal strain ~4% at 150 MV/m, the irradiated sample is not easy fabricated. Therefore, it is worthwhile to explore the field-induced strain in processable terpolymers consisting of the VDF, TrFE, and chloro-containing fluoro-monomers.

As mentioned above, the longitudinal field-induced strain was obtained from the displacement of the polymer film thickness using a modified Sawyer-Tower circuit with linear variable differential transducer (LVDT) as a sensor. However, because of the softness of the polymer (compared to ceramics), the displacement of the polymer under the electric field is force dependence. The higher the applied force, the lower the displacement will be (the strain is inverse proportional to the applied force). Therefore, at each electric field the reported strain was taken from the extrapolation to zero force of the plot between the inverse displacement and the contact force. Figure 4.16 shows plot of the contact force and the inverse displacement of the VDF/TrFE/CDFE (63.6/31.4/5.0) terpolymer at the electric field

of 100 MV/m. The detailed experimental results of field induced strain of all terpolymers are summarized in Table 4.3.



Figure 4.16 the plot of the contact force and inverse displacement of the 63.6/31.4/5.0 VDF/TrFE/CDFE at electric field of 100 MV/m.

Sample	Composition/	Strain (%)	Strain (%)	Strain (%)
no.	termonomer	E = 50 MV/m	E = 100 MV/m	E = 150 MV/m
A-1	60.0/36.0/4.0 CTFE	0.9	2.5	
A-2	58.0/35.1/6.9 CTFE	0.8	2.2	3.2
A-3	59.3//32.9/7.8 CTFE	1.6	3.4	4.1
A-4	57.3/31.2/11.5 CTFE	1.0	2.5	
A-5	54.6/35.1/10.3 CTFE	0.9	2.9	4.0
A-6	64.9/26.1/9.0 CTFE	1.5	3.2	4.5
A-7	68.4/19.9/11.7 CTFE	1.2	3.0	4.5
A-8	72.2/17.8/10 CTFE	0.3	2.0	4.0
B-1	63.6/31.4/5.0 CDFE		3.0	3.5
B-2	64.5/30.2/5.3 CDFE	0.7	3.2	4.7
B-3	62.5/30.9/6.6 CDFE	1.0	2.3	3.8
B-4	72.2/21.3/6.5 CDFE	1.0	2.8	3.5
B-5	77.6/16.2/6.1 CDFE	0.6	1.7	2.4
C-1	58.3/34.7/7.0 VC	1.2	3.3	4.3
D-1	63.7/27.6/8.7 /1,1-CFE	0.4	2.0	3.5
D-2	60.1/29.3/10.6/1,1CFE	0.5	1.7	2.8

TABLE 4.3 Summary of the field induced strain of several terpolymers containing VDF, TrFE and chloro-fluoromonomers, including CTFE, CDFE, VC and CFE, at different field.

In general, the VDF/TrFE/CTFE terpolymers, with a VDF content at ~60 mol% and T_c of about ambient temperature, show a high field induced strain, about 2-3 % at electric field of 100 MV/m and about 4-4.5% at electric field of 150 MV/m. The terpolymers with higher T_c (also harder material) show smaller strains. On the other hand, it is not very conclusive to show the effects of the termonomer. The terpolymers based on the CDFE appear to show slightly smaller stain at 150 MV/m, which may also be associated with the slightly hardness of the VDF/TrFE/CDFE terpolymers. Probably, the high field part of the field induced strain is attributed to the Maxwell stress induced strain that is dependent on the Maxwell strein is shown in the following equation:

$$S_3 = -\epsilon s_{11} E_3^2$$

where s_{11} is the elastic compliance of the polymer and is equal to s_{33} for an isotropic polymer and the ε is the permittivity of the sample.

Garrett and Roland at NRL also studied the electrostrictive behavior of the same set of the terpolymers in the relative low field (10 MV/m). They concluded that the observed field induced 1% longitudinal stain is not related to Maxell strain, due to the terpolymer's high mechanical modulus (10 to 100 MPa). However, based on the above equation, the Maxwell strain can have significantly higher contribution in the high field range.

Figure 4.17 (a) shows a typical field induced strain curves of the VDF/TrFE/CTFE. The butterfly shape like strain curve is usually seen in the terpolymers, which is the shape of the electrostrictive materials. Figure 4.17 (b), however, shows the field induced strain curve with the round edge at high electric field. This round edge could be due to the thermal expansion of the terpolymer.



Figure 4.17 Typical field induced strain curves of the terpolymers (a) VDF/TrFE/CTFE and (b) VDF/TrFE/CDFE.

Figure 4.18 compares the longitudinal strain of several terpolymers containing various Cl-termonomers, with similar terpolymer compositions and about 7 mol% termonomer units. All terpolymers show similar trend of the strain toward the applied field (about 4% strain at 150 MV/m). It is very difficult to deduce any definite explanation for the small deviation, which may be due to small difference in composition, polymer molecular weight, or molecular weight and composition distributions. However, it is interesting to compare the field induced strain of the same terpolymer with different termonomer concentrations. Figures 4.19 and 4.20 show the plots of longitudinal stain vs. electric field for several VDF/TrFE/CTFE and VDF/TrFE/CDFE terpolymers, respectively.



Figure 4.18 The longitudinal strain as a function of applied electric field of several terpolymers that are composed of VDF/TrFE (60/40 mole ratios) and about 7 mol% termonomers containing of CTFE, CDFE, VC and CFE.



Figure 4.19 Longitudinal field induced strains of several VDF/TrFE/CTFE terpolymers with different CTFE concentrations.



Figure 4.20 Longitudinal field induced strains of several VDF/TrFE/CDFE terpolymers with different CDFE concentrations.

Although the strain is high in some terpolymers, it seems that there is no correlation between the strain and the termonomer concentration. Figure 4.21 shows longitudinal field induced strain of VDF/TrFE/CTFE terpolymers with high VDF contents. It is also found that there is no direct correlation between the strain and the percentage of the VDF content. At ambient temperature, the longitudinal strain reached about 4.0% under an electric field of 140 MV/m. As shown in Figure 4.22, a nearly straight line of S vs. P² for 72.2/17.8/10 VDF/TrFE/CTFE indicating the electrostrictive response in the terpolymer. Based on the electrostrictive relationship $S = QP^2$, this equation yields the electrostrictive coefficient (Q) of about -5.57 m⁴/C².



Figure 4.21 Comparison of three longitudinal field-induced strains of VDF/TrFE/CTFE terpolymers with different VDF content.


Figure 4.22 Electrostrictive relation between strain and polarization square measured at electric field from 0-100 MV/m of the VDF/TrFE/CTFE terpolymers (66.0/22.5/11.5)

4.4 Conclusion

The experimental results in the previous Chapter, indicate that the homogeneous incorporation of a controlled amount of bulky chlorine units into the VDF/TrFE copolymer, gradually alters both the molecular structure, and the morphology resulting in a stable ferroelectric γ -phase, with reduced Curie transition temperature and very small activation energy for the phase transition. As a result, the terpolymers exhibit several common features of a typical relaxor ferroelectric behavior, such as high dielectric constant at ambient temperature, diffuse phase transition and dielectric relaxation (large frequency dependence) and the slim polarization hysteresis loop. The dielectric constant and the polarization used, but also on the choice of termonomers. The dielectric constant tends to be higher for less

destructive dipole termonomers, for example, the CFE \sim CDFE \sim VC > CTFE. The large expanding and contracting of new ferroelectric phase under external electric field, coupled with a large difference in the lattice strain between the polar and non-polar crystal phases, generate a large electrostrictive strain response.

4.5 References

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Chapter 5

Synthesis and characterization of the functional fluoropolymers

5.1 Background

As discussed in Chapter 2, fluoropolymers, such as the poly(tetrafluoroethylene) (PTFE), poly(vinylidine fluoride) (PVDF), poly(vinylidine difluoride-co-trifluoroethylene) (VDF/TrFE copolymer), and the poly(vinylidine difluoride-co-hexafluoropropene) (VDF/HFP elastomer) exhibit a unique combination of properties. These include thermal stability, chemical inertness (acid and oxidation resistances), low water and solvent absorptivities, self-extinguishing, excellent weatherability, and very interesting surface properties. They are commonly used in many high-end applications, such as aerospace, automotive, textile finishing, and microelectronics. However, fluoropolymers also have some drawbacks, being their limited processability, poor adhesion to substrates, lack of crosslinking chemistry, and inertia to chemical modifications limiting their applications where both the interactive and reactive properties are paramount.

As discussed in Chapter 2, in the past decades most of research activities have been focused on the copolymerization of fluorinated monomer with non-fluorinated or fluorinated co-monomers to improve their processability (in melt or solution). However, the lack of functional groups and curable sites still remains a major problem that hinders even wider spread application of fluoropolymers in many areas. As mentioned earlier, there are two general research approaches in the functionalization of fluoropolymers, including (i) control polymerization using functional initiators or chain transfer agents to prepare telechelic fluoropolymers containing terminal functional groups, and (ii) copolymerization of fluorinated monomer with functional comonomers to form functional fluoro-copolymers containing pending functional groups.

Our interest in the functionalization of fluoropolymers is two-fold: (i) the development of a general functionalization chemistry for fluoropolymers, and (ii) the improvement of the interactive properties of our newly developed ferroelectric VDF/TrFE/chloro-containing terpolymers discussed in Chapter 3 and 4. It was pointed out that many desirable properties, such as high dielectric constant, narrow hysteresis, and high field induced strain at ambient temperature, were observed, in the VDF/TrFE/chlorocontaining terpolymers. However, an extremely high electric field (MV/m) is required to achieve high strain, which is a major concern for many applications, especially in biological areas. To reduce this high electric field requirement, there was the need to either reduce the space between the electrodes or increase the dielectric constant of the terpolymer. In both cases, some foreign materials have to be introduced into the system, such as imbedding a conducting material (could be a conducting polymer) serving as electrodes in the first approach, or blending high dielectric ferroelectric inorganic nano-particles in the second approach. In both cases, the synthesis of functionalized terpolymers containing some specific functional groups would be a crucial step in achieving the research objective.

As discussed in this Chapter, our functionalization approach has focused on the preparation of telechelic VDF/TrFE/chloro-containing terpolymers having functional (polar and reactive) terminal groups, and the diblock copolymers containing a VDF/TrFE/chloro-containing terpolymer and functional polymers. Such telechelic and block polymer structures not only provide the needed interactive properties but also preserve the existing desirable

properties, because of the undisturbed polymer backbone structure. Two chemical methods have been studied: (i) the use of functional borane/oxygen initiators that carries functional groups and exhibit living radical polymerization mechanism, and (ii) the investigation of an improved iodine transfer polymerization (ITP) method to prepare telechelic fluoropolymers containing two terminal iodine groups. The chemistry is based on the combination of a specific radical initiator and a reversible addition-fragmentation chain transfer (RAFT) process involving an α, ω -diiodoperfluoroalkane (I-R_F-I) chain transfer agent.

5.2 Experimental

5.2.1 Materials

All solvents used in the synthesis were dried over CaH₂ and freshly distilled before being used. The starting materials for the synthesis of borane initiators, including 3-chloro-2methypropene, 4-bromo-1butene, allylacetate, allyltrifluoroacetate, allyltrichlorosilane, allydichlorolmethylsilane, allylchlorodimethylsilane, were obtained from the Aldrich Chemical Company and were distilled before they were used. Boron hydride was purchased from the Aldrich Chemical Company. All the chemicals used for the synthesis of the low temperature initiators, including the trichloroacetyl chloride, 2-bromoethyl chloroformate, allyl chloroformate, and sodium peroxide, were also obtained from the Aldrich Chemical Company and were used as received. The conventional peroxide initiators, such as benzoyl peroxide (BPO), hydrogen peroxide, and azobis(isobutylonitrile) (AIBN), were also purchased from the Aldrich Chemical Company and were used as received. The chain transfer agent, diiodo perfluorobutane, was kindly supplied by the Daikin American Inc. All fluoro-monomer gases were obtained either from the PCR (Lancaster) Company or the Synquest Laboratory Company and were purified by the freeze-thaw process before being used.

5.2.2 Synthesis of the functional Borane initiators

Several functional borane initiators were prepared by hydroboration of functional alkenes, such as 3-chloro-2-methypropene, 4-bromo-1butene, allylacetate, allyltrifluoro acetate, allyltrichlorosilane, allydichlorolmethylsilane, and allylchlorodimethylsilane, with boron hydride (3:1 mole ratio). Hydroboration reaction was conducted at 0°C for 4 hours in tetrahydrofuran (THF). In a typical example, the reaction was carried out in dried flask containing 20 ml dried THF and 8.7ml (0.06 mol) allyltrichlorosilane. The solution was then cooled down to 0°C, and 20 ml (0.02 mol) of 0.1 M boron hydride in THF was then dropped slowly via the air-tight syringe into the reaction flask. The solution was stirred at 0°C for 4 h. After that the THF was removed under high vacuum pump to obtain about 80-90% yield tri(trichlorosilyl propyl)borane initiator. The initiator was stored in a dried box under argon atmosphere. Other borane initiators were prepared by the same procedure.

5.2.3 Synthesis of the functional low temperature initiators

All low temperature initiators were synthesized by modifying the Leffer and Gibson's method.³ A typical example is as follows: a mixture of 6 g sodium chloride in 25 ml water was cooled down to 0°C before slowly adding 0.28 g (3.6 mmol) sodium peroxide. After completing the addition, the solution was cooled down to -25°C and stirred vigorously. Trichloroacetyl chloride 0.9 g (5 mmol) was added slowly by syringe within 1 min and stirred at -25°C for 5 min. The solution was then extracted with 15 ml chloroform (or with ether in the cases of allyl chloroformate and 2-bromo-ethylchloroformate). The catalyst

solution was then dried under high vacuum to get about 80% yield of white solid product and was ready to use for the polymerization.

5.2.4 Polymerization initiated by functional borane initiator

The polymerization was carried out in a 75ml stainless steel bomb reactor. In a typical reaction, 240 mg (4.4×10^{-4} mol) of tri(trichlorosilyl propyl)borane initiator was added to the reactor in a dry box under argon atmosphere. The reactor was then moved out from the dry box and connected to a vacuum line. After that, 25 ml (0.24 mol) of VDF, 12.5 ml (0.19 mol) of TrFE, and 1.3 ml (0.15 mol) of CTFE were vacuum distilled into the reactor at the liquid nitrogen temperature. A known amount of oxygen (1:0.5 mole ratio of boron: oxygen) was then introduced into the reactor, which was then naturally warm up to room temperature and was kept at this temperature for 18 h. After that, the reactor was cooled down and the unreacted monomer was recovered. The solid polymer was dissolved in acetone and precipitated in the mixture of the water/methanol several times and was vacuum dried at 70°C to obtain about 5.8 g (22% conversion).

5.2.5 Polymerization initiated by functional low temperature initiators

In one example, a 10 ml (contains about 1.0×10^{-4} mol of the catalyst) of the 2bromo-ethyl acetyl peroxide catalyst in ether solution was injected into a 75 ml stainless steel bomb reactor. The solvent was then removed by vacuum distillation at -30°C. After that, 20 ml (0.19 mol) of VDF, and 10 ml (0.1mol) of HFP were vacuum condensed into the reactor at liquid N₂ temperature. The reactor was then slowly warmed up to 50°C and maintained at this polymerization temperature for 18 h, before vacuum removal of the unreacted monomer(s). The polymer obtained, 5 g (about 18 % conversion), was then dissolved in acetone and precipitated with water/methanol several times to remove the impurities, and finally vacuum dried at 70°C. In the preparation of the copolymer and terpolymer cases, the reactions were usually stopped at less than 20% monomer conversion to ensure the constant comonomer ratios during the polymerization.

5.2.6 Polymerization initiated by hydrogen peroxide initiator

Polymerization was performed in a 200 ml stainless steel bomb reactor. In one example, 0.2 ml (1.8×10^{-3} mol) of aqueous hydrogen peroxide (30% weight/volume concentration) and 100 ml acetonitrile were mixed in the reactor. The reactor was vacuumed to remove air, then, 25 ml (0.24 mol) of VDF, 12.5 ml (0.19 mol) of TrFE, and 1.3 ml of (0.15 mol) CTFE was vacuum distilled into the reactor at the liquid nitrogen temperature. The reactor was then rapidly heated up to 100° C and maintained at this temperature for 4 h. After that, the unreacted monomer was then vacuum recovered, and the polymer solution was precipitated in methanol/water mixture to obtain the white solid powder. The polymer solid was then dissolved in acetone and precipitated with methanol/water several times to remove the impurities, and finally vacuum dried at 70° C to get 8.6 g (32.6% conversion). The composition of the terpolymer measured by ¹H NMR and elemental analysis is 62.9/30.3/6.8 VDF/TrFE/CTFE. Mole average molecular weight (Mn) of polymer was in the range of about 15000 with molecular weight distribution of 2.0, as indicated by the GPC.

5.2.7 Polymerization initiated by AIBN/diiodide system

In a typical reaction, the AIBN initiator 0.3 g (1.83×10^{-3} mol) was dissolved in 30ml acetonitrile solvent and was placed into a 75 ml stainless steel reactor. Diiodoperfluorobutane chain transfer agent 0.4 g (0.84×10^{-3} mole) was then added to the solution

in the reactor. After the reactor was vacuumed to remove air, 25 ml (0.24 mol) of VDF, 12.5 ml (0.19 mol) of TrFE, and 1.3 ml of (0.15 mol) CTFE monomers were then vacuum distilled into the reactor at liquid nitrogen temperature. The reactor was rapidly heated up to 80°C and maintained at this temperature for 4 h. After that, the unreacted monomer was vacuum recovered, and the polymer solution was precipitated in methanol/water mixture and purified twice by dissolving in acetone and reprecipitated with water/methanol mixture. The composition of the polymer obtained, 16.0 g (48.5% conversion), was 68.7/25.5/5.8 VDF/TrFE/CTFE with a mole average molecular weight (Mn) of about 20000 and molecular weight distribution of 1.7. The calculation of the result from iodine analysis shows that the polymer contains 2 iodine functional groups/polymer chain.

5.2.8 Synthesis of block copolymer containing P(VDF/HFP) and PMMA

The polymerization was conducted in a 75ml stainless steel bomb reactor. In a typical reaction, tributyl borane initiator of about 100 mg (1 x 10^{-4} mol) was placed in the reactor in dry box under argon atmosphere. The reactor was then moved out from the dry box and connected to a vacuum line. A 25 ml (0.24 mol) of VDF and 15 ml (0.15 mol) HFP were vacuum distilled into the reactor at the liquid N₂ temperature. After a known amount of oxygen (1:0.5 of boron: oxygen) was introduced into the system, the reactor was then naturally warmed up to room temperature and was kept at this temperature for about 4 h. After that, the reactor was cooled down to liquid N₂ temperature again, and 5 ml (0.05 mol) of MMA monomer was subsequently distilled into the reactor, and the polymerization was kept at room temperature for 12 h. The polymer obtained, 4.9 g, was precipitated and washed with methanol several times and vacuum dried at 70°C. The resulting polymer was subjected to the fractionalization by dissolving in acetone and titrated with methanol (non-solvent). The

first precipitating fraction is PMMA homopolymer (2.5 g, 50 wt%), and the second precipitating fraction is the P(VDF/HFP)-b-PMMA diblock copolymer, 1.7 g (35 wt%). The soluble fraction is unblocked P(VDF/HFP) 0.7 g (15 wt%), which is recovered by the evaporation of the solvent.

5.2.9 Synthesis block copolymer containing P(VDF/TrFE/CTFE) terpolymer and PVDF homopolymer

In a 75 stainless steel bomb reactor, 1 g of the telechelic 67.2/27.6/5.2 VDF/TrFE/CTFE terpolymer containing two terminal iodine groups (sample A-1 of Table 5.5, prepared by the method shown in section 5.2.7) and 0.2 g (1.2 x 10^{-3} mol) of AIBN initiator were dissolved in 30 ml acetonitrile. After air was removed, 20 ml (0.19 mol) of VDF monomer was vacuum distilled into the reactor at the liquid N₂ temperature. The block copolymerization was taken place at 70-80°C for 10 h. After that, the unreacted monomer was removed, and the polymer solution was precipitated in methanol/water mixture. The trace amount of PVDF homopolymer (insoluble in acetone) was removed by dissolving the polymer solid in acetone and filtered out. The total amount of block copolymer after purification was 1.5 g (run no. 4 of the Table 5.6).

5.2.10 Characterization of polymer initiated by functional initiators

The compositions both the copolymers and terpolymers, as well as the terminal functional groups, were examined by a combination of ¹H NMR, ¹³C NMR and ¹⁹F NMR at 300 MHz. Typically about 128 scans were recorded using 20% polymer solution in either d⁷-dimethylsulfoxide or d⁶-actone. The chemical shifts were referenced to the external standards, trimethylchlorosilane for ¹H NMR, and fluorotrichloromethane for ¹⁹F NMR. The

IR spectrum was recorded with the polymer thin film on KBr window, which was prepared by solution casting from the THF solution. The molecular weight and the molecular weight distribution of polymers were measured by the GPC using Waters 710B delivery system with 410 refractive index detector, and compared with the monodisperse polystyrene standards. The melting and the Curie temperatures were determined using the Perkin-Elmer DSC-7 at the scanning rate of 20°C/min, and data were taken from the second heating cycle, in order to eliminate the thermal history of the sample. Indium was used to calibrate the melting temperature and heat of fusion.

5.3 Results and discussions

5.3.1 Synthesis of functional fluoropolymers by functional borane initiators

As discussed in chapter 3, borane/oxygen radical initiators have several distinctive advantages over the traditional ones. The most outstanding advantage is that they possess pseudo-living characteristic during the radical polymerization process, with no detectable chain transfer and termination reactions. It is anticipated that, if the radical polymerization was carried out by a functionalized borane initiator containing a specific functional group, the resulting polymer chain should contain the specific functional group located at the beginning of the polymer chain.

It is very interesting to note that the well-known borane chemistry provides simple and facile reaction process to prepare functional borane initiators. As illustrated in scheme 5.1, the Cl-functionalized borane initiator was prepared in one-pot reaction process via the hydroboration of a chlorinated olefin with BH₃.THF reagent.

$$\begin{array}{cccc} CH_2 = CHCH_2CI + BH_3.THF & \xrightarrow{THF} B(CH_2CHCH_2CI)_3 \\ CH_3 & CH_3 \end{array}$$

Scheme 5.1

The hydroboration reaction was completed at 0°C within 4 hours, and the product obtained was very pure thus required no further purification. This reaction is also suitable for the olefins containing various functional groups, such as Br, silane, and acetyl group (precursor for OH group), to prepare several functional borane initiators (shown in scheme 5.2).

$$\begin{array}{c} \mathsf{R} & \mathsf{C}\mathsf{H}_{3} \\ \mathsf{B}\mathsf{-}\mathsf{C}\mathsf{H}_{2}\mathsf{C}\mathsf{H}\mathsf{C}\mathsf{H}_{2}\mathsf{C}\mathsf{H}_{2}\mathsf{-}\mathsf{C}\mathsf{I} \\ \mathsf{R} \end{array} \tag{I}$$

$$\begin{array}{c} \mathsf{R} \\ \mathsf{B}\text{-}\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\text{-}\mathsf{Br} \\ \mathsf{R} \end{array} \tag{II}$$

$$\begin{array}{c} \mathsf{R} & \mathsf{C}\mathsf{H}_{3} \\ \mathsf{B}\mathsf{-}\mathsf{C}\mathsf{H}_{2}\mathsf{C}\mathsf{H}_{2}\mathsf{-}\mathsf{Si}\mathsf{-}\mathsf{C}\mathsf{I} \\ \mathsf{R} & \mathsf{C}\mathsf{H}_{3} \end{array} \tag{III)}$$

Scheme 5.2

Figure 5.1 shows the ¹¹B NMR spectra of several functional borane initiators (I), (III), and (IV) in Figure 5.1(a)-(c), and that of a partially oxidized Si-borane initiator (I) in Figure

5.1(d). The major peak at 86 ppm corresponds to trialkylboran moieties, indicating the boron atom connected to three alkyl groups, consistent to the functional borane initiator structures. Upon the partially oxidation by a small amount of oxygen, two additional new peaks shown at 56 and 30 ppm, corresponding to the mono-oxidized (boron connected to one oxygen and two alkyl groups) and the double-oxidized (boron connected to two oxygen atoms and one alkyl group) borane moieties, respectively. As discussed in chapter 3, the mono-oxidized boron moieties are responsible for initiating the living radical polymerization, and in the presence of monomers and controlled amount of oxygen (usually less than stoichiometric amount of oxygen) most of the mono-oxidized borane species formed in situ immediately react with monomers and initiate the polymerization process, instead of further oxidation.

Figure 5.2 shows two examples of the ¹H NMR spectra of the polymers that were initiated by the functional borane initiators: (a) the VDF/TrFE/CTFE terpolymer produced by the B(CH₂CH₂CH₂CH₂SiCl(CH₃)₂)₃ initiator, and (b) the VDF/HFP copolymer produced by the B(CH₂CH(CH₃)CH₂Cl)₃ initiator. Both functional groups at the beginning of each polymer chains, although they are very small due to high molecular weight of the polymer, are clearly observed in the ¹H NMR spectra. In Figure 5.2 (a), a small peak at the chemical shift of 0.1 ppm corresponds to three protons connected to the silane atom (-Si(CH₃)₂Cl), whereas the major peaks at the chemical shift of 2.2-3.2 ppm and 5.2-6.2 ppm represents protons from the VDF and the TrFE, respectively. A small peak in Figure 5.2 (b), at the chemical shift of 0.9 ppm, represents three protons (-CH(CH₃)CH₂Cl) of the end group of the polymer produced from the B(CH₂CH(CH₃)CH₂Cl)₃ initiator, whereas the peak at the chemical shift of 3.6 ppm indicates two protons adjacent to the chlorine atom (-CH(CH₃)CH₂Cl).



Figure 5.1 ¹¹B NMR spectra of several functional borane initiators (a) B(CH₂CH₂CH₂SiCl(CH₃)₂)₃, (b) B(CH₂CH(CH₃)CH₂Cl)₃, (c) B(CH₂CH₂CH₂CH₂CH₂OAc)₃, and (d) the partially oxidized B(CH₂CH₂CH₂CH₂SiCl(CH₃)₂).



Figure 5.2 Two typical ¹H NMR spectra of the polymer produced by functional borane initiators (a) VDF/TrFE/CTFE terpolymer produced by $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$ initiator, and (b) VDF/HFP copolymer produced by $B(CH_2CH(CH_3)CH_2Cl)_3$ initiator.

Catalyst/	Monomers feed/	Time	Conversion	[η] in MEK, 35°C or			
Amount	Mole ratio	(hrs)	(%)	Mn/Mw			
$(mol \ x \ 10^{-3})$				$(x \ 10^{-3} \text{ g/mole})$			
I-1/0.4	VDF/HFP / 80:20	1	1.3	0.09			
I-2/0.4	VDF/HFP / 80:20	3	3.8	0.12			
I-3/0.4	VDF/HFP / 80:20	5	4.5	0.16			
I-4/0.4	VDF/HFP / 80:20	7	6.1	0.17			
I-5/0.4	VDF/HFP / 80:20	9	6.6	0.18			
II-1/0.4	VDF/HFP/70:30	18	1.5	-			
II-2/0.6	VDF/HFP/70:30	18	2.0	-			
II-3/1.0	VDF/HFP/70:30	18	3.7	-			
III-1/0.5	VDF/HFP / 80:20	5	2	8.9/15.3			
III-2/0.5	VDF/HFP / 80:20	8	2.5	10.1/20.2			
III-3/0.5	VDF/HFP / 80:20	10	6	14.6/31.7			
III-4/0.5	VDF/HFP / 80:20	12	7	23.5/65.3			
III-5/0.5	VDF/HFP / 80:20	15	11	29.6/60.0			
IV-1/0.4	VDF/HFP/70:30	18	1.3	-			
IV-2/0.9	VDF/HFP/70:30	18	3.0	-			
IV-3/1.0	VDF/HFP/70:30	18	4.0	-			

 Table 5.1
 Summary of the copolymers prepared by using the functional borane initiators*

* Initiators: I=B(CH₂CH(CH₃)CH₂Cl)₃, II= B(CH₂CH₂CH₂CH₂Br)₃, III =

 $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$, $IV = B(CH_2CH_2CH_2OAc)_3$. Polymerization conditions: at room temperature with monomer feed ratio: 25 ml VDF/10 ml HFP (70:30 mol ratio), and 25 ml VDF/5 ml HFP (80:20).

Table 5.1 summarizes the radical polymerization results by using functional borane initiators (I)-(IV). Despite the formation of the desirable functional group (i.e. Cl, Br, Si-Cl, and acetyl group) terminated copolymers, the copolymerization reactions of the VDF and the HFP are generally very slow. The low monomer conversion of the polymer initiated by the functional borane was probably due to the intramolecular interaction between the functional borane initiator, as illustrated in scheme 5.2.



Scheme 5.2

Boron is an electron deficient element, which is opposite to most of the functional groups containing oxygen and halogens that are electron rich elements. The intramolecular acid-base interaction can occur and reduce the availability of free borane species, which certainly leads to low initiator efficiency. As we changed the functional groups from ester group to the silane group, this effect seemed to reduce. Although the monomer conversion still remained relatively low, it may have also been due to the low reactivity of the HFP itself that contained 6 electron-withdrawing fluorine atoms. Despite the slow polymerization rate, the functional borane initiators show the long-life propagation site leading to the linear increase of polymer molecular weight with monomer conversion and narrow molecular weight distribution, similar to those shown in regular trialkylborane initiators (discussed in chapter 3).

Figure 5.3 shows two linear plots of the average molecular weight of the VDF/HFP copolymers versus the monomer conversion initiated by the B(CH₂CH₂CH₂Si(CH₃)₂Cl)₃, and the B(CH₂CH(CH₃)CH₂Cl)₃, respectively. In both cases, the polymer molecular weight increases with the monomer conversion, with the intercept at near origin, a strong indication of pseudo-living polymerization.



Figure 5.3 shows plots of monomer conversion vs. average weight of the VDF/HFP copolymer initiated by the $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$ and the $B(CH_2CH(CH_3)CH_2Cl)_3$, respectively.

It was very interesting to take advantage of the pseudo-living polymerization characteristic in the borane/oxygen initiator system to prepare the block copolymers, especially the synthesis of new block copolymers containing both fluorinated polymer segments with non-fluorinated polymer segment. One example is the P(VDF/HFP-b-MMA) diblock copolymer containing the VDF/HFP copolymer block and the PMMA homopolymer block, which was prepared by the tributylborane/oxygen initiator with sequential monomer addition (VDF/HFP, then MMA). After completing the polymerization process, the polymer mixture was subjected to solvent-fractionated and separated into 3 fractions, including the PMMA homopolymer fraction, the P(VDF/HFP-b-MMA) diblock copolymer fraction, and the unblocked P(VDF/HFP) fraction.

Figure 5.4 compares the ¹H NMR spectrum spectra of these three fractions. Figure 5.4 (a) shows a typical ¹H NMR spectrum of PMMA homopolymer with three major peaks at 1.2-1.4 ppm (-CH₂-C(CH₃)-), 2.7 ppm (CH₂-C(CH₃)-) and 4.0 ppm (-CH₂-C(COOCH₃). On the other hand, Figure 5.4 (c) shows a major peak at 2.8-3.2 (-CH₂-CF₂-), indicating the unblocked P(VDF/HFP) copolymer. Figure 5.4 (b) shows all the peaks for both PMMA and P(VDF/HFP) polymers, which strongly suggest the formation of P(VDF/HFP-b-MMA) diblock copolymer.



Figure 5.4 ¹H NMR spectra of three polymer fractions (a) the PMMA homopolymer fraction, (b) the P(VDF/HFP-b-MMA) diblock copolymer fraction, and (c) the unblocked P(VDF/HFP) fraction.

Figure 5.5 compares the GPC curves of the P(VDF/HFP-b-MMA) diblock copolymer and the unblocked P(VDF/HFP) polymer. The P(VDF/HFP-b-MMA) diblock copolymer shows higher molecular weight than the unblocked P(VDF/HFP) polymer. It is interesting to note that the GPC curve of the unblocked P(VDF/HFP) shows a negative peak whereas after the block copolymerization with the PMMA, the GPC curve changes to a positive peak.



Figure 5.5 GPC curves of (a) PMMA homopolymer, (b) P(VDF/HFP-b-MMA) fraction and (c) PVDF homopolymer fraction.

To demonstrate that the P(VDF/HFP) macro-radical has a long life propagation site and was protected by the coordinated boron species, the MMA monomer was further polymerized at different polymerization time. Table 5.2 summarizes several block copolymers of the P(VDF/HFP-b-MMA), in which the MMA polymerization was carried out for 2, 5, and 12 hours. Figure 5.6 compares the ¹H NMR spectra of the resulting three P(VDF/HFP-b-MMA) block copolymers.



Figure 5.6 ¹H NMR spectra of P(VDF/HFP-b-MMA) block copolymers with different polymerization time (a) 2 h, (b) 5 h, and (c) 12 h, during MMA polymerization.

Run	Reaction time (h)		Polymer weight fraction (%)			mol%MMA	Mn/Mw/PD
no.	1 st block	2 nd block	1^{st}	2^{nd}	$3^{\rm rd}$	In diblock	Of diblockx 10 ⁻⁴
1	5	2	27	55	18	16.0	7.5/22.1/2.9
2	5	5	34	52	14	20.0	9.5/28.9/3.0
3	5	12	50	35	15	23.5	11.5/32.2/2.8

Table 5.2 Summary of the P(VDF/HFP-b-MMA) diblock polymers prepared by controlling the polymerization time of the MMA.

Reaction conditions: tributylborane initiator (1x 10^{-3} mole); sequential monomer addition by adding 25 ml VDF and 5 ml HFP in first block and 5 ml MMA in second block.

Comparing the ¹H MR spectra of the three P(VDF/HFP-b-MMA) block copolymers in Figure 5.6, the integrated intensity at the chemical shift 4.0 ppm, corresponding to MMA units, increases from 16.0 mol% to 23.5 mol% as the polymerization time increases from 2 to 12 h. However, the PMMA homopolymer fraction also increases, which indicates some new polymer chains formed after adding MMA. The MMA monomer is significantly higher reactivity toward the borane initiator due to the acid-base interaction.

Although the borane initiator shows many advantages, including the ease of introducing a functional group at the polymer chain end without disturbing other properties of the polymer, and the potential for modification of the fluoropolymer with the non-fluoropolymer. However, there are some drawbacks, such as low polymerization yield and low efficiency of the block copolymer. It is worthwhile to explore other initiator systems toward our objectives.

5.3.2 Synthesis of telechelic fluoropolymers by functional peroxide initiators

5.3.2.1 By using acetyl peroxide functional initiators

Several conventional functional peroxide initiators were also investigated, although they are known to be very unstable and can involve various side reactions that are detrimental to the preparation of a chain end functionalized polymer. To minimize the side reactions, low temperature peroxide initiators bearing bromine and double bond were chosen, with the use of the bulk process that has pure monomers in the condensed phase. Table 5.3 summarizes the experimental results involving 3 acetyl peroxide initiators, i.e. (Br-CH₂CH₂OC(=O)O-)₂, (CH₂=CHCH₂OC(=O)O-)₂, and (CH2=CHOC(=O)O-)₂.

Catalyst	Monomer	Polymerization conditions		Conversion
	(feed ratio)	Catalyst (mol)	Temp/Time	(%)
A-1	VDF/HFP/70:30	1.0 x 10 ⁻³	50°C/20h	12
A-2	VDF/HFP/70:30	$4.0 \ge 10^{-3}$	70°C/20h	7
A-3	VDF/TrFE/CTFE/54/42/4	$1.0 \ge 10^{-3}$	50°C/20h	15
A-4	VDF/TrFE/CTFE/54/42/4	$4.0 \ge 10^{-3}$	50°C/20h	31
		2		
B-1	VDF/TrFE/CTFE/54/42/4	$4.0 \ge 10^{-3}$	50°C/20h	5
B-2	VDF/TrFE/CTFE/54/42/4	$4.0 \ge 10^{-3}$	70°C/20h	Trace
		2		
C-1	VDF/TrFE/53/47	$1.0 \ge 10^{-3}$	50°C/20h	5
C-2	VDF/TrFE/CTFE/54/42/4	$4.0 \ge 10^{-3}$	50°C/20h	8

Table 5.3 Summary of the polymerization results by three low temperature peroxide initiators

Catalyst A: $(Br-CH_2CH_2OC(=O)O_2)$, B: $(CH_2=CHCH_2OC(=O)O_2)$, C: $(CH2=CHOC(=O)O_2)$. Monomer feed: 25 ml VDF/10 ml HFP (70:30 mol ratio), 25 ml VDF/12ml TrFE/1.3 ml CTFE (54/42/4), and 25 ml VDF/12.5 ml TrFE (53/47).

In general, monomer conversions are quite poor and polymer molecular weight are very low, only the $(Br-CH_2CH_2OC(=O)O_{-})_2$ initiator with high concentration produces polymer with decent yield. Figure 5.7 shows infrared spectra of two polymers (samples A-1 and B-1) that were synthesized by $(Br-CH_2CH_2OC(=O)O_{-})_2$ and $(CH_2=CHOC(=O)O_{-})_2$ functional initiators, respectively. The weak absorbance peaks around 1780 cm⁻¹, which is the characteristic peak of the carbonyl group that exists in both functional initiators, whereas

the absorbance peak at 1640 cm⁻¹ corresponds to the double bond, indicating some unsaturated chain ends in the polymers produced by the $(CH_2=CHOC(=O)O_{-})_2$ initiator.



Figure 5.7 Infrared spectra of polymers synthesized by the functional initiator (Br- $CH_2CH_2OC(=O)O_2$, and ($CH_2=CHOC(=O)O_2$).

The detail molecular structures were examined by the ¹H NMR technique. Figure 5.8 shows the ¹H NMR spectra of two polymers (A-1 and B-1 in Table 5.3) that were synthesized by the (Br-CH₂CH₂OC(=O)O-)₂ and the (CH₂=CHOC(=O)O-)₂ functional initiators, respectively. In Figure 5.8 (a), two major chemical shifts were observed at 2.5 -3.5 ppm (-CH₂CF₂- in the VDF/HFP copolymer) and at 3.8 and 4.5 ppm, corresponding to the BrCH₂CH₂O- and BrCH₂CH₂O-, respectively, located at the polymer chain end. In Figure 5.8 (b), several broad chemical shifts were observed at 2.5-3.5 and 4.8-5.8 ppm, corresponding to -CH₂CF₂- and -CHFCF₂- in the VDF/TrFE/CTFE terpolymer backbone. The polymer chain ends were also observed at 4.2 ppm (-OCH₂CH=CH₂), 4.8 ppm (-OCH₂CH=CH₂), and the overlapping peak at 5.2 ppm (-OCH₂CH=CH₂).



Figure 5.8 ¹HNMR spectra of polymers initiated by different catalysts (a) by the (Br-CH₂CH₂OC(O)O-)₂ sample (A-2), and (b) by the (CH₂=CHCH₂OC(O)O-)₂ sample B-1.

Overall, these functional initiators produced mixed results. Some of the polymers obtained exhibited terminal functional groups (i.e. Br, and $CH_2=CH$ -). However, despite the effort of using low temperature polymerization and pure monomer conditions, some chain transfer reactions did take place, which reduced the polymer yield and the polymer molecular weight. In addition, some more reactive functional end groups still remain unattainable.

5.3.2.2 By hydrogen peroxide initiator

As discussed in section 2.3.2, the other traditional functional radical initiator is H_2O_2 that potentially can afford the polymer with OH terminal groups. Table 5.4 summarizes several VDF/HFP copolymers and VDF/TrFE/CTFE terpolymers prepared by the hydroperoxide initiator.

Table 5.4 Summary of the VDF/HFP copolymers (A) and the VDF/TrFE/CTFE terpolymers (B) prepared by the H_2O_2 initiator.

Run	Monomer	Polymer	Catalyst	Conversion	Appearance	Mn/Mw/PDI
no.	feed	composition	$[H_2O_2]/[M]$	(%)		x10 ⁻³
	(mol ratio)	(mol ratio)	(%)			
A-1	65/35	87.5/12.5	30	20.8	soft wax	0.6/1.0/1.6
A-2	35/35	88.7/11.3	20	60.0	hard wax	1.3/2.1/1.6
A-3	65/35	89.6/10.6	10	69.5	hard wax	2.0/4.0/2.0
A-4	65/35	88.8/11.2	5	52.7	powder	5.7/13.5/2.4
A-5	65/35	91.6/8.4	1	22.7	powder	6.2/11.1/1.8
B-1	54/42/4	63.0/30.4/6.6	10	60.9	powder	3.1/6.8/2.2
B-2	54/42/4	60.2/32.6/7.2	5	77.5	powder	6.6/11.9/1.8
B-3	54/42/4	69.5/24.7/5.8	2	90.0	powder	10.0/16.3/1.6
B-4	54/42/4	62.9/30.3/6.8	0.4	51.6	powder	14.7/29.6/2.0

Polymerization conditions: temperature = 100° C, time = 4 h., solvent = 100 ml acetonitrile

Overall, the polymer yields are reasonably good and are dependent on the concentration of $[H_2O_2]$ that has an optimum value of about 10 % of $[H_2O_2]/[monomer]$ for the VDF/HFP copolymer and about 2 % for the VDF/TrFE/CTFE terpolymer. The polymer molecular weight is basically controlled by the ratio of the [catalyst]/[monomer], the higher the ratio the lower the molecular weight. The resulting polymers range from low molecular weight (white soft wax) to high molecular weight (white powder). Figure 5.9 shows several ¹HNMR spectra of the resulting VDF/HFP copolymers (A-1, A-2, A-3, and A-4 in Table 5.4) with different molecular weight.



Figure 5.9 ¹HNMR spectra of the VDF/HFP copolymers initiated by various $[H_2O_2]/[monomer]$ initiator concentrations, (a) = 30%, (b) = 20%, (c) = 10% and (d) = 5 %.

All four ¹HNMR spectra show two major chemical shifts at 2.8-3.2 ppm (-CH₂CF₂-) and 2.2-2.6 ppm (-CF₂CH₂CH₂CF₂-) from the VDF/HFP backbone. The triplet peaks centered at 3.8 ppm associate with the hydroxyl terminal group (-CH₂OH). Some uncontrolled termination process, by disproportionation reaction that produced unsaturated chain ends (CF₂=CHCF₂CH₂-), was also observed at 4.9-5.5 ppm. The small triplet-triplet peaks centered at 6.1 ppm (CFH=CFCF₂-) are due to the rearrangement of fluorine atom. It is interesting to note that the distinctive disproportionation reaction between two propagating radical chain ends may be associated with the bulky hexafluoropropene comonomer. Two hexafluoropropene macro-radicals can not be coupled due to steric hindrance, preferring the disproportional reaction to form an unsaturated chain end, as discussed in Scheme 5.3.



Figure 5.10 Infrared spectra of VDF/HFP copolymers (A-1, A-3, and A-4 in Table 5.4) initiated by hydrogen peroxide at various concentrations.

$$H_2O_2 + n CF_2=CH_2 + m CF_2=CF \longrightarrow HO \left[CF_2-CH_2]-[CF_2-CF] \\ CF_3 \\$$

where G represents hydroxyl or carboxylic acid groups

initiation

$$H_{2}O_{2} \longrightarrow 2 \text{ OH}^{*} \text{ (major)}$$

$$I + CH_{2}=CF_{2} \longrightarrow \text{HOCH}_{2}CF_{2}^{*} \xrightarrow{\text{n (II, IV, VI, VIII)}} \text{Propagation}$$

$$I + CF_{2}=CH_{2} \longrightarrow [\text{HOCF}_{2}CH_{2}^{*}] \xrightarrow{\text{HF}} [\text{FOCCH}_{2}^{*}] \xrightarrow{\text{Hg}} \text{HOOCCH}_{2}^{*} \longrightarrow$$

$$I + CF_{2}=CF_{3} \longrightarrow [\text{HOCF}_{2}CF_{3}^{*}] \xrightarrow{\text{-HF}} [\text{FOCCF}^{*}] \xrightarrow{\text{Hg}} \text{HOOCCF}^{*} \xrightarrow{\text{n (II, IV, VI, VIII)}} \text{Propagation}$$

$$I + CF_{2}=CF_{3} \longrightarrow [\text{HOCF}_{2}CF_{3}^{*}] \xrightarrow{\text{-HF}} [\text{FOCCF}^{*}] \xrightarrow{\text{Hg}} \text{HOOCCF}^{*} \xrightarrow{\text{n (II, IV, VI, VIII)}} \text{Propagation}$$

$$I + CF_{2}=CF_{2} \longrightarrow [\text{HOCF}_{2}CF_{3}^{*}] \xrightarrow{\text{-CF}_{3}H} [\text{FOCCF}_{2}^{*}] \xrightarrow{\text{Hg}} \text{HOOCCF}^{*} \xrightarrow{\text{n (II, IV, VI, VIII)}} \text{Propagation}$$

$$I + CF_{2}=CF_{2} \longrightarrow [\text{HOCF}_{2}CF_{2}^{*}] \xrightarrow{\text{-CF}_{3}H} [\text{FOCCF}_{2}^{*}] \xrightarrow{\text{Hg}} \text{HOOCCF}^{*} \xrightarrow{\text{n (II, IV, VI, VIII)}} \text{Propagation}$$

Termination



Scheme 5.3 Postulated mechanism of the polymerization of the VDF/HFP initiated by H_2O_2

Figure 5.10 shows infrared spectra of the VDF/HFP copolymers (A-1, A-3, and A-4 in Table 5.4) synthesized by the hydrogen peroxide initiator. Both the hydroxy and the carboxylic chain end functional groups are clearly observed in these spectra. The absorbance bands at 1730 cm⁻¹ is intrinsic to the C=O stretching of the carboxylic functional group, whereas the broad bands from 3500-2900 cm⁻¹ indicates the O-H stretching from both the carboxylic acid and the hydroxy groups. As expected, the intensity of the C=O stretching peak increases as the catalyst concentration increases. It is noted that the shadow peak at 1640 cm⁻¹, which is characteristic to the C=C-H stretching is also observed at the polymer chain ends.

Similar results were also observed in the VDF/TrFE/CTFE terpolymer system prepared by the H_2O_2 initiator. Figure 5.11 shows several ¹H NMR spectra of the VDF/TrFE/CTFE terpolymers (B-2, B-3, and B-4 in Table 5.4) using different initiator concentrations. It is interesting to note the absence of the unsaturated chain end (CF₂=CHCF₂CH₂) in these terpolymers. Without the bulky HFP monomer, the terminal process is more likely to proceed through the coupling reaction rather than the disproportionation reaction.

The possible reaction mechanism during the polymerization of the VDF/HFP by the hydrogen peroxide was postulated in scheme 5.3. In addition to the intended OH terminal groups, there are high concentrations of the COOH terminal groups due to the unstable $-CF_2$ -OH chain end and the substantial amount of terminal double bonds due to the disproportional reactions. Overall, this H₂O₂ initiator system, although provides an easy process of producing the polymer with the high yield, the terminal functional groups are very complicated due to some inevitable side reactions.



Figure 5.11 ¹HNMR spectra of several VDF/TrFE/CTFE terpolymers (B-2, B-3, and B-4) with different initiator concentrations (a) $[H_2O_2]/[monomer] = 5\%$, (b) 2%, and (c) 0.4%

5.3.3 Synthesis of telechelic fluoropolymers having two terminal iodine groups by AIBN/α, ω-diiodo perfluorobutane initiator system

As discussed in Chapter 2, several attempts using functional initiators only achieved very limited success. This section examines the iodine transfer polymerization (ITP) method (the basic mechanism discussed in section 2.3.3) that can prepare telechelic fluoropolymers containing two terminal iodine groups. The terminal iodine chain ends are reactive for crosslinking and coupling reactions. The chemistry is based on the combination of a reversible addition-fragmentation chain transfer (RAFT) process and an α , ω -diiodoperfluoro alkane (I-R_F-I) chain transfer agent. As shown in section 2.3.3, the existing iodine transfer polymerization process, developed by the Daikin Kogyo Company in 1979, has some drawbacks, in terms of the quality of the product. Not all polymer chains contain two terminal iodine groups due to the imperfect chain ends from the initiators. The conventional process involving the initiator, such as the sodium persulfate, produces the dead-end polymer chain. To minimize the dead end polymer chains, a small initiator is usually used, which leads to very long reaction time.

To address these problems, we have discovered a combined initiation system involving an AIBN initiator and an α, ω -diiodoperfluoroalkane (I-R_F-I) chain transfer agent. Since AIBN is known to be a poor initiator for initiating fluoromonomers, which has to react with the chain transfer agent before initiating the polymerization, therefore, there is no dead end polymer chain. Along this improvement of the chemistry for preparing the telechelic fluoropolymers containing two terminal iodine groups, including telechelic terpolymers having desirable electric properties, we also utilized this process to prepare block fluoropolymers that could not be achieved by other existing methods.



Scheme 5.4 Polymerization mechanism using the combination of the AIBN initiator and the diiodoperfluorobutane as chain transfer agent.

Scheme 5.4 shows the proposed reaction mechanism during the polymerization of the VDF by using the AIBN initiator and diiodo-compound as the chain transfer agent. The AIBN is first, thermally decomposed at 70°C (half life of AIBN at 70°C is 4.8 hr.) to create a relatively stable carbon radical (I), which is a poor initiator for the fluoromonomers, including the VDF. However, in the presence of the diiodo-chain transfer agent (II), the

carbon free-radical (I) abstracts iodine atom from (II) and creates new carbon free-radical (III), which then can initiate the polymerization of the VDF monomers. The propagation process is continued by a repeated addition of the monomers until the monomers are depleted. Several termination modes can take place during the reaction by either coupling of the two macro-radicals (V) or with iodo-compounds (III) or (IV), which lead to product (VI), (VII), and (VIII), respectively. All the PVDF polymer chains formed have both ends capped with the iodine groups. The only potential undesirable reaction is the coupling between the macro-radical and the AIBN radical, which leads to the polymer with only one iodine terminal group. However, this reaction is unlikely to occur due to the small amount of the AIBN at any given time during the reaction. In addition, this reaction can be avoided by increasing the ratio of the diiodo-compound to the AIBN concentration.

It is significant to note that this iodine chain transfer polymerization, using AIBN/diiodo-compound system, has a unique living characteristic resembling the radical living polymerization with reversible iodine-capped chain ends. As expected, we should be able to prepare the telechelic polymers with narrow molecular weight distribution and the polymer molecular weight increases with the monomer conversion. Table 5.5 summarizes several VDF/TrFE/CTFE terpolymers prepared by the AIBN/ α , ω -diiodoperfluorobutane system. Figure 5.12 shows plots of the number average molecular weight of the terpolymer vs. the monomer conversion. The combination of the linear relationship of the molecular weight with the monomer conversion and the narrow molecular weight distribution indicates the living characteristic of this polymerization system.

Run	Polymer	$I(CF_2)_2I$	Conversion	Mn/Mw/PDI	Wt % iodine	Iodine/chain	Melting temp.		Curie temp.	
no.	composition	$(x10^{-3} mol)$	/Time (h)	x10 ⁻³			Tm (°C)	$\Delta H (J/g)$	Tc (°C)	$\Delta H_{c} (J/g)$
A-1	69.2/25.7/5.1	0.82	48.5/18	19.7/43.3/1.7	1.4	2.1	128.1	22.2	33.9	6.1
A-2	60.4/33.6/6.0	1.76	81.9/18	16.7/32.1/1.9	0.7	0.9	132.7	21.6	34.8	4.1
A-3	62.9/30.2/6.4	3.3	90.0/18	12.5/20.0/1.6	2.28	2.2	126.6	28.9	35.5	5.9
A-4	63.7/29.6/6.7	4.4	56.1/8	9.5/13.6/1.4	2.86	2.1	110.8	26.7	28.3	4.5
A 5	60 2/22 2/7 5	176	26.1/2	0 6/19 2/1 7	266	2.0	1127	20.0	727	2.2
A-3	09.3/23.2/1.3	1.70	20.1/3	9.0/18.2/1.7	2.00	2.0	113.7	20.9	23.7	5.5
A-6	62.9/29.4/7.7	1.76	30.0/4	9.8/19.0/1.9	2.61	2.0	118.2	23.2	27.6	4.9
A-7	72.7/21.3/6.0	1.76	36.4/6	11.1/19.1/1.7	1.29	1.1	117.9	24.3	28.6	5.1
A-8	67.7/26.7/5.6	1.76	51.2/8	16.1/35.7/2.0	1.28	1.6	125.3	26.9	32.5	7.0
A-9	67.2/27.6/5.2	1.76	64.8/10	20.2/32.1/2.1	0.97	1.4	126.0	27.6	33.0	6.3

Table 5.5 Summary of the VDF/TrFE/CTFE terpolymers initiated by AIBN/ α , ω -diiodoperfluorobutane

Polymerization conditions: polymerization temperature $=80^{\circ}$ C, polymerization time = 4 h., solvent = 30 ml acetonitrile, AIBN amount $= 1.83 \times 10^{-3}$ mol.


Figure 5.12 The relationship of the number average molecular weight and the monomer conversion.

The chain ends of the VDF/TrFE/CTFE terpolymers were detected by the ¹⁹F NMR spectra shown in Figure 5.13. The chemical shift at -35 ppm indicates the two fluorine next to the iodine atom (- CF_2CF_2I). The amount of chain ends, as well as the molecular weight of the terpolymers, can be controlled by controlling the chain transfer agent concentration. The higher the concentration, the higher the amount of the chain ends and the lower the molecular weight would be. Figure 5.14 shows the ¹H NMR spectra of the same set of the VDF/TrFE/CTFE terpolymers with different chain transfer agent concentrations. All telechelic terpolymers are very pure with almost no detectable chemical shift at 1.5 -1.8 ppm [(CH₃)₂C(CN)], associated with the AIBN fragment. In addition to the major peaks at 2.2-3.2 and 5.2-5.8 ppm for the -CH₂CF₂- and -CFHCF₂-, respectively, the new additional peaks between 3.5 and 4.0 ppm correspond to the -CF₂CH₂I group due to the chain transfer reaction of the propagating (VDF/TrFE)-CF₂CH₂* macro radical with the iodine atom in the ICF₂CF₂I chain transfer agent.



Figure 5.13 ¹⁹F NMR spectra of several VDF/TrFE/CTFE terpolymers with different chain transfer agent concentrations (a) 0.8×10^{-3} mol, (b) 2.2×10^{-3} mol and (c) 4.4×10^{-3} mol.



Figure 5.14 ¹H NMR spectra of VDF/TrFE/CTFE terpolymers initiated by AIBN/I(CF₂)₂I with I(CF₂)₂I concentrations (a) 0.8×10^{-3} mol, (b) 2.2×10^{-3} mol and (c) 4.4×10^{-3} mol.

By using the end group analysis method, it becomes difficult to see the terminal iodine chain ends due to the high molecular weight of the polymer. However, the preparation of the block copolymer by sequential monomer addition provided a strong evidence for the living radical polymerization and the terminal iodine groups at both polymer chain ends. In addition, the block copolymer structure offers many distinctive properties, especially mechanical properties that are relatively weak in the ferroelectric terpolymers. The block copolymer or the VDF/TrFE copolymer (with higher crystallinity and tensile strength) would be very interesting, which would not only enhance mechanical properties but also preserve the desirable electric properties of the terpolymer discussed in chapter 4.



Scheme 5.5 Block copolymer by chain extension of iodine-terminated VDF/TrFE/CTFE terpolymer with sequential monomer addition.

Scheme 5.5 shows the reaction mechanism of the preparation of the block copolymer with the combination of the telechelic VDF/TrFE/CTFE polymer having two iodine terminal end groups, and the addition of the VDF (and TrFE) monomers. Table 5.6 summarizes the resulting triblock copolymers that have the VDF/TrFE/CTFE centered block and two PVDF end blocks. The molecular weight of the triblock copolymer (measured by the GPC) increases with the reaction time, without changing molecular weight distribution (PDI) during the polymerization, which strongly suggests the living characteristic of this polymerization system.

Run	VDF/TrFE	Yield (g)	Mn/Mw/PD	Center block		end block		Curie temp.	
no.	composition	/Time (h)	x10 ⁻³	Tm	ΔH	Tm	ΔH	Tc	ΔHc
				(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
1	70/30	1.0/0	11.9/22.6/1.9	126.0	27.6	-	-	33.0	6.3
2	75/25	1.2/5	16.6/29.1/1.8	123.4	10.8	165.1	10.3	38.4	2.7
3	80/20	1.6/10	18.9/31.6/1.7	124.6	14.2	167.9	17.9	37.2	3.2
4	-	2.0/24	21.8/39.6/1.8	123.7	10.2	170.3	26.7	42.1	2.7

Table 5.6Summary of the VDF/TrFE/CTFE -b-VDF copolymers

Center block polymer: 67.2/27.6/5.2 VDF/TrFE/CTFE terpolymer, amount 1.0 g, solvent: 40 ml acetonitrile, polymerization temperature: 80°C, catalyst: 1.2 x 10⁻³ mol AIBN



Figure 5.15 Comparison of DSC curves of (a) VDF/TrFE/CTFE terpolymer (the starting polymer) and three triblock copolymers of PVDF-b-P(VDF/TrFE/CTFE)-b-PVDF prepared with different reaction times, (b) 5 h., (c) 10 h., (d) 24 h., and (e) PVDF homopolymer.

Figure 5.15 compares the DSC curves of three PVDF-b-P(VDF/TrFE/CTFE)-b-PVDF triblock copolymers prepared with different polymerization time with the starting terpolymer and the PVDF homopolymer. As the polymerization time increases, the heat of fusion (Δ H) of the PVDF's melting peak increases indicating the increase of the VDF units in the triblock copolymer chains. Two distinctive melting temperatures in the triblock copolymers imply a clear phase separation between the PVDF homopolymer and the P(VDF/TrFE/CTFE) terpolymer blocks in the polymer morphology.

Other examples of demonstrating the chain extension of the telechelic polymer with two iodine terminal chain ends are the triblock copolymerization of the P(VDF/TrFE/CTFE) with the P(VDF/TrFE) copolymer or the P(VDF/TrFE/CTFE) terpolymer comprising a similar composition. Table 5.7 summarized the experimental results of these triblock copolymers.

Run no.	Ratio of	Mn/Mw/PDI	Melting	g temp.	Curie temp.	
	Center/End	x10 ⁻³	Tm	ΔH	Tc	ΔHc
	Blocks		(°C)	(°C)	(°C)	(°C)
Set 1						
Centered block	4:0	11.6/24.0/2.1	118.8	22.4	22.8	2.7
1 st block	4:1	13.4/27.3/2.0	120.0	23.7	30.9	3.8
2 nd block	4:2	17.7/39.8/2.2	146.9	25.9	42.0	6.0
3 rd block	4:3	18.2/40.4/2.2	147.0	25.1	51.7	7.6
4 th block	4:4	19.3/47.7/2.5	148.5	24.5	54.6	7.8
Set 2						
Centered block	1:0	10.9/28.4/2.6	118.0	14.1	27.0	3.3
1 st block	1:1	23.3/51.1/2.2	129.5	24.2	29.0	3.4
Centered block	1:0	9.5/20.9/2.2	125.4	27.5	32.8	6.4
1 st block	1:1	22.4/50.4/2.3	130.4	26.9	36.8	7.7

Table 5.7 Summary of the triblock copolymers having a P(VDF/TrFE/CTFE) center block and two P(VDF/TrFE) end blocks (Set 1) or two P(VDF/TrFE/CTFE) end blocks (Set 2).

Set 1 is the triblock copolymers prepared by starting with the diiodo-terminated P(VDF/TrFE/CTFE) terpolymer having 60/32/8 mol%, which becomes the center block, and

following with the copolymerization of VDF and TrFE to form two P(VDF/TrFE) end blocks, with about 60/40 mol %. It is significant to note that the molecular weight of the terpolymer as well as its melting and Curie temperatures increase systematically as the ratio of the consecutive block increases. Figure 5.16 compares the DSC curves of several triblock copolymers containing different ratios of center P(VDF/TrFE/CTFE) block and P(VDF/TrFE) end blocks. Only a single Curie transition was observed, and the temperature systematically increased with the addition of the P(VDF/TrFE) end blocks. On the other hand, the melting peak, which also increases with the increase of the P(VDF/TrFE) end blocks, comprising a shoulder, indicates a somewhat mixing phase between the two crystals of the terpolymer and the copolymer. These results are very different from those of simple solution blending of the VDF/TrFE/CTFE terpolymer and the VDF/TrFE copolymer with similar composition, shown in Figure 5.17. Both the melting and the Curie temperatures of the polymer blends show a clear phase separation, with two sets of phase transitions for two type crystals. Basically, both the melting and the Curie temperatures of the polymer blend stay at the same positions and change their relative intensity as the VDF/TrFE copolymer increases its content. Figure 5.18 shows the GPC curves of the center P(VDF/TrFE/CTFE) block and the three consecutive P(VDF/TrFE) copolymer end blocks. The increase of the average molecular weight of the consecutive end blocks is clearly demonstrated. The overall results clearly indicate the formation of the triblock copolymers. It is highly anticipated that by adjusting the ratios between the P(VDF/TrFE/CTFE) terpolymer center block and the P(VDF/TrFE) copolymer end blocks, the mechanical properties of the terpolymer, such as the tensile strength, could be enhanced, whereas, the electrical properties of the P(VDF/TrFE/CTFE) terpolymer are still preserved.



Figure 5.16 DSC curve comparison among two P(VDF/TrFE)-b-P(VDF/TrFE/CTFE)-b-P(VDF/TrFE) triblock copolymers including (b) 1/1 and (c) 2/1 mole ratios between P(VDF/TrFE/CTFE) and P(VDF/TrFE) blocks and the corresponding (a) VDF/TrFE (55/45) copolymer and (d) VDF/TrFE/CTFE terpolymer.



Figure 5.17 DSC comparison of two solution blended samples including (b) 1/1 and (c) 2/1 mole ratios between P(VDF/TrFE/CTFE) terpolymer and P(VDF/TrFE) copolymer and the corresponding (a) VDF/TrFE (55/45) copolymer and (d) VDF/TrFE/CTFE terpolymer



Figure 5.18 GPC curve comparison of the triblock copolymers (a) center block, (b) 1^{st} block, (c) 3^{rd} block, and (d) 4^{th} block.

One minor concern of the functional P(VDF/TrFE/CTFE) terpolymer is its molecular weight (in the range of the 10,000-20,000) after a batch reaction, which is not very high. To address this problem and demonstrate the chemistry of the telechelic fluoro-terpolymer with terminal iodines, we synthesized two consecutive block copolymer of the VDF/TrFE/CTFE terpolymer containing similar composition. The experimental results are summarized in Table 5.7 (Set 2). Basically, by block copolymerization, the molecular weight of the terpolymer can easily increase to more than double. The increase of the average molecular weight of the block copolymer is clearly seen in the GPC curve comparison in Figure 5.19. Figure 5.20 shows the DSC curves of two terpolymers before and after the chain extension, respectively. Both the melting and the Curie temperatures are almost identical.



Figure 5.19 GPC curve comparison of the VDF/TrFE/CTFE terpolymer (a) before block, and (b) after block



Figure 5.20 DSC comparison of two VDF/TrFE/CTFE terpolymers (a) before and (b) after chain extension.

5.3.4 Electrical properties of functional fluoropolymers

As discussed in section 5.1, we postulated that the telechelic VDF/TrFE/chlorocontaining terpolymers containing terminal functional (polar and reactive) groups could provide the needed interactive properties but also preserve the existing desirable properties, because of the undisturbed polymer backbone structure. All functionalization approaches, including (i) functional borane/oxygen initiators and (ii) iodine transfer polymerization (ITP) method, were geared to prepare the telechelic fluoropolymer structures.

Figure 5.21 shows dielectric constant of three telechelic VDF/TrFE/CTFE terpolymers prepared by (a) functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo compounds, respectively. The dielectric constant curves during the heating-cooling cycles with various frequencies are almost identical with those of the corresponding VDF/TrFE/CTFE terpolymers that have no terminal functional group. The dielectric constant as high as 100 was observed in some systems. Figure 5.22 shows the polarization hysteresis loop of the same three VDF/TrFE/CTFE terpolymers. Basically, the coercive field of these terpolymers are very small as well as the ramanent polarization. Table 5.8 summarized their thermal properties and electrical properties. With different initiator systems, the telechelic terpolymers still possess high dielectric constant and narrow hysteresis polarization loop.

Table 5.8Summary of the thermal and the electrical properties of the telechelicVDF/TrFE/CTFE terpolymers prepared by various initiator systems.

Catalyst	Thermal properties		Dielectric constant@1kHz		Polarization loop@RT		
	Tm	Tc	DK/	Loss	Ec	Pmax (mC/m ²)	
	(°C)	(°C)	Peak (°C)		(MV/m)		
Borane	125	25	75/33	0.05	11.5	70	
$(Cl_3CCOO)_2$	128	26	65/38	0.04	12.5	50	
H_2O_2	122	29	95/38	0.05	7.2	50	
AIBN/I	113	26	90/30	0.05	11.2	55	

Polymer:VDF/TrFE/CTFE with the composition about 60/22/8



Figure 5.21 Dielectric constant of the telechelic VDF/TrFE/CTFE terpolymers prepared by (a) functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo compounds.



Figure 5.22 Polarization loops of the telechelic VDF/TrFE/CTFE terpolymers prepared by (a) functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo compounds.

5.4 Conclusion

In this Chapter, we have investigated several new initiator systems, including (a) functional borane initiator, (b) functional low temperature peroxide initiator, (c) hydrogen peroxide initiator, and (d) AIBN/diiodo compounds, which allow the preparation of the telechelic polymers containing terminal functional group(s). Although the borane initiator shows many advantages, including the ease of introducing functional group at the polymer chain end and the potential for modification of fluoropolymer with non-fluoropolymer, there are some drawbacks, such as low polymerization yield and low efficiency of block copolymerization. On the other hand, both peroxide initiators suffer from many side reactions, such as chain transfer reactions and functional group conversion, which result in a complicated molecular structure and mixed end groups. The most reliable method may be the modified iodine chain transfer polymerization using the combination of the AIBN and diiodo compound, which forms the telechelic terpolymers containing two iodine terminal groups with high yields and good control of polymer molecular weight and narrow molecular weight distribution. The combination of this system and sequential monomer addition provides the best method to prepare block copolymers.

Overall, functional borane initiator produces polymers with one terminal functional group, whereas, the iodine chain transfer polymerization yields polymer with two iodine terminal groups. Both functionalization methods only change the polymer chain ends, the properties of the fluoropolymer (thermal stability, acid and oxidation stability, low water absorptivity, crystallinity, and electric and mechanical properties) are all preserved. The formation of block copolymers is also useful, especially in enhancing the mechanical properties (modulus) of the terpolymers.

5.5 References

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Chapter 6

Conclusion and future work

In the first part of my research program (Chapter3 and 4), I focused on the development of a new family of fluoroterpolymers comprising VDF, TrFE, and chlorocontaining termonomers, including vinyl chloride (VC), chlorodifluoroethylene (CDFE), chlorofluoroethylene (CFE), and chlorotrifluoroethylene (CTFE). The novel polymerization process involves a combination of a low temperature borane/oxygen initiator and the bulk reaction condition, which allows the thorough mixing of all monomers during the terpolymerization reaction, resulting in the homogeneous distribution of the termonomer units in the polymer chain. A chloro-containing termonomer, especially CDFE and CTFE, having comparative reactivities with VDF and TrFE, lead to the terpolymer with a relatively narrow molecular weight and composition distributions. The homogeneous incorporation of the chloro-containing termonomers in the VDF/TrFE copolymer chain is crucial in modifying its polymer chain conformation and crystal structure. With ~7 mol% of the termonomer units, the copolymer alters the crystalline phase from the ferroelectric β phase (all-trans conformation) toward another ferroelectric γ phase ($tttg^+tttg^-$ conformation), without significant reduction of the overall crystallinity. The new ferroelectric γ phase of the terpolymer, with shorter trans-sequence and smaller crystalline domains, reduces Curie phase transition temperature with a much smaller energy barrier for phase transition. The unique combination in this new ferroelectric γ phase, with a small energy barrier and the large unit expansion or contraction during the crystal phase transition, results in high electromechanical response and behaves like a ferroelectric relaxor. The terpolymer shows high dielectric

constant, as high as 100, with narrow hysteresis and high field-induced longitudinal strain (up to 4-5% at 150 MV/m) at ambient temperature.

Despite achieving many desirable properties, the lack of the functional group in the terpolymers limits the possibility of further improving their properties such as the mechanical strength, adhesion, miscibility, compatibility, and curability. In addition, the electric field used to drive high longitudinal strain is very high, which is a major concern for many applications, especially in the biological and medical systems.

The second part of my research (Chapter 5) tries to address this shortfall by developing telechelic VDF/TrFE/chloro-containing terpolymers having functional (polar and reactive) terminal groups, and diblock copolymers containing a VDF/TrFE/chloro-containing terpolymer and functional polymers. These telechelic and block polymers not only provide the interactive properties but also preserve the existing desirable properties due to the undisturbed polymer backbone. Two chemical methods have been studied, including (i) the use of functional borane/oxygen initiators that carry functional groups and exhibit living radical polymerization mechanism, and (ii) the investigation of an improved iodine transfer polymerization (ITP) method to prepare telechelic fluoropolymers containing two terminal iodine groups. The former method although has some advantages in terms of ease and high purity of the polymer with the desirable reactive functional groups such as acetyl (can be converted to hydroxy group), silane and bromine groups, the polymerization yield is not very high due to the intramolecular interaction between the boron atom and the functional groups. The latter method, the iodine transfer polymerization (ITP), provides a very effective method with high yield, good catalyst efficiency, and well-defined telechelic polymer structure with two reactive terminal iodine functional groups on both chain ends. The chemistry involved an

improved iodine transfer polymerization process using the combination of the AIBN imitator and a diiodo-compound chain transfer agent. Both initiation systems also show a living radical polymerization characteristic leading to the well-defined polymer with narrow molecular weight and composition distribution. The living characteristic was demonstrated by the block copolymerization of the terpolymer with the non-fluoropolymer (such as the PMMA homopolymer), or the fluoropolymer (including the PVDF homopolymer and the VDF/TrFE copolymer). The material from the latter case is very useful in terms of the improvement of the mechanical strength of the terpolymer. The combination of the complementary properties from the PVDF homopolymer or the VDF/TrFE copolymer (mechanical strength) and the terpolymer (low Curie phase transition temperature and low energy barrier), make the block copolymer one of the most interesting materials for further study.

With the availability of telechelic fluoro terpolymers having the reactive terminal groups at one or both chain ends and preserving the desirable properties, we can start to address the major issue of the high electric field requirement to achieve high strain. As mentioned above, to reduce this high electric field requirement, we have to either reduce the space between the electrodes or increase the dielectric constant of the terpolymer. In both cases, some foreign materials is needed to introduce into the system, such as imbedding conducting material (could be a conducting polymer) serving as electrodes in the first approach or blending high dielectric ferroelectric inorganic nano-particles in the second approach.

In respect to the reduction of the electrode gap, the functional fluoropolymer containing terminal iodine chain ends is very useful. The iodine chain ends are very reactive

for further block copolymerization with the conducting polymer such as the polythiophene under specific conditions. A proposed reaction route of preparing block copolymer containing both ferroelectric and conducting polymer blocks is illustrated in Scheme 6.1.



Scheme 6.1

The chemistry of the preparation of the block copolymer could be based on the coupling reaction of the polythiophene with the fluoropolymer containing iodine terminal chain ends in the presence of the nickel catalyst. It is expected that by self assembly of the block copolymer, each conducting block is sandwiched between the terpolymer and serves as an electrode. Hence an electrode gap would significantly be reduced (from micro scale to nano scale) resulting in low electric field input.

The second approach is the composite of the inorganic high dielectric constant material with the fluoropolymer carrying hydroxy functional groups. The most interesting high dielectric constant is the metallophthalocyanines, especially copper-phthalocyanine (CuPc), which is the inorganic material carrying the peripheral carboxylic groups as illustrated below (from ref. 1).



Scheme 6.2

The CuPc is a sheet-like polymer with highly conjugated double bond and has a large planar structure. Our preliminary work shows that the high dielectric constant, as high as 100,000 at 100 Hz and room temperature, could be obtained as can be seen in Figure 6.1. The high dielectric constant can be explained in terms of the long-range electron orbital delocalization, so called nomadic polarization.² Figure 6.2 shows the postulated reaction of the CuPc with the terpolymer barring the hydroxyl functional group. It is anticipated that by condensation or coupling reaction of the peripheral carboxylic groups of the CuPc with the hydroxy group of the fluoropolymer, the dielectric constant of the terpolymer could be

drastically increased. In addition, the high dielectric loss, due to the stack of the phthalocyanine sheet, could be reduced due to the separation between the sheets by the terpolymer.



Figure 6.1 Dielectric constant (a) and the dielectric loss (b) of the copper-phthalocyanine



Figure 6.2 The postulated reaction of the copper-phthalocyanine with the terpolymer barring hydroxyl group.

The earlier work of the composite of the CuPc with the fluoropolymer was done by H. S. Xu et al.³ A large amount of the CuPc, as much as 55 wt%, was introduced into the

polymer matrix to increase the dielectric constant of the VDF/TrFE copolymer to 1000 (at 100 Hz and room temperature). This may cause the stiffness problem in the composite resulting in the processing problem. It was also found that the dielectric constant the composite largely depends on the homogeneity of the composite. By simply mixing of the CuPc with the polymer, the inhomogeneity problem can not be avoided. To address those problems, it is suggested that the chemical reaction of the CuPc with the polymer could lead to the better properties, higher dielectric constant and more homogeneous material, with less amount of the material used.

References

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