A Modular Approach to Ferroelectric Polymers with Chemically Tunable Curie Temperatures and Dielectric Constants

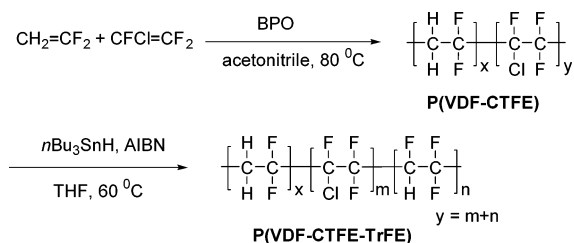Yingying Lu,[†] Jason Claude,[†] Bret Neese,[†] Qiming Zhang,[†,‡,§] and Qing Wang*,[†,§]

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High dielectric constant polymers are becoming crucial components in advanced electronic devices, such as memory and gate dielectrics for integrated circuits, and stationary power generation, and miniature capacitors for telecommunication.[1] The exchange of electrical energy and mechanical energy in sensors, transducers, and actuators also benefits from the materials with high dielectric constants.[2] Compared to the traditional electroactive ceramics, polymeric dielectric materials enjoy inherent advantages, such as high mechanical elasticity, high electrical breakdown strength, ease of processing in large areas, low cost, and self-healing ability. However, unlike their inorganic counterparts, the permittivities of most polymers are in a limited region ranging from 2 to 12.[1a] Ferroelectric poly(vinylidene fluoride) (PVDF) and its copolymers are the most interesting dielectric polymers due to the strong polarization originating from C−F bonds and the spontaneous orientation of dipoles in the crystalline phases.[3] Since ferroelectric materials typically exhibit dielectric anomaly near the Curie temperature, a phase transition point between ferroelectric (polar) and paraelectric (nonpolar) crystalline domains, many research efforts have been devoted to a general goal of moving the Curie transition close to the application temperatures for a high electric-field response.[4] The incorporation of trifluoroethylene (TrFE) into PVDF induces the appearance of a ferroelectric-to-paraelectric (F−P) transition below the melting temperature of the polymer crystals.[5] More recently, it was demonstrated that by introducing a small amount of disparate chlorinated monomer, such as chlorotrifluoroethylene (CTFE), into P(VDF-TrFE) copolymers, the resulting P(VDF-TrFE-CTFE) terpolymers show very high dielectric constants at room temperature.[6] The presence of the slightly bulky chlorine atoms in the terpolymers moves the Curie transition to near ambient temperature through the reduction of the crystalline domain size and the energy barrier in phase transition.

However, significantly different thermal and electronic properties have been revealed on the reported P(VDF-TrFE-CTFE) terpolymers.[6,7] This is due to a strong dependence of the dielectric properties of the polymers on their chemical compositions. The terpolymers are usually prepared by free radical polymerization using emulsion, suspension, and solution methods at various temperatures. Compared to that of VDF and CTFE, TrFE exhibits quite a different reactivity in free radical polymerization.[8] The considerable difference in reactivity ratios results in the terpolymers having a broad composition distribution and inhomogeneous crystalline domains, as evidenced by a broad F−P transition depending on reaction conversion.[7a] Furthermore, it is difficult to control and tune the polymer composition via changing monomer feeding ratios in the direct polymerization of three co-monomers. These restraints limit the expansion of the known library of the ferroelectric fluoropolymers and assessment of the impact of

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Scheme 1

P(VDF-CTFE)

P(VDF-CTFE-TrFE)

chemical structures on their dielectric properties. In this communication, we describe a modular approach allowing a systematic and straightforward development of the ferroelectric fluoropolymers with precisely controlled chemical structures and dielectric properties.

As shown in Scheme 1, our synthetic method comprises a two-step reaction, including the copolymerization of VDF and CTFE, and a subsequent hydrogenation reaction. Due to the similar reactivity ratios between VDF ($r_1 = 0.70$) and CTFE ($r_2 = 0.72$),[9] the structures of the P(VDF-CTFE) copolymers are kept homogeneous during the polymerization. In addition, the compositions of the copolymers are readily controlled by the monomer feeding ratios. The second step is to introduce TrFE segments into the copolymers by partial dechlorination of CTFE segments to afford the P(VDF-CTFE-TrFE) terpolymers. Because hydrogenation of CTFE segments occurs quantitatively,[10] the concentrations of TrFE in the resulting terpolymers can thus be accurately tuned by controlling the ratio between the reduction reagent (e.g., Bu₃SnH) and the content of CTFE in P(VDF-CTFE) copolymers. The randomly distributed TrFE and CTFE components in the terpolymers from the hydrogenation reaction also lead to uniform molecular structures and polymer morphologies, as evidenced by relatively sharp thermal transition temperatures displayed in differential scanning calorimetry (DSC).

In the present investigation, a library of 47 P(VDF-CTFE-TrFE) terpolymers with different chemical compositions has been prepared. The chemical structures and compositions of the polymers were determined by ^1H and ^{19}F NMR spectra. The thermal properties, such as melting point, crystallization temperature, and Curie temperature, were measured by DSC. The dielectric properties were evaluated by a multifrequency impedance analyzer equipped with a temperature chamber. As expected, the polymer compositions impose a significant effect on both the thermal and dielectric properties. A broad range of Curie transition temperatures from 22 to 106 °C and room temperature dielectric constants from 11 to 50 at 1 kHz were revealed for the terpolymers with different chemical compositions. The results for all 47 terpolymers are tabulated in the Supporting Information. A three-dimensional plot of the room temperature dielectric constants for the terpolymer library is shown in Figure 1. The terpolymer of 78.8 mol % of VDF, 7.2 mol % of TrFE, and 14 mol % of CTFE exhibits the highest room temperature
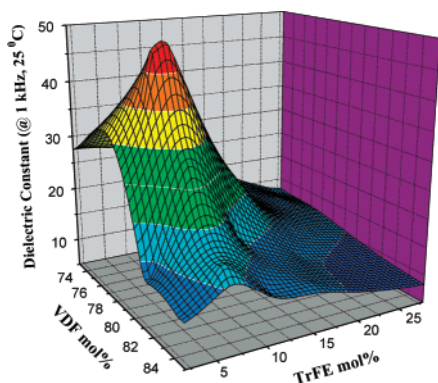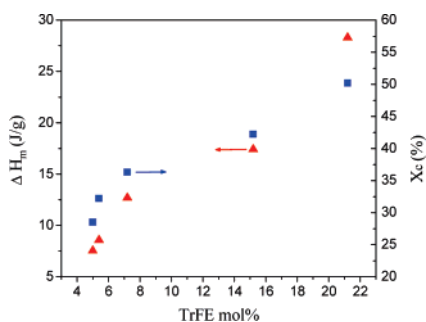
Figure 1. A three-dimensional plot of room temperature dielectric constants at 1 kHz for the P(VDF-CTFE-TrFE) terpolymers.

Figure 2. The heats of melting (ΔH_m) and degree of crystallinity (X_c) as a function of the TrFE contents in the polymers containing 78.8 mol % of VDF.

dielectric constant of 50 and a low dielectric loss (tan δ < 0.05) measured at 1 kHz.

The correlation between dielectric and thermal properties and polymer structures has been carefully investigated. With the introduction of CTFE into PVDF, the melting and crystallization temperatures of the resulting P(VDF-CTFE) copolymers systematically decrease with the increase of CTFE content and eventually disappear at compositions of more than 15 mol % of CTFE. By converting more than 20% CTFE to TrFE through the hydrogenation reaction, the crystallinity of the polymers is regenerated. As shown in Figure 2, the degree of crystallinity, X_c, and the melting endotherm, ΔH_m, determined by wide-angle X-ray diffraction (WXRD) and DSC, respectively, gradually increases with the increase of TrFE concentrations. Concomitantly with the changes in crystallinity, the Curie temperature continuously increases, for example, from 23 °C at 5 mol % of TrFE content to 98 °C at 21 mol % of TrFE content for the polymers containing 78.8 mol % of VDF, while the room temperature dielectric constant varies from 48 to 14. The evolution of polymer chain conformation with CTFE and TrFE concentrations has been followed by FTIR spectroscopy. The intensities of the absorption band at 1288 cm^{-1} corresponding to the CF$_2$ stretching vibration modes of all-trans ($t_{m>4}$) conformation in the β-phase increase with the increase of TrFE content, whereas the bands at 505 cm^{-1} attributed to the CF$_2$ vibration of $tttg^+tttg^-$ conformation in the γ-phase decrease in relative intensity. The γ-phase with shortened trans sequence in the polymer chains results in a reduced activation energy barrier for phase transition and in turn a low Curie temperature. This is consistent with previous studies, indicating that the bulky CTFE components in the terpolymers act as random defect fields and alter the crystalline phase from ferroelectric β-phase to γ-phase.[11] Indeed, for the compositions showing the highest room temperature dielectric constant, the vibration bands for the all-trans conformation are almost completely absent, and $tttg^+tttg^-$ conformation becomes a dominant ferroelec-

tric phase. These polymers exhibit a Curie phase transition at ambient temperature. On the other hand, the P(VDF-TrFE) copolymers yielded from complete hydrogenation of P(VDF-CTFE)s exhibit largely all-trans conformation with Curie temperatures around 100 °C.

The dielectric properties of the terpolymers could also be tuned between a normal ferroelectric and ferroelectric relaxor state by controlling the chemical compositions, with the particular state dependent on the CTFE contents. For example, the terpolymer with a composition of 80.5 mol % of VDF, 6.9 mol % of CTFE, and 12.6 mol % of TrFE exhibits normal dielectric behavior with a relatively sharp F−P transition and a dielectric peak position that is unrelated to frequency. By increasing the CTFE content to 12.5 mol %, the resulting terpolymer shows a much broader dielectric constant peak that shifts progressively to high temperature as frequency increases, a typical feature of ferroelectric relaxors.[12] This is consistent with the observation of the decreased Curie temperatures with the increase of CTFE content.

In summary, we have developed a highly efficient and practical route to the ferroelectric fluoropolymers exhibiting high dielectric constants. This approach allows the dielectric properties of the polymers to be tuned by exquisite control over chemical compositions. The ability to tailor these polymers permits, for the first time, a systematic study of the structure−property correlations and may provide unprecedented insight into the factors governing the dielectric responses in organic electroactive materials. A full investigation of the electronic and physical characteristics of the ferroelectric fluoropolymers presented herein will be reported in due course.

Supporting Information Available: Experimental details pertaining to the synthesis and characterization and the dielectric properties of the new polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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