“Telechelic” Ferroelectric Fluoro Terpolymers With High Chemical Reactivity and Large Electromechanical Response at Ambient Temperature

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Abstract

This paper discusses a new family of telechelic ferroelectric polymorphs fluoro-terpolymers having OH and COOH terminal groups. The polymer backbone comprises of vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a small amount of chlorine-containing third monomers. The slightly bulky chlorine atoms serve as the kinks, which alters the chain conformation from all-trans (β-phase) to $tttg^{+}tttg^{-}$ (γ-phase), without reducing crystallinity. Consequently, the terpolymers exhibit low Curie temperature, high dielectric constant (>80) and large electrostrictive response (>5%) at ambient temperature. On the other hand, the reactive terminal groups provide the terpolymers chemical reactivity to form super-structures that may further enhance their electric performance.

Introduction

Poly(vinylidiene fluoride) (PVDF)[1, 2] and its copolymers[3-6], especially vinylidiene fluoride/ trifluoroethylene (VDF/TrFE), are the most investigated ferroelectric polymer system with high piezoelectricity and pyroelectricity. Their interesting electric properties originate from the strong dipole in the constituted CF_2 units along the polymer chain and the orientation of dipoles in some of the crystalline phases (such as β- and γ-phases)[7, 8]. They exhibit polymorphic structure across the whole composition range, with high crystallinity and only slight differences in the melting temperature. Although, the crystallization of PVDF homopolymer from the melt form trans-gauche ($tg^{+}tg^{-}$) polymer chain conformation, which results in a paraelectric phase (α-phase), the VDF/TrFE copolymer with > 20% TrFE units changes to all-trans ($t_{m>4}$) chain conformation with a ferroelectric phase (β-phase). The extra fluorine atoms in TrFE comonomers prevent the polymer chain from adopting trans-gauche ($tg^{+}tg^{-}$) conformation and result in an extended planer zigzag all-trans conformation. The ferroelectricity in the copolymer was strongly evidenced by the existence of Curie (ferroelectric-paraelectric) phase transition temperature (T_c). In this transition, the all-trans polymer chain conformation in the ferroelectric β-phase changes to trans-gauche chain conformation in paraelectric α-phase.

One major drawback in VDF/TrFE copolymers is the relatively high Curie

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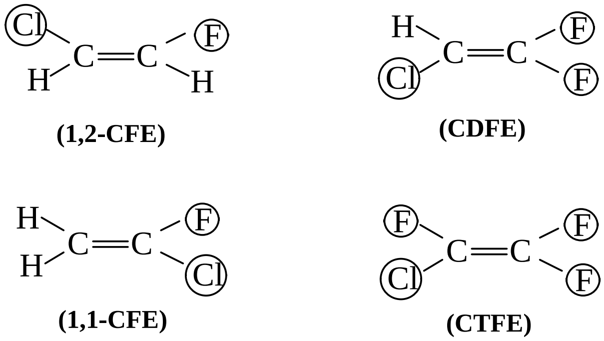
temperature. Although it is very dependent on the copolymer composition, the lowest T_c observed is > 60^o C in VDF/TrFE (55/45) copolymer[9], which is well above ambient temperature (the most convenient application temperature). Therefore, the dielectric response of the dipoles to the electric field is very small at ambient temperature despite the VDF/TrFE copolymer exhibiting a high piezoelectric constant (d_{31} = 15-30 pC/N).[10] The small response to the electric field is also revealed in a low dielectric constant and a large polarization hysteresis loop[11, 12] due to the high energy barrier of switching the dipole direction at ambient temperature.

In the past decade, many researchers have devoted their efforts related to PVDF and VDF/TrFE copolymers to the general goal of reducing the Curie transition temperature, narrowing the polarization hysteresis loop, and generating a large electromechanical response at ambient temperature. The direct correlation between the reduced polar domain size and lower energy barrier, shown in ferroelectric ceramic materials,[13] led to many attempts to alter copolymer morphology. The methods include mechanical deformation,[14] electron-irradiation,[15, 16] uniaxial drawing,[17] crystallization under high pressure,[18] and crystallization under high electric field.[19]

Termonomer Approach

In our laboratory[20, 21], we introduced a new chemical approach by incorporating some slightly bulky chloro-containing third monomer units into the VDF/TrFE copolymer structure, which include vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), and chlorotrifluoroethylene (CTFE), as illustrated in Scheme 1. The terpolymers formed by a combination of a control radical polymerization mechanism and homogeneous reaction conditions (bulk or solution process) feature relatively narrow molecular weight and composition distributions and solution and melt processible.



Scheme 1

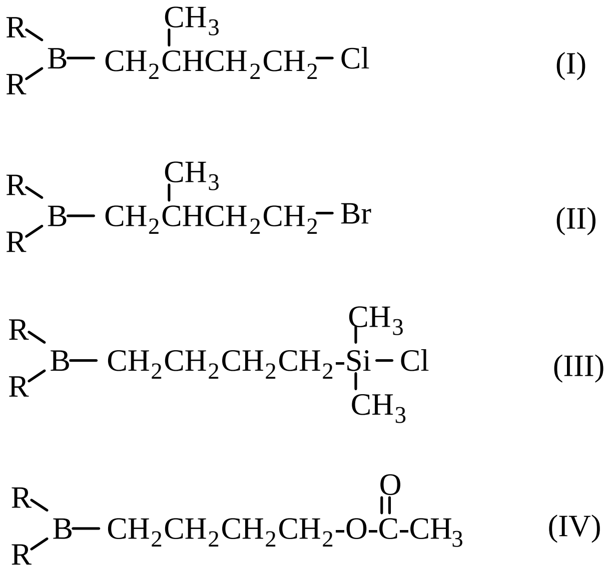
The slightly bulky chlorine atoms (radius of F and Cl are 1.19 and 1.67 A, respectively) homogeneously located along the VDF/TrFE polymer chain introduce the kinks (with gauche conformation) into the otherwise planer zigzag all-trans chain conformation. As a result, they spontaneously alter the crystalline phase from ferroelectric β-phase ($t_{m>4}$) 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 phase transition, and the terpolymers show high dielectric constant, strong ferroelectricity, and large electromechanical response at ambient temperature. Therefore, the terpolymers exhibited a slim polarization hysteresis loop and large electrostrictive response (> 4%) at ambient temperature.

Functionalization of Fluoropolymers

Although new fluoroterpolymers exhibit interesting electrical properties, there are two concerns, 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 fluoroterpolymer 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 for either chemical or physical interactions with the external materials. Unfortunately, fluoropolymers are generally 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 many applications of fluoropolymers, especially in coating, polymer blends, and composites. In addition, the reactive functional groups in the terpolymers could be used as the coupling sites for preparing block and graft copolymers, or crosslinking sites for forming 3-D network. Both approaches could achieve better mechanic properties.

Telechelic polymer having functional groups at the polymer chain ends is a very desirable functional polymer structure, which provides the needed reactive functional groups but also preserve the existing properties of the polymer. The telechelic polymer is also the ideal structure for preparing block and graft copolymers. Unfortunately, the existing chemical methods in the preparation of telechelic fluoropolymers are very limited. The most valuable method involves iodine transfer polymerization (ITP process)[22, 23] that 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; 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.

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 VDF/TrFE/chloro-containing terpolymers. With the objective of preparing telechelic fluoropolymers, two chemical methods have been studied, including (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.



$R_2B-CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2-Cl$ (I)

$R_2B-CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2-Br$ (II)

$R_2B-CH_2CH_2CH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}-Cl$ (III)

$R_2B-CH_2CH_2CH_2CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$ (IV)

Scheme 2

As illustrated in Scheme 2, several functional group containing borane imitators have been synthesized and evaluated in the polymerization of fluoromonomers. ^{11}B NMR spectra of the functionalized borane initiators (I), (II), (III), and (IV) show a major chemical shift at 86 ppm, corresponding to trialkylboran moieties 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. 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.

Usually, the molecular weight of the polymer linearly increases with the reaction time, indicating a pseudo-living radical polymerization process. Figure 1 shows two examples of the ^{1}H NMR spectra of the polymers that were initiated by the functional borane initiators: (a) the VDF/TrFE/CTFE terpolymer produced by the $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$ initiator, and (b) the VDF/HFP copolymer produced by the $B(CH_2CH(CH_3)CH_2Cl)_3$ initiator. Both functional groups at the beginning of each polymer chains, although are very small due to high molecular weight of the polymer, are clearly observed in the ^{1}H NMR spectra. In Figure 1 (a), a small peak at the chemical shift of 0.1 ppm corresponds to three protons connected to the silane atom ($-Si(C\mathbf{H}_3)_2Cl$), 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 1 (b), at the chemical shift of 0.9 ppm, represents three protons (-

$CH(C\mathbf{H}_3)CH_2Cl)$ of the end group of the polymer produced from the $B(CH_2CH(CH_3)CH_2Cl)_3$ initiator, whereas the peak at the chemical shift of 3.6 ppm indicates two protons adjacent to the chlorine atom ($-CH(CH_3)C\mathbf{H}_2Cl$).

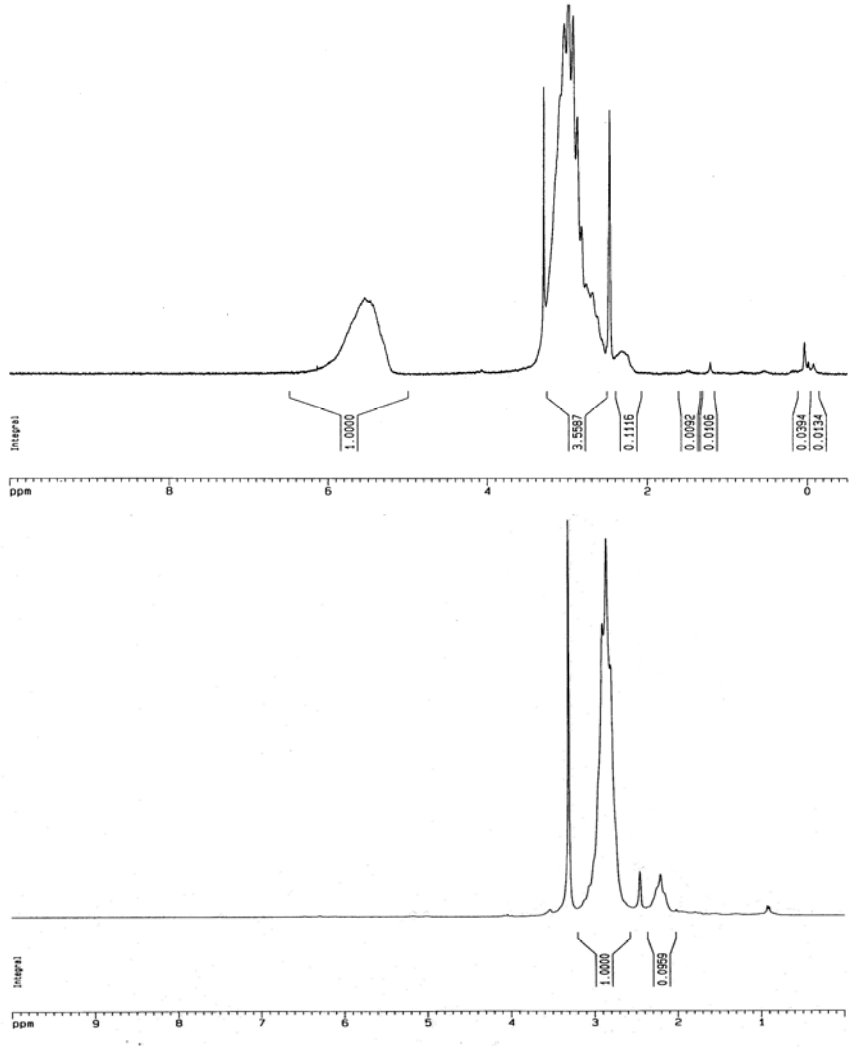


Figure 1 Two typical ^1H NMR spectra of the polymer produced by functional borane initiators (a)VDF/TrFE/CTFE terpolymer produced by $B(CH_2CH_2CH_2SiCl(CH_3)_2)_3$ initiator and (b) VDF/HFP copolymer produced by $B(CH_2CH(CH_3)CH_2Cl)_3$ initiator.

It was very interesting to take advantage of the pseudo-living polymerization characteristic in the borane/oxygen initiator system to prepare new block copolymers. 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 sequential monomer addition of VDF/HFP, then MMA. Figure 2 compares the ^1H NMR spectrum spectra of PMMA homopolymer, P(VDF/HFP-b-MMA) diblock copolymer, and P(VDF/HFP) copolymer. Figure 2 (b) shows all the peaks for both PMMA and P(VDF/HFP) polymer segments, including 1.2-1.4 ppm ($-CH_2-C(C\mathbf{H}_3)-$), 2.7 ppm ($C\mathbf{H}_2-C(CH_3)-$) and 4.0 ppm ($-CH_2-C(COOC\mathbf{H}_3)$ for PMMA and a major peak at 2.8-3.2 ($-C\mathbf{H}_2-CF_2-$) for

P(VDF/HFP).

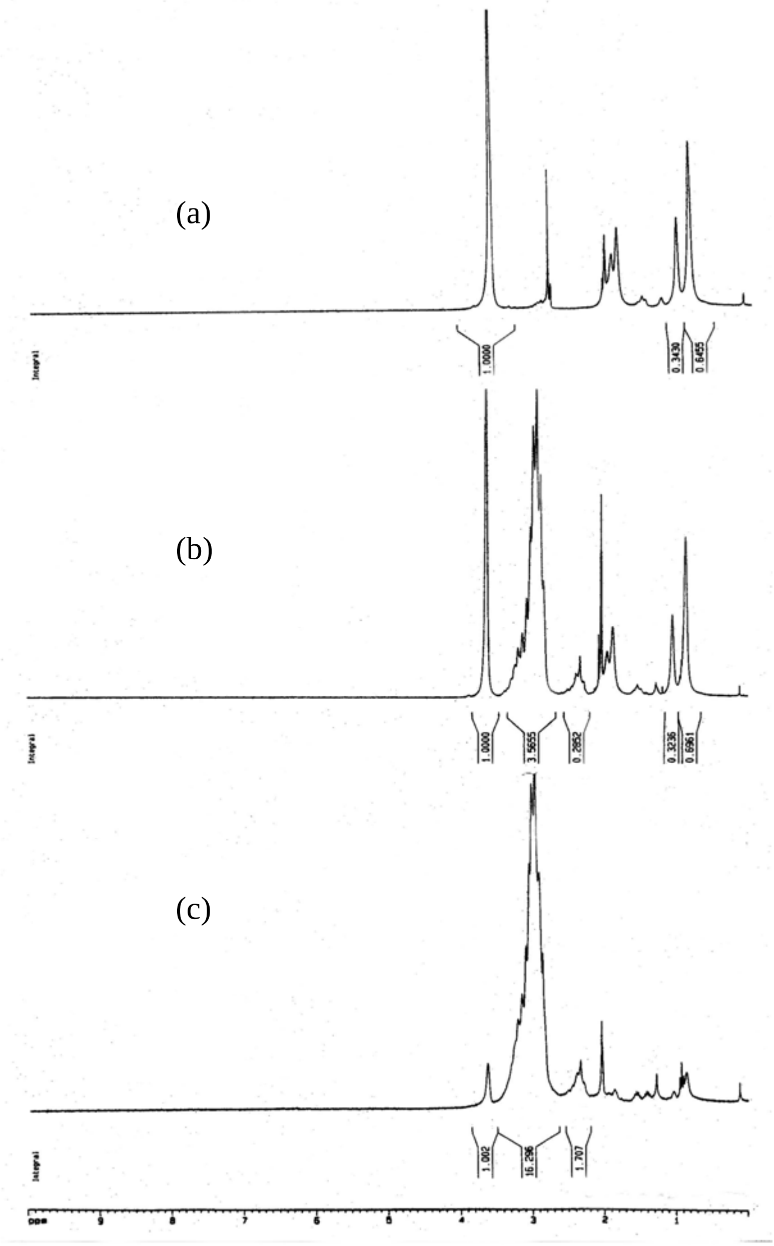


Figure 2 ^{1}H NMR spectra of (a) PMMA homopolymer, (b) P(VDF/HFP-b-MMA) diblock copolymer, and (c) P(VDF/HFP) copolymer.

Figure 3 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.

Overall, the results strongly suggest the formation of P(VDF/HFP-b-MMA) diblock copolymer.

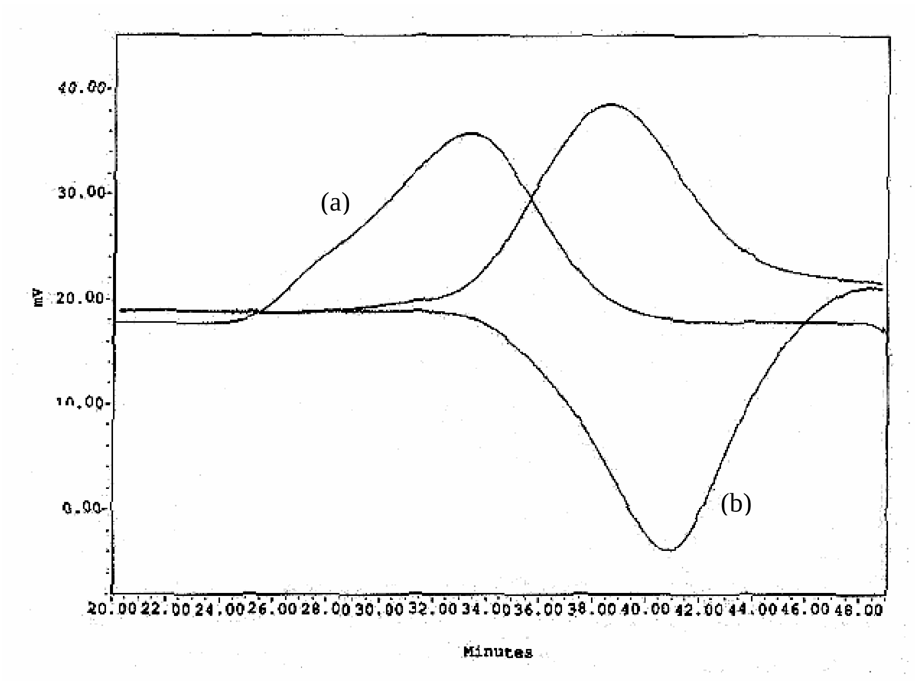
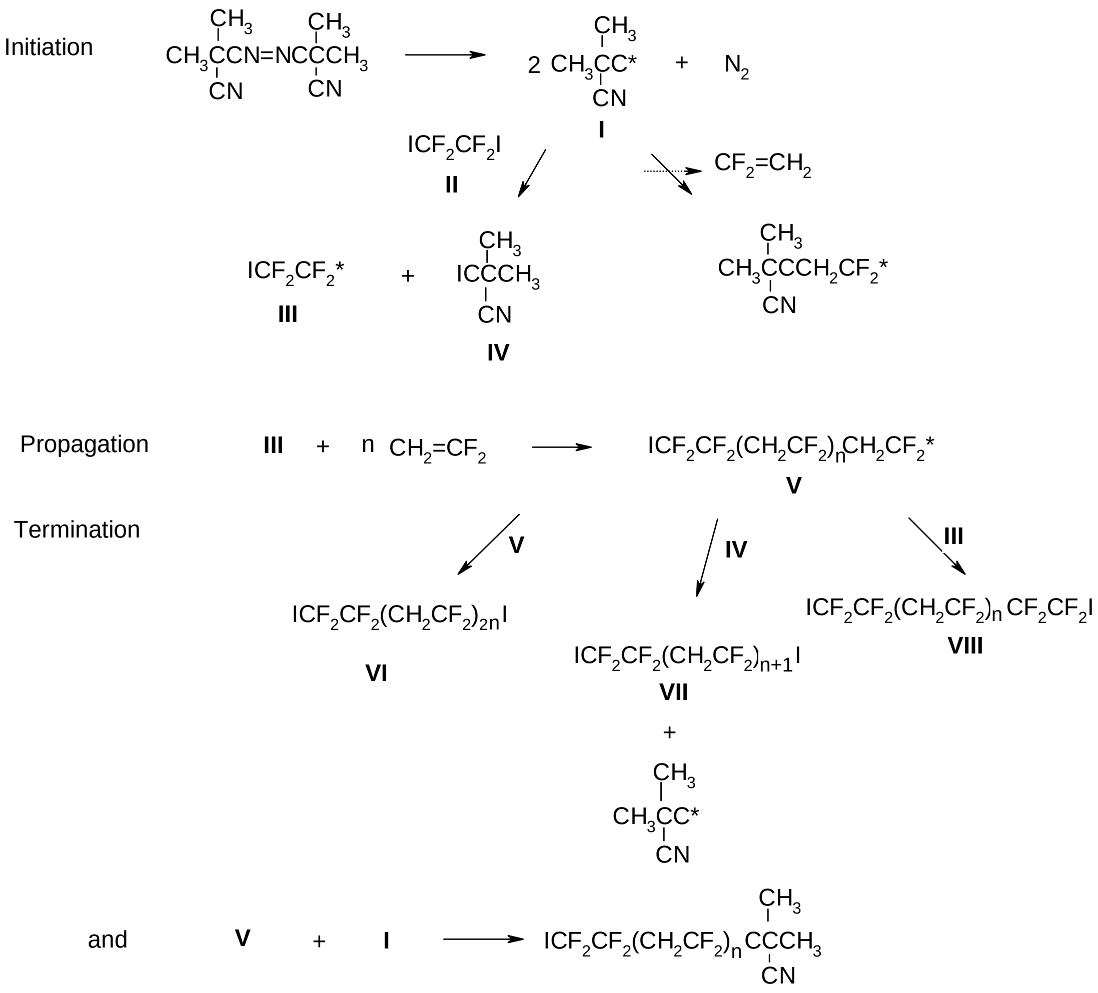


Figure 3 GPC curves of (a) P(VDF/HFP-b-MMA) diblock copolymer and (b) P(VDF/HFP) copolymer.

The other approach in the preparation of telechelic fluoropolymers involving a combined initiation system containing AIBN and α,ω-diiodoperfluoroalkane (I-R_F-I). Scheme 3 illustrates the reaction mechanism during the polymerization of the VDF. 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. Overall, there is almost no dead end polymer chain.



Scheme 3

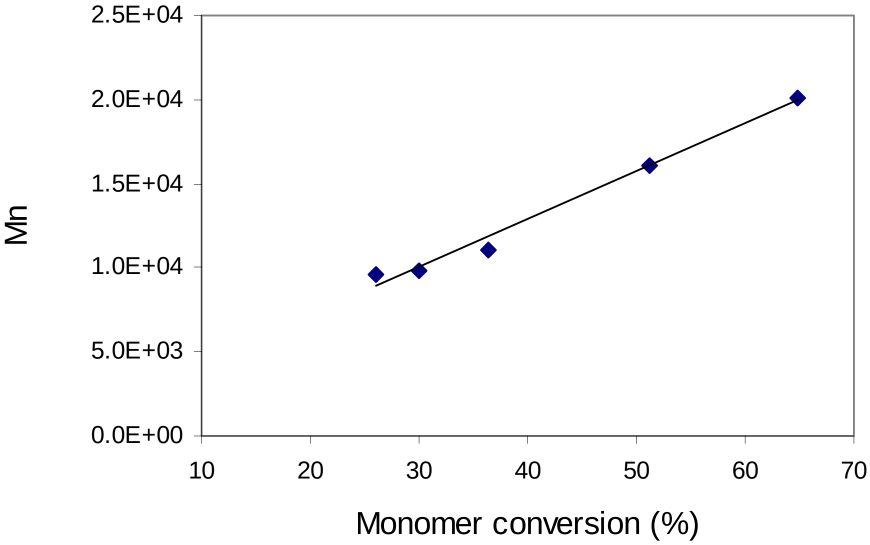


Figure 4 Molecular weight of VDF/TrFE/CTFE terpolymer vs. monomer conversion.

It is significant to note that this improved 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. Figure 4 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.

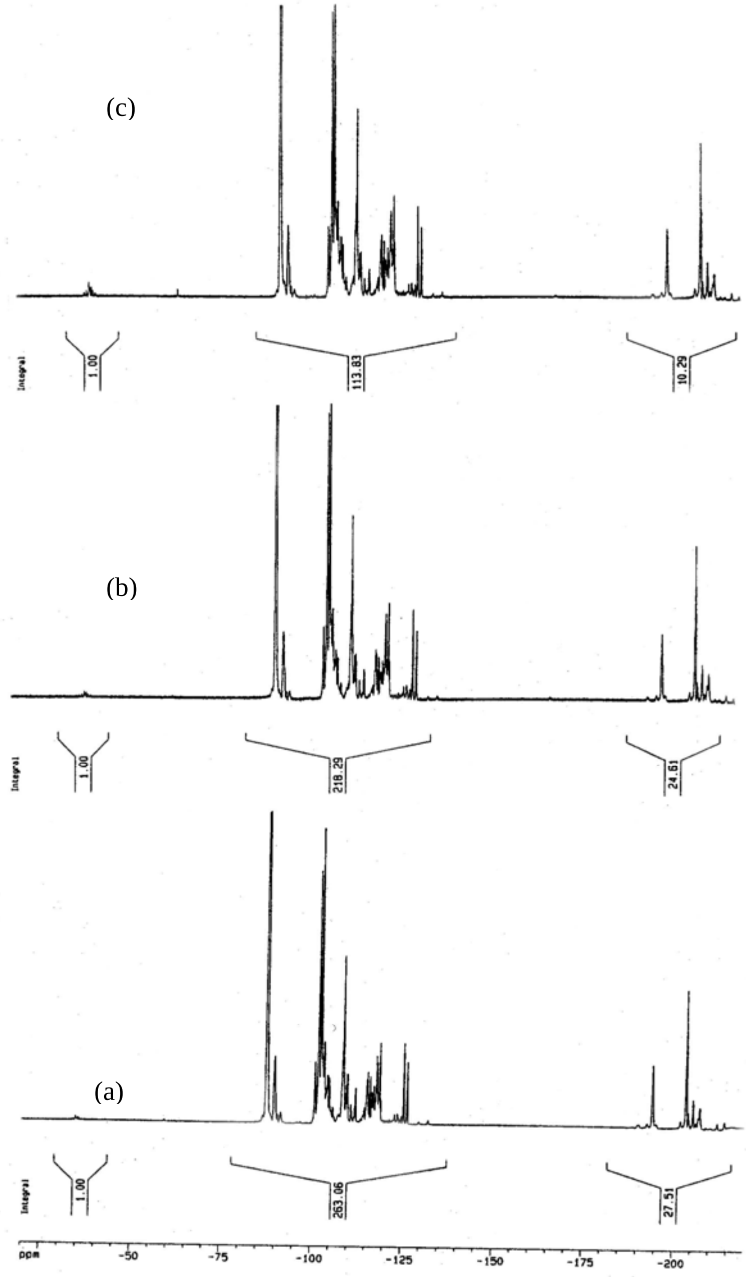


Figure 5. ^{19}F NMR spectra of several VDF/TrFE/CTFE terpolymers with different chain transfer agent concentrations (a) 0.8 x 10^{-3} mol, (b) 2.2 x 10^{-3} mol and (c) 4.4 x 10^{-3} mol.

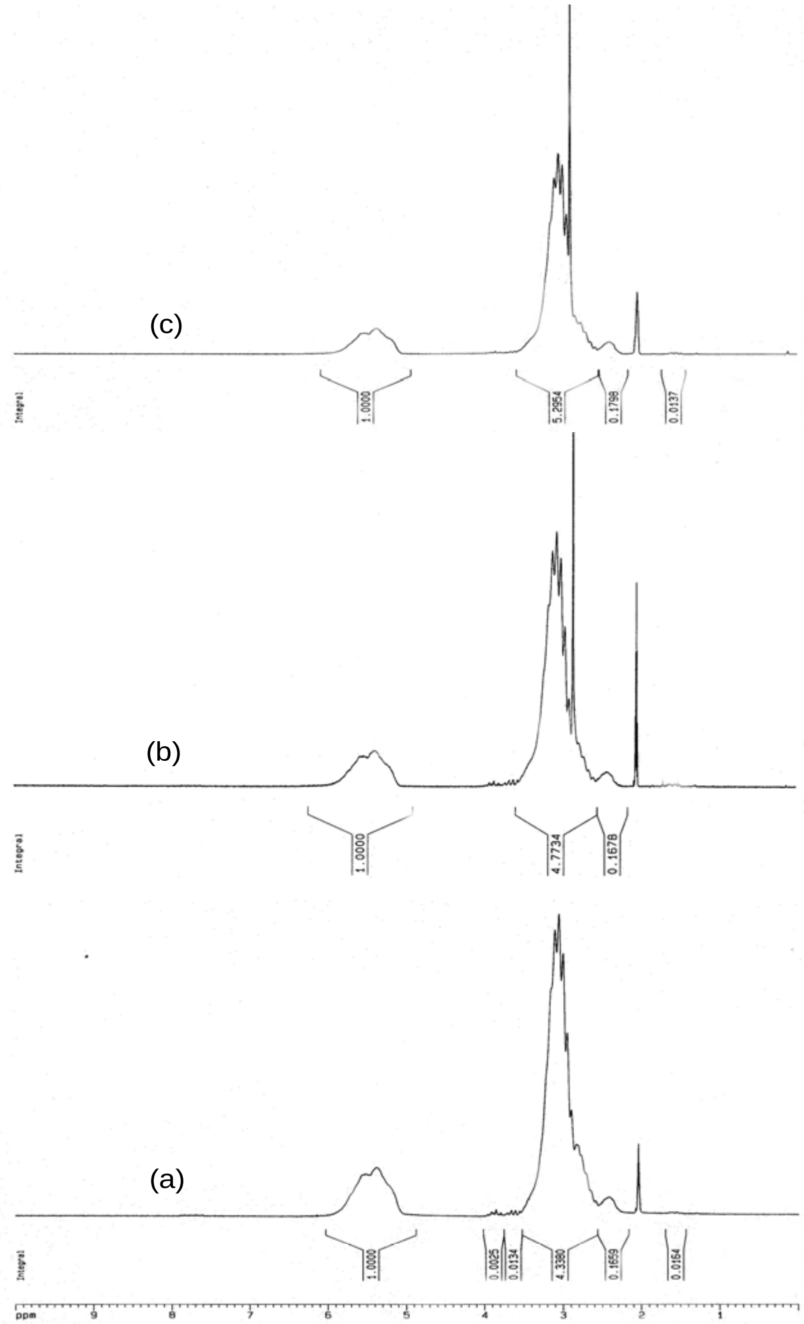


Figure 6 ^1H NMR spectra of VDF/TrFE/CTFE terpolymers initiated by AIBN/I(CF_2)$_2$I with I(CF_2)$_2$I concentrations (a) 0.8 x 10^{-3} mol, (b) 2.2 x 10^{-3} mol and (c) 4.4 x 10^{-3} mol.

Three VDF/TrFE/CTFE terpolymers were examined by ^{19}F and ^1H NMR spectra shown in Figures 5 and 6, respectively. The chemical shift at -35 ppm indicates the two fluorine next to the iodine atom (-C**F**$_2$C**F**$_2$I). The amount of chain ends, as well as the molecular weight of the terpolymers, can be controlled by the concentration of chain transfer agent, higher the concentration, higher the amount of the chain ends, and lower the molecular weight. All ^1H NMR spectra indicate high purity of the VDF/TrFE/CTFE terpolymers with almost no detectable chemical shift at 1.5 -1.8 ppm [(C**H**$_3$)$_2$C(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 -C**H**$_2$CF$_2$- and -CF**H**CF$_2$-, respectively, the new additional peaks between 3.5 and 4.0 ppm correspond to the -CF$_2$C**H**$_2$I group due to the chain transfer reaction of the propagating (VDF/TrFE)-CF$_2$CH$_2$* macro radical with the iodine atom in the **I**CF$_2$CF$_2$I chain transfer agent.

Electrical properties of functional fluoropolymers

As discussed before, we postulated that the telechelic VDF/TrFE/chloro-containing 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.

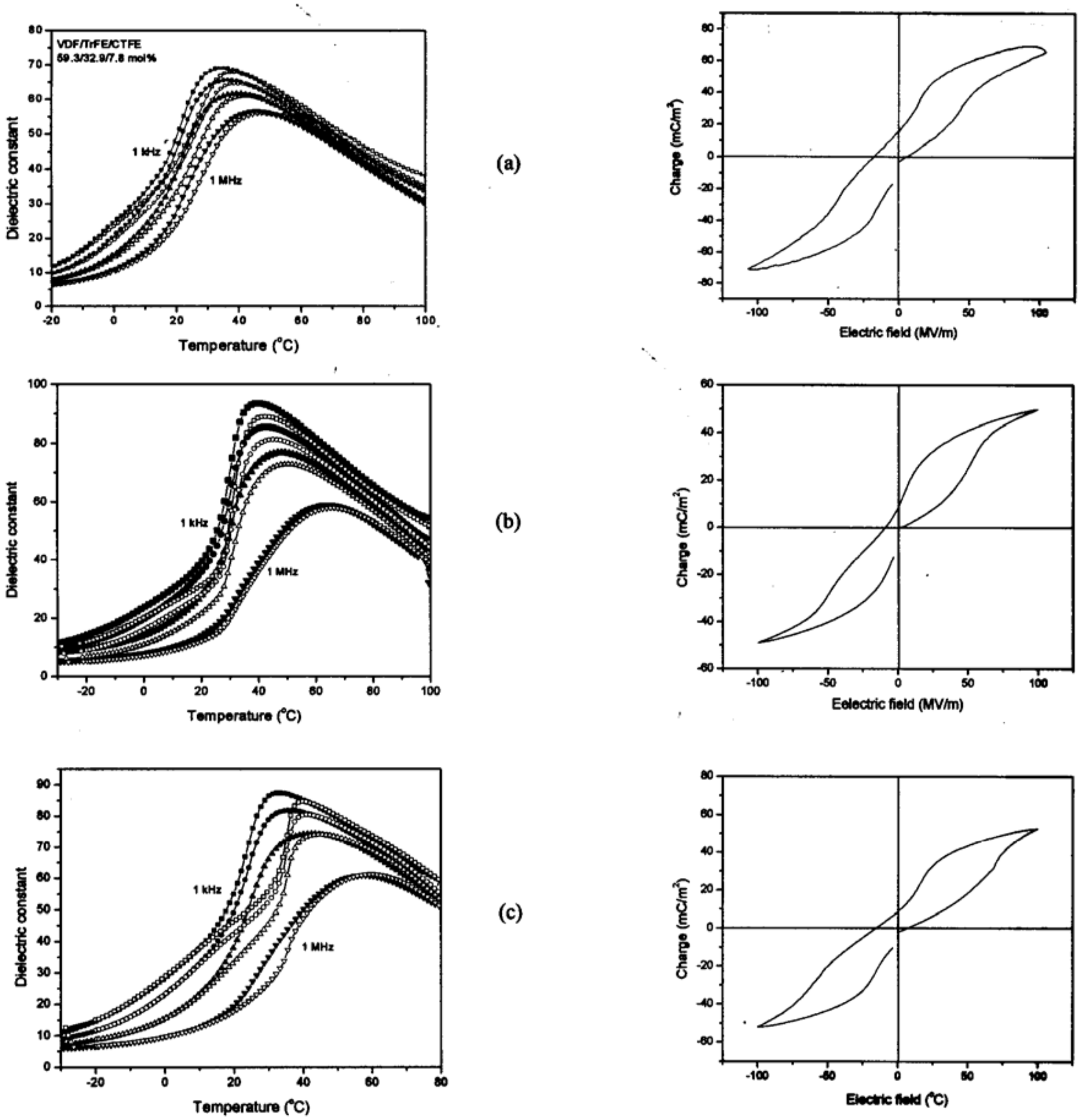


Figure 7. Dielectric constant and polarization loops of three telechelic VDF/TrFE/CTFE terpolymers prepared by (a) functional borane initiator, (b) hydrogen peroxide, and (c) AIBN/diiodo compounds.

Figure 7 shows dielectric constant and polarization loops 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. All polarization curves show slim hysteresis loops. Basically, the coercive field of these terpolymers are very small as well as the ramanent polarization. With different initiator systems, the telechelic terpolymers still possess high dielectric constant and narrow hysteresis polarization loop.

Conclusion

In this paper, we have investigated two radical initiator systems, including functional borane initiator and 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. 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.

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