distribution is assumed; the present data do not distinguish between the two choices. The disparity in the NMR and mechanical relaxation results can be removed by assuming that the phenylene ring reorients by rotational diffusion with a root-mean-square jump of 3° (inhomogeneous distribution) or 40° (homogeneous distribution). Such jumps less than 180° do couple mechanically and may reflect one of the molecular processes responsible for the secondary relaxation in this epoxy polymer. Whether this is the actual loss mechanism and whether this process contributes in other bisphenol polymers will be better resolved as the highly specific information available from variable-temperature ^{13}C NMR supplements mechanical relaxation spectroscopy.

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Magnetic Resonance and Relaxation in a Vinylidene Fluoride/Trifluoroethylene Copolymer

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ABSTRACT: NMR T_1, T_2, and $T_{1\rho}$ relaxation data for poly(trifluoroethylene) (TrFE) and a 52/48 mol % vinylidene fluoride/trifluoroethylene copolymer (PVDF/TrFE) are reported. Three relaxations are observed in TrFE, in contrast to the two reported previously. The NMR results for the copolymer are broadly consistent with current interpretations of behavior in PVDF/TrFE reported in the literature. However, NMR reveals that both amorphous and crystalline regions are affected at the "70 °C transition". Immediately below the 70 °C transition the copolymer exhibits behavior that resembles that of glassy material.

Introduction

Considerable research effort has been expended in more clearly understanding the remarkable pyro- and piezoelectric properties of poly(vinylidene fluoride) (PVDF).[1,2] The trans-planar configuration of molecules, which characterizes the β polymorph (form I) is an important ingredient in achieving useful electrical properties. Not surprisingly, the copolymer of VDF with trifluoroethylene (TrFE)[3-5] is of special interest since TrFE in proportions greater than 10% induces the VDF component to preferentially crystallize in the β form.[5,6] Its properties are indeed intriguing and, in particular, a ferroelectric phase transition near 70 °C in the 55/45 mol % PVDF/TrFE copolymer has been proposed.[7] The transition is presumed to manifest cooperative rotation of dipoles in steps of $n\pi/3$ or $n\pi$.[1,2] The proposed ferroelectric transition is deduced

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chiefly from the following observations: (i) the dielectric relaxation strength peaks near 70 °C[6,7] and there are indications of a "slowing down" of molecular motions as the transition is approached,[7] (ii) remanent polarization disappears in the temperature range 70–80 °C,[7] (iii) an anomalous peak, which shifts to higher temperatures with increasing VDF content, is observed at about the transition temperature in DSC measurements,[6,8] (iv) hysteresis in D vs. V disappears above 70 °C,[7] and, finally, (v) the crystal lattice spacing increases rapidly between 65 and 80 °C.[5,9-11]

Recent X-ray measurements[10,11] reveal two disordered crystalline phases in which the random copolymer molecules adopt trans-planar and 3/1-helical configurations. From the nature of the reflections, the crystallinity is determined to be significantly lower than in neat PVDF. When drawn and poled at low temperatures, the molecules reorient and, in addition, both disordered phases transform into one well-ordered trans phase, with a reduced *d* spacing of ~4.53 Å. When heated above 70 °C (80–85 °C for the poled or oriented material), all conformations transform into the 3/1-helical structure, which characterizes neat TrFE. As the transition temperature is approached, the *d* spacings that describe both low-temperature disordered phases increase rapidly and ultimately achieve the spacing observed in neat TrFE. For the poled sample, the increase in spacing occurs abruptly at 85 °C.

In a study on the relaxation behavior of the copolymer, Yagi and co-workers[6] observed three transitions, β_1, β_2, and γ, in dielectric and mechanical measurements, all of which are deemed to be amorphous in character. Because of high ionic conduction, the β_1 relaxation is observed only in mechanical relaxation data. β_1 and β_2 are ascribed to micro-Brownian motion in TrFE-rich and VDF-rich regions, respectively. In keeping with similar assignments in the homopolymers,[3,12,13] the γ relaxation is assigned to local molecular motion in the amorphous regions.

Dielectric measurements of Furukawa et al.[11,14] reveal three relaxations, α, β, and γ. The β_1 relaxation remains undetected but there is an additional relaxation (α) at high temperatures, crystalline in origin and ascribed to thermal rotation or torsion motion. As reported above, this transition has been described as ferroelectric, involving cooperative rotation of molecules. There is a broad distribution of relaxation times at temperatures below ~70 °C.[7]

No doubt, the "70 °C transition" in the copolymer involves a complex interplay of conformational and molecular motional events that are not fully understood. Evidence on the precise nature of molecular motions is sparce and it is opportune to carry out an investigation by nuclear magnetic resonance, a technique both that is sensitive to the scale of lattice spacing changes observed in PVDF/TrFE and that is capable of probing molecular motions in a number of motional frequency domains.[15,16] Motions in PVDF are reasonably well understood through the collated results of diverse studies.[1,2] TrFE, on the other hand, has received little attention[3,12,17-19] and a prerequisite study has been carried out on this polymer in the hope of facilitating interpretation of motional events and structural changes in the copolymer.

Experimental Section

The copolymer, 52/48 mol % PVDF/TrFE, was prepared by the Daikin Kogyo Co. of Japan and is believed to possess a statistically random molecular configuration in which head-to-tail VDF–TrFE or TrFE–VDF sequences are predominant.[4,20,21] The TrFE homopolymer was prepared by the National Bureau of Standards.

Proton resonances were detected with a Bruker spectrometer operating at 60 MHz. Procedures for data acquisition and analysis have been described elsewhere.[16] A significant departure, however, involved the use of a Commodore PET computer to signal average the weak resonances observed in materials of low proton content, pertinent to this study. T_2 was determined directly from the free induction decay following a 90° pulse as the time for the signal amplitude to fall to $1/e$ of the initial observed magnitude. This procedure is only strictly correct for Lorentzian FIDs and represents an approximation when the decay has Gaussian character, as is usually the case at low temperatures. In such cases, too, an inability to observe the first 4 μs (the recovery time of the spectrometer) of the FID results in an underestimate of T_2. 180°–τ–90° and 90°–90° (phase shift) spin-locking pulse sequences provided T_1 and $T_{1\rho}$, respectively.[16]

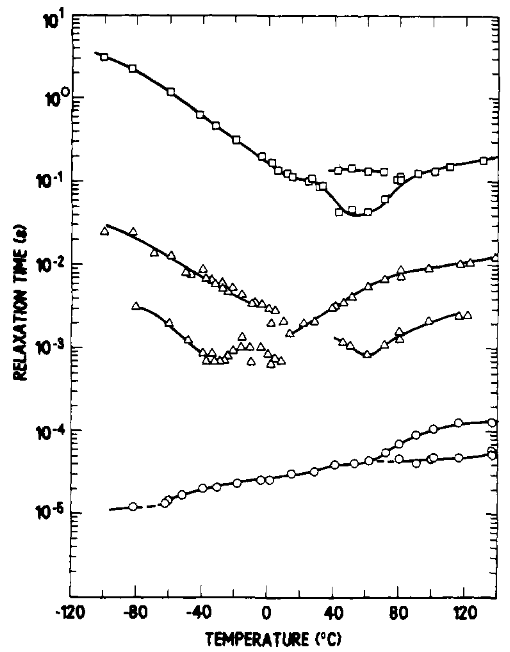

Figure 1. T_1 (60 MHz) (□), $T_{1\rho}$ (H_1 = 10 G) (△), and T_2 (○) data for TrFE as a function of temperature.

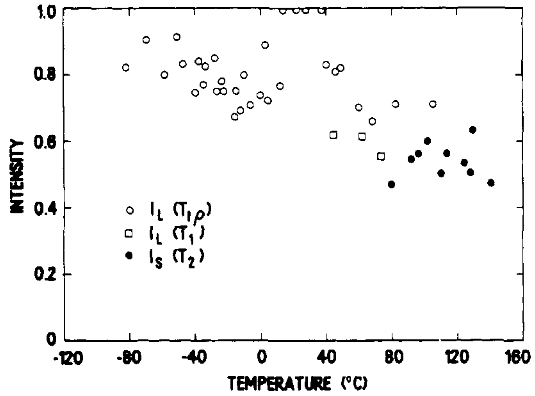

Figure 2. T_1, T_2, and $T_{1\rho}$ component intensity data as a function of temperature for TrFE.

Results and Discussion

Trifluoroethylene. Spin–spin (T_2), spin–lattice (T_1), and rotating-frame ($T_{1\rho}$) relaxation data are presented as a function of temperature in Figures 1 and 2. T_2 increases almost continuously, beginning about −60 °C, with only subtle and barely detectable changes in slope. Thus it is difficult to delineate relaxation processes operative at temperatures below ~60 °C. At this temperature, however, motions of the amorphous protons become significantly more rapid than those in the crystalline regions. This fact coupled with an ability to follow the free induction decay over 3 decades, a consequence of signal averaging, allowed decomposition of the FID into two components. The intensity of the shorter, crystalline

Table I
NMR Relaxation Data for TrFE[a]

relaxation process	T_1(min) log ν_c = 7.75 A	T_1(min) log ν_c = 7.75 C	$T_{1\rho}$(min) log ν_c = 4.6 A	$T_{1\rho}$(min) log ν_c = 4.6 C	T_2 transitions log ν_c = 3.6 A	T_2 transitions log ν_c = 4.1 A	T_2 transitions log ν_c = 4.1 C	act energy, kcal/mol
α	(100)		60		~70			78
β		55	(10)	10		( )		28
γ	20		-30			-50		23

Temperature, °C.

[a] A and C denote amorphous and crystalline, respectively. Assignment of the β relaxation to the crystalline regions is tentative (see text).

component indicated a crystallinity of ~55%. It is interesting to observe that while the molecular motions responsible for the long amorphous T_2 are rapid at the highest temperature studied, they have not yet attained large-amplitude, liquid-like, proportions characteristic of polymers above their glass transition temperature, T_g, for which T_2 is of the order of milliseconds. Similar behavior was observed in PTFE.[22] The formation of a T_2 plateau implies motional constraints typical, for example, of the behavior of folds and cilia on the surface of crystallites.[23] Either the amorphous material as a whole is undergoing rapid, though constrained, motions or the long component represents unresolved contributions to T_2 from constrained interfacial molecules and from molecules in a truly amorphous phase undergoing liquid-like motions typical of a polymer above T_g.

As explained in the Experimental Section, T_2 of 13 μs at the lowest temperatures is underestimated. This is borne out in calculations of the proton rigid lattice T_2, which is of the order of 18 μs. Of particular interest is the magnitude of short T_2 above the transition at 70 °C, which is typically equal to or greater than twice the rigid lattice estimate, indicating that the chains in the crystalline regions are rotating and possibly translating.[16] The change in T_2 around -50 °C is consistent with the onset of chain rotation in the amorphous regions.[24]

The $T_{1\rho}$ data are more revealing and indicate the presence of three relaxation processes, as opposed to the two relaxations observed in dielectric and dynamic mechanical measurements.[3,12] Two components are resolved over the greater part of the temperature range. An inability to resolve T_2 components renders absolute $T_{1\rho}$ assignments difficult. Nor is it possible to ascertain with certainty whether or not the $T_{1\rho}$ curves cross over in the vicinity of room temperature. Nonetheless, it is reasonable to assume that the short $T_{1\rho}$ below room temperature indicates amorphous behavior. Equally, the minimum observed in the short $T_{1\rho}$ at 60 °C is also associated with the onset of more general motions in the amorphous regions since it is accompanied by an increase in the long, amorphous T_2 component. This is possibly the glass transition. It is difficult to decide with certainty that a third $T_{1\rho}$ minimum is developed in the vicinity of 10 °C. Accuracy of the decomposition procedure deteriorates rapidly when component relaxation times converge to within a factor of 2 of each other. Recall, however, that the crystalline chains are in motion at higher temperatures, as indicated by the magnitude of the resolved short T_2 component. It is primarily on this basis that the, albeit tentative, assignment of motional events in the vicinity of 10 °C to the crystalline regions is favored. Indeed, the transition map of Figure 3 also implies that there should be a $T_{1\rho}$ transition in this temperature region. As a consequence of spin diffusion, intensities of component $T_{1\rho}$ data (Figure 2) bear no obvious relationship to the amount of material contributing to a particular relaxation process.[15,16] Limited rotational or torsional motions facilitated by the high defect content are the likely candidates.[3]

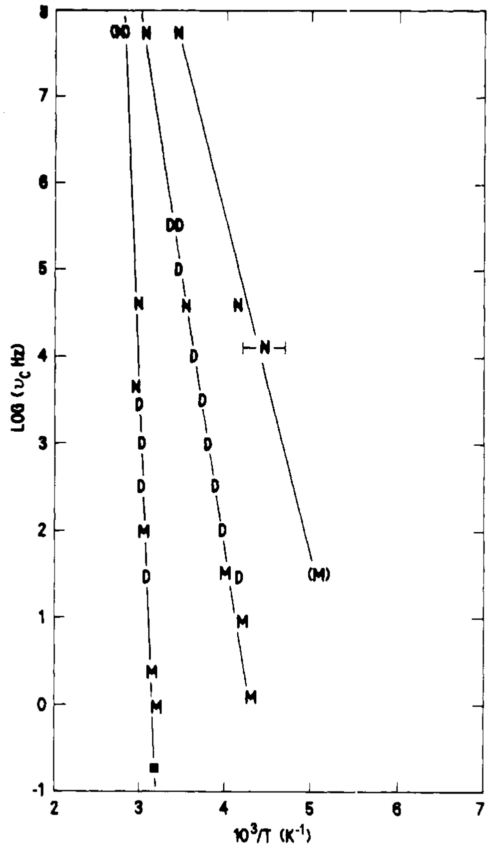

Figure 3. Transition map describing relaxation in TrFE. D, N, and M signify dielectric, NMR, and dynamic mechanical data, respectively. The low correlation frequency point (■) refers to a heat capacity measurement reported in ref 19.

The T_1 data are generally consistent with the above assignments, which are summarized in Table I. The transition map of Figure 3 collates the available relaxation data for TrFE.[3,12,17-19] The γ relaxation detected in the NMR data is unresolved from the β relaxation in the dielectric and dynamic mechanical experiments. The tensile modulus results of Yagi[3] do in fact indicate the presence of the γ relaxation in the form of a shoulder on the low-temperature side of the β relaxation, in keeping with our conclusions.

The observation that $T_{1\rho}$ and T_1 have minima near 10 °C coupled with the small change in T_2 in the same temperature region affords the possibility that the changes in the three relaxation times result from a structural phase transition, as opposed to motional events. This suggestion is consistent with observations in PTFE[22] but must remain tentative.

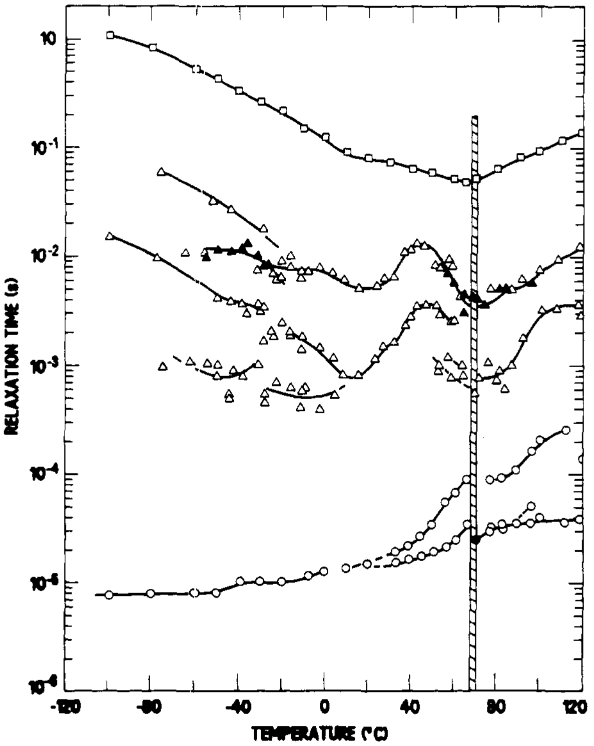

Figure 4. T_1 (60 MHz) (□), $T_{1\rho}$ (H_1 = 10 G) (△), and T_2 (○) data for the PVDF/TrFE copolymer. The filled triangles denote unresolved components.

PVDF/TrFE Copolymer. The NMR response of the copolymer is shown in Figures 4 and 5. A number of observations are pertinent to our discussion:

(1) There is an obvious discontinuity at 70 °C, which is most pronounced in the T_2 data.

(2) Below 70 °C the results, although complex, can be interpreted as a superposition of PVDF and TrFE responses.

(3) The discontinuity in T_2 in the form of a shoulder (or a maximum) occurs in both long and short components. The latter supports the notion of crystal reorganization,[10,11] and it is further interesting to observe that the magnitude of the short T_2 above the transition is comparable to the neat TrFE crystalline T_2. Note also the absence of a T_2 characteristic of the crystalline phase of neat PVDF. On the basis that the random copolymer in a 3/1-helical configuration exhibits motions comparable to those of neat TrFE in a similar configuration, conversion of the low-temperature crystalline phases into the 3/1-helical configuration characteristic of TrFE would appear to be substantiated.

(4) The intensities of the long T_2 and short $T_{1\rho}$ components tend to zero as the transition temperature is approached. Conventional interpretation of the observed discontinuity in the magnitude of the long T_2 indicates that the amorphous regions are also affected profoundly at the 70 °C transition. Therefore the proposal that this transition is purely a crystalline one is not confirmed. However, it would also seem possible to interpret the increase in T_2 in terms of fluctuations associated with approach to an order–disorder transition such as the proposed ferroelectric transition. While the behavior of T_1 near a ferroelectric transition has received substantial experimental and theoretical attention,[25] definitive work on T_2 seems lacking.

(5) There is evidence of a third T_2 component above the transition of magnitude comparable to the mobile T_2 observed in neat TrFE. If such is the case, the integrity of the *amorphous* TrFE-rich and VDF-rich phases may well be maintained above the transition. The short $T_{1\rho}$ characteristic of neat amorphous TrFE appears to be unaffected at 70 °C.

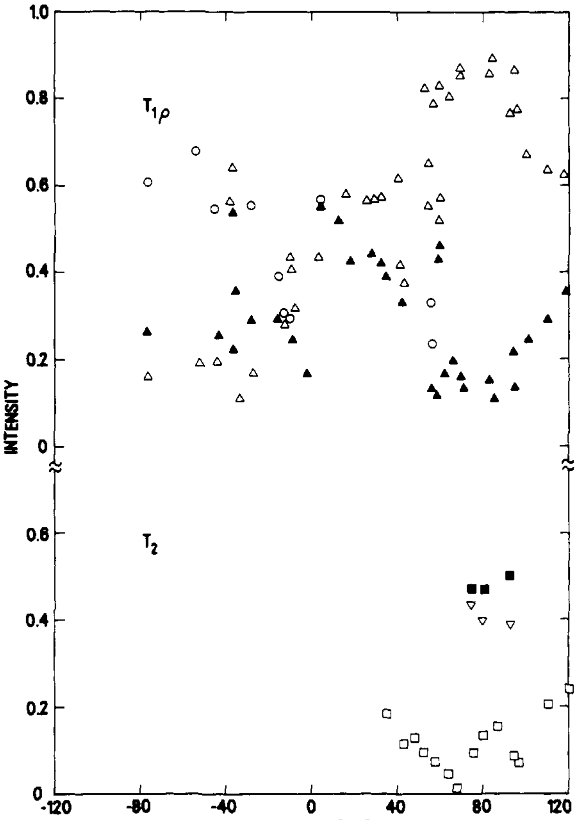

Figure 5. $T_{1\rho}$ and T_2 component intensity data as a function of temperature: (□) T_2(long); (■) T_2(short); (▽) T_2(intermediate); (△) $T_{1\rho}$(long); (▲) $T_{1\rho}$(short); (○) $T_{1\rho}$(intermediate).

Figure 6 contains the available relaxation data for the copolymer.[6,7,18,19] Special features of the transition map are, first, the locus of infinite slope characteristic of the first-order 70 °C transition and, second, the nature of the locus of the β transition. As the transition temperature is approached, the curvature of the locus behaves in a way that is consistent with motional retardation. It is tempting, however, to postulate that at temperatures below the transition, one is observing WLF behavior[26] characteristic of a glass and at temperatures in excess of 70 °C the process is Arrhenius in character.

Resolution of the basic question regarding the presence or absence of a ferroelectric state centers upon the degree of stabilization, or destabilization, of the ordered state by an internal field. The evident stabilization of the more dense trans-planar phases of PVDF and the TrFE/VDF copolymer by an external field would then seem to lead to a rephrasing of the question: Is the stabilization by an internal field an important influence in maintaining the ordered state when the external field is subsequently removed? Whether the internal field is important or not, one is also concerned with the stability or metastability of the ordered state in the absence of the applied field. If the internal field plays a significant role, one expects some order–disorder character to the transition and the characteristic spectral density associated with critical fluctuations near the transition to be manifested in relaxation measurements. Thus far it appears that the 70 °C transition may be interpreted in terms of either motional spectra exhibited by metastable glass-like material or order–disorder fluctuations. It has been shown that in the

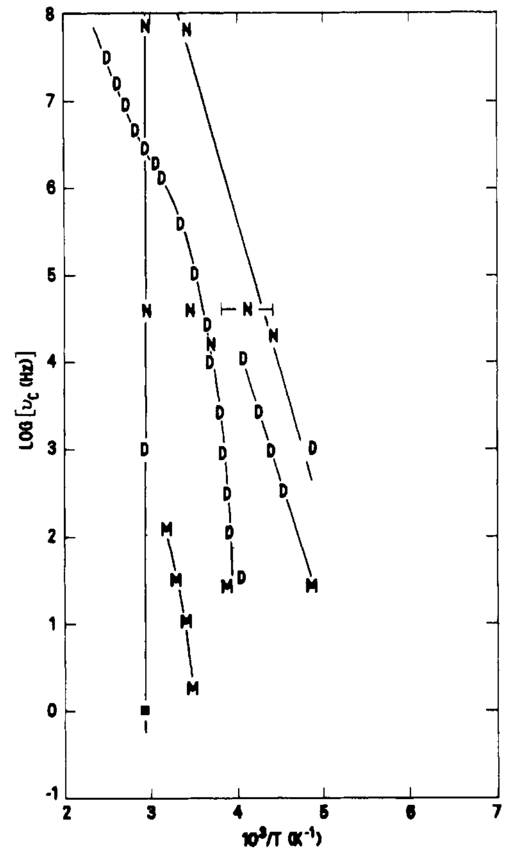

Figure 6. Transition map describing relaxation in PVDF/TrFE. The low correlation frequency point (■) refers to a DSC measurement.

case of ferroelectric single crystals T_1 vs. temperature exhibits a cusp-like maximum at the transition.[25] However, in the copolymer T_1 behavior is almost certainly controlled by the presence of efficiently relaxing amorphous material that acts as a sink to relax the small crystalline regions via spin diffusion.[15,16] Therefore, it is not possible on the basis of these NMR data to distinguish between the two possibilities.

The broad distribution of motional processes in this, as in most polymeric material, necessarily means that assignment of any given transition entirely to a single specific process is, at best, a first approximation. Nevertheless, the existent data in the literature and the data herein lead one to feel that the internal field may well play a significant role in PVDF and the copolymer. Interpretation of the data in terms of critical fluctuations deserves continued attention, with due consideration of the special problems introduced by the polymeric nature of the polymer. One might add that in view of the large number of defects in the copolymer, it may be exceedingly difficult to achieve spontaneous nucleation of large domains in the absence of an appreciably developed internal field.

While one may not be able to attain a picture fully correspondent with the usual perception of the ferroelectric state in crystals, it may be possible to characterize the copolymer by a temperature-dependent order parameter. If one assumes that the order develops via $n\pi/3$ reorientations within crystalline regions, there must be a distribution of order parameters relative to the macroscopic internal field even in a poled sample.

At this point it is clear that studies of poled material should be carried out with particular attention given to the interesting behavior of the long T_2 component, herein indexed as amorphous, in the vicinity of the 70 °C transition.

In summary, the NMR results for the copolymer are broadly consistent with current interpretations based on other relaxation experiments and on X-ray measurements. NMR reveals, however, that both amorphous and crystalline regions are affected at the 70 °C transition. The alternative proposal that the copolymer may be exhibiting glassy behavior below 70 °C is suggested.

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