103134-51-6; **11**, 108090-21-7; **12**, 117371-51-4; **13**, 117371-52-5; **14**, 117371-53-6; **15**, 104156-79-8; **16**, 117371-54-7; **18**, 117371-49-0; **19**, 103229-97-6; **20**, 117371-50-3; **21** (copolymer), 108090-24-0; **21** (SRU), 117371-55-8; **22** (copolymer), 103134-52-7; **22** (SRU), 103083-29-0; **23** (copolymer), 108090-22-8; **23** (SRU), 117371-56-9; **24**, 70183-18-5; $PhNH_2$, 62-53-3; p-$H_3COC_6H_4NH_2$, 104-94-9; 3-$H_2NC_6H_4NH_2$, 108-45-2; 4,4'-$H_2NC_6H_4OC_6H_4NH_2$, 101-80-4; 3-$ClCOC_6H_4COCl$, 99-63-8; 4-$ClCOC_6H_4COCl$, 100-20-9; 4-$ClCOC_6H_4SO_2C_6H_4COCl$, 4462-61-7; H_2O, 7732-18-5; benzoyl chloride, 98-88-4; malononitrile, 109-77-3; 4-phenoxyaniline, 139-59-3.

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Spectroscopic Analysis of the Electric Field Induced Structural Changes in Vinylidene Fluoride/Trifluoroethylene Copolymers

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ABSTRACT: The electrical poling behavior of a uniaxially drawn random copolymer of 75 mol % vinylidene fluoride and 25 mol % trifluoroethylene has been examined by infrared spectroscopy at various temperatures. Vibrational assignments are clarified by examining the effects of annealing, orientation, temperature, and electric field on the spectrum. Bands sensitive to specific conformations are used as indicators of structural and orientation changes induced by an electric field. Intensity changes due to orientation demonstrate that the crystalline units are aligned in the draw direction by mechanical drawing, while molecular chains are rotated by the application of the electric field. Under a cyclic field of 2.2 MV/cm, the infrared intensity exhibits a hysteresis similar to that seen previously for PVDF. The shape of the hysteresis is sensitive to temperature with a large reversible intensity change observed above the Curie temperature. Below the Curie temperature bands show irreversible changes that suggest an improvement in chain packing and a disruption of long trans sequences by the applied field.

Introduction

Ferroelectric and piezoelectric polymers are a subject of great interest today. These materials exhibit lower piezoelectric activity than ferroelectrics such as quartz but can be processed easily and are light weight and flexible.[1] Polymers such as poly(γ-benzyl glutamate),[2] copolymers of vinylidene cyanide with vinyl acetate,[3] and methyl methacrylate[4] as well as the odd nylons[5] are known to be piezoelectric. Poly(vinylidene fluoride) (PVDF) has received much attention as it contains polar and nonpolar crystal phases which control the piezoelectric activity. The relative amounts of each phase can be altered by the application of a high strength electric field,[6] and studies have been reported on the structural change induced by poling and its field strength and temperature dependences.[7-10]

Our current interest is focused on PVDF and its copolymers with trifluoroethylene (TrFE). These copolymers have been the subject of much study since the addition of trifluoroethylene produces a trans structure similar to the β phase of PVDF and exhibiting greater piezoelectric activity.[11] In these materials a Curie phase transition is observed in which the planar trans ferroelectric phase containing ordered dipoles undergoes a solid–solid phase

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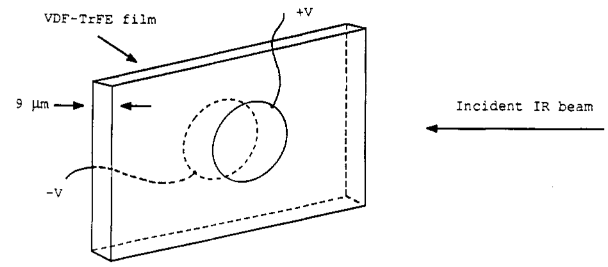

Figure 1. Schematic drawing of experimental geometry.

transition to a paraelectric phase with conformational disorder and loss of dipole orientation.[12-14]

The application of a high strength electric field is known to raise the Curie temperature[14,15] and is frequently employed to increase piezoelectric activity. Previous X-ray analyses have been carried out to determine structural changes occurring at the Curie transition and the effects of poling.[13-17] Several theories have been proposed for the mechanism by which chain dipoles couple to the field and produce conformational change;[18-20] however, this mechanism is still uncertain.

We are interested in the microstructural change occurring in VDF/TrFE copolymers due to an applied electric field. Such information is important in order to gain an understanding of the mechanism of piezoelectricity in these materials. Vibrational spectroscopy is our primary structural characterization technique; however, the vibrational assignments for this material are unclear. Therefore we have examined the effects of annealing, temperature, orientation, and electric field application in order to clarify these assignments. In the infrared spectra of these materials there are absorptions representative of specific conformations that provide information about structural changes in the presence of an electric field. These vibrations show substantial intensity changes at the Curie transition and are monitored as a function of field strength and temperature. A cyclic electric field is applied to observe reversible structural changes due to dipole orientation under the field, as well as irreversible conformation and molecular packing changes. Such information will complement earlier X-ray and spectroscopic studies.[13-15,21,22] Poling behavior is compared with that of PVDF and is related to the microstructural disorder present in the copolymer satructure due to the presence of TrFE units.

Experimental Section

Samples used in this study are a 75 mol % VDF–25 mol % TrFE copolymer provided by Pennwalt Corp. in the form of 9-μm uniaxially oriented films. In order to remove the effects of prior poling treatments, the films used in our experiments were annealed for 2 h at 130 °C. The Curie temperature for this composition is broad and depends on the experimental parameters. The onset of transition in our DSC scans starts at 116 °C.

It is difficult to obtain infrared data for the 9-μm films for quantitative analysis since many bands show high absorbance values. Therefore a 2% solution was prepared by dissolving pellets of the 75/25 copolymer in acetone. Films were cast in aluminum pans and annealed or drawn at room temperature to a maximum draw ratio of 5. An annealing experiment was carried out by placing the unoriented cast film in a sample holder placed in a 130 °C oven. In order to observe in situ structural changes produced by the electric field, as described in previous studies, gold–palladium electrodes were evaporated directly onto the as received copolymer films or onto polished KBr windows.[8-10] The electrodes were thick enough to conduct electricity yet thin enough to allow transmittance of the infrared beam. The KBr windows and sample were held together by a clamp and placed in a heating cell for high-temperature poling experiments. The temperature was maintained to within 1 °C of the setting temperature. A high voltage power supply was used to generate fields up to 2.2 MV/cm. A schematic diagram illustrating the experimental poling setup is found in Figure 1. Infrared spectra were obtained with an IBM IR32 and a Nicolet 60SXB FTIR spectrometer. To obtain spectra with high signal-to-noise ratio, 500 scans were collected at a resolution of 2 cm^{-1}. In general, electric fields were applied for 10 min before spectra were obtained.

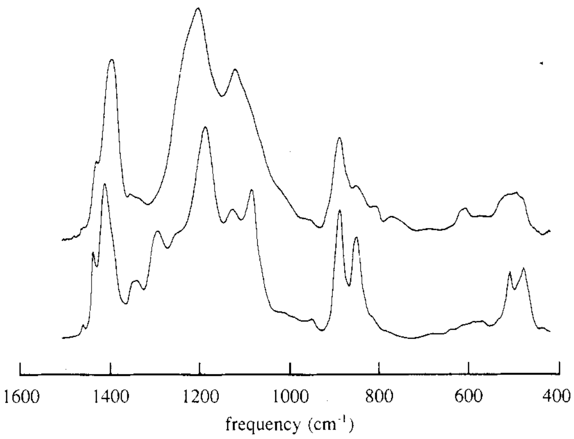

Figure 2. Infrared spectra of 75/25 PVDF/TrFE film as a function of temperatue (1600–400 cm^{-1}; 2 cm^{-1} resolution): (top) 125 °C spectrum; (bottom) room-temperature spectrum.

Results and Discussion

Unlike PVDF, the chain conformation and packing are not well understood for PVDF–TrFE copolymers. It is generally agreed, however, that the electrically active crystalline phase has a nearly planar zigzag chain conformation and packing similar to the β phase found for PVDF.[11,12] It has been suggested that the TrFE units may be excluded from the β form crystalline unit cell.[20] However, X-ray and DSC studies suggest both subunits of the copolymer can be incorporated into the unit cell.[11,24] It is uncertain what structure is present above the Curie transition, for this polymer, approximately 116 °C. It is generally agreed that this chain conformation is a statistical distribution involving tt, tg, tg′, t_3g, and t_3g' rotational isomers.[12,15] However recent studies suggest that the paraelectric phase exists in a tgtg′ conformation similar to the α phase of PVDF with some trans isomers remaining.[25,26] The available X-ray data suggest that chains are packed in a hexagonal array.[11,12]

The participation of the β phase of PVDF in the piezoelectric effect is well established.[6] Transformation between the various phases has also been characterized for PVDF;[6-10] however, relatively little information is available for the copolymer of PVDF and TrFE. The main objective of this spectroscopic study is to characterize the conformation of the various phases of a PVDF–TrFE copolymer and to determine how the chain segments in these phases respond to an applied electric field. The principal advantage of vibrational spectroscopy when compared to other physical techniques is its ability to measure localized chain orientation, packing, and conformation. In addition, the large dipoles of the chain couple strongly to the applied field; thus the spectroscopic technique is sensitive to the small structural subunits change induced by an electric field. In Figures 2 through 4 are shown the infrared spectra of the copolymer as a function of temperature, annealing treatment, and electric field application. Spectral changes arise either from a change in the chain conformation or in the orientation of the transition dipoles or functional groups.

In an earlier experiment, the response of the electrically active or nonactive phases in PVDF to an external field

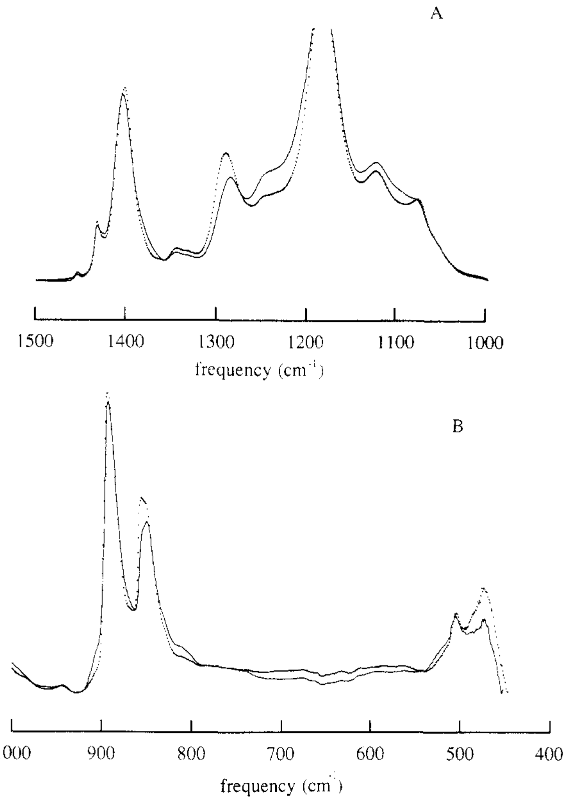

Figure 3. Infrared spectra of 75/25 PVDF/TrFE film before and after annealing at 130 °C for 2 h: (A) 1500–1000 cm^{-1} region; (B) 1000–400 cm^{-1} region; (···) annealed sample; (—) as cast film.

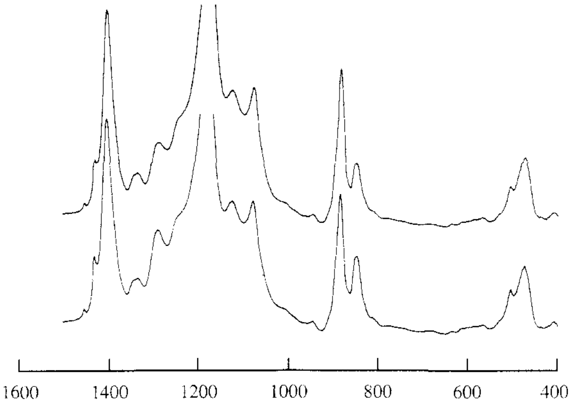

Figure 4. Infrared spectra of 75/25 PVDF/TrFE film as a function of electric field; (top) E = 2.2 MV/cm; (bottom) E = 0.0 MV/cm.

was directly interpretable from the intensity changes in the infrared spectra.[8-10] Unlike PVDF, nearly all the bands in PVDF–TrFE copolymers change in frequency or intensity as a function of electric field strength and polarity. However, for the same field strength and measurement temperature the changes observed for the copolymer are much smaller than those observed for PVDF.[10] The rather insignificant intensity changes can be interpreted as weaker coupling to the applied field as a result of the inherently smaller effective dipole of the copolymer chain, since for each TrFE unit the CF_2 dipole is partially compensated by a CFH unit. However, the fact that nearly all the observed infrared active vibrations are sensitive to the applied field suggests that the β chain conformation is indeed the most favorable one due to the stabilizing factor of the TrFE units. It can also be speculated that the chains do not pack in such a fashion that all effective dipoles cancel completely, as in the case for the α phase of PVDF.

Table I
Characteristics of Vibrational Bands Chosen for Analysis

freq (cm^{-1})	polarization	assignment	conformation
3014	$\perp$	$\nu_a(CH_2)$	
2977	$\perp$	$\nu_s(CH_2)$	
1290	$\perp$	$\nu_a(CF_2)$, $\nu_s(CC)$, δ (CCC)	T_m ($m > 4$)
883	$\perp$	$r(CH)_2$, $\nu_a(CF_2)$, $r(CF_2)$	T
850	$\perp$	$\nu_a(CF_2)$	T_m ($m > 3$)
802	$\perp$	$r(CH_2)$	TG
612	$\parallel$	$\delta(CF_2)$, δ(CCC)	TG

Band Assignments. In order to have a more detailed interpretation of the field induced structural changes, band assignments need to be more certain. In comparison to what we know about polyethylene or normal alkanes, there really has been very limited normal vibrational analysis for the fluorinated polymers due to the unclear chain structure and ill defined force field. Analysis of vibrational spectra has been carried out for poly(tetrafluoroethylene)[27-31] and for PVDF.[32-36] These studies have proven to be enormously useful to select the vibrations in order to interpret the molecular structure changes giving rise to the piezoelectric effect for PVDF.

Since such normal vibrational analysis is unavailable for the copolymer, our understanding of the vibrational spectra associated with PVDF–TrFE copolymers is far from complete. Due to the large mass of the fluorine atom, most infrared-active vibrations for the copolymer are concentrated in a rather narrow region, 1500–400 cm^{-1}. Virtually all the vibrations are coupled delocalized vibrations involving many atoms making exact band assignments difficult. Clearly the more complete the vibrational analysis, the more detailed is our explanation for the molecular mechanism. Therefore band assignments for the copolymer are dependent upon our interpretation of the spectra obtained for various deuterated polymers and copolymers, annealed versus unannealed samples, and highly oriented samples. Detailed analysis of these spectra will be presented in a subsequent publication.[37]

Several vibrational bands for the copolymer have been assigned to specific conformations by Tashiro et al.,[12,16,17,26] and these assignments will be employed in this study. These bands exhibit changes as a function of temperature, field strength, or orientation and therefore are used in this study to interpret the response of a PVDF–TrFE copolymer to an external electric field. The assignments and polarizations of the selected bands are listed in Table I.

The 1290, 883, 850 (doublet), 802, and 612 cm^{-1} bands showed the most interesting and interpretable changes. One of our original candidates, the 507 cm^{-1} band, may correspond to the 510 cm^{-1} CF_2 bending band observed for trans sequences associated with either the β or γ phases of PVDF. However, Davis et al. have observed a band at this position for P(TrFE),[14] making it difficult to employ for structural interpretation.

As seen in the table, the 1290 cm^{-1} band has been assigned to the symmetric CF_2 stretching vibration coupled to the backbone stretching and bending vibrations.[35,36] It is assigned to sequences of four or more VDF units corresponding to trans isomer sequences four or more units long and is therefore characteristic of the chain extended or β structure.[12,16,17] As seen in Figure 2 this band is absent in the high-temperature paraelectric phase. It should have a perpendicular polarization as observed for our oriented film shown in Figure 5.

The 883, 850 (doublet), and 612 cm^{-1} bands, assigned to CH_2 rocking and CF_2 asymmetric stretching, CF_2 symmetric stretching, and CF_2 bending coupled to skeletal bending, respectively, are useful for structural character-

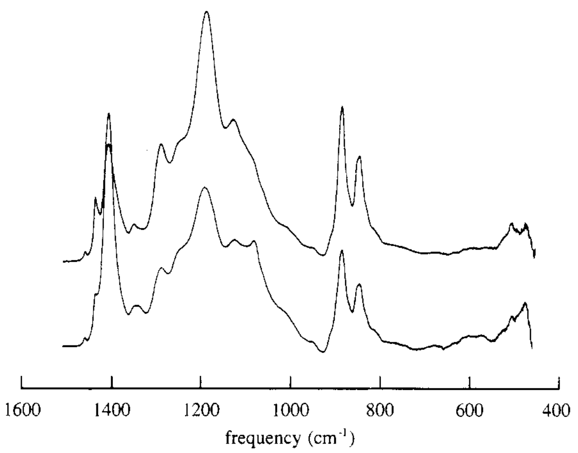

Figure 5. Polarized infrared spectra of 75/25 PVDF/TrFE film at a draw ratio of 1.6 (1600–400 cm^{-1}; 2 cm^{-1} resolution): (top) perpendicular polarization; (bottom) parallel polarization.

ization.[26,34–36] Although not used extensively in our study, the 802 cm^{-1} band assigned to the CF_2 symmetric stretching vibration is extremely strong in the Raman spectrum of these copolymers.[25,26] The dichroic ratios of these bands measured for the highly oriented films are all consistent with the expected polarization characteristics. It should be emphasized that these vibrations are characteristic of conformations of PVDF sequences. Strictly speaking, we cannot directly interpret the overall chain conformation; however, we feel the molecular response of the comonomers cannot be separated. The two bands near 850 cm^{-1}, similar to the 1290 cm^{-1} band, are characteristic of long sequences of at least three trans isomers.[12,16,17] In contrast, the bands at 802 and 612 cm^{-1} are characteristic of gauche conformers.[12,16,25,26] The relative amount of chain conformations in our study are based on the relative intensity of the different bands. We have not been able to measure the intrinsic absorption coefficients of each vibration, and therefore we have assumed them to be the same as done previously.[17]

There has been some controversy regarding the assignments of the bands listed above. Originally, the assignments of the 880 and 840 cm^{-1} bands for PVDF were unclear.[34] In a recent poling experiment and normal vibrational analysis, the new assignment is consistent with polarized Raman studies on rolled PVDF films, with the 880 cm^{-1} band assigned to the CH_2 rocking, CF_2 asymmetric stretching, and CF_2 rocking vibrations, while the 840 cm^{-1} band is assigned to the CF_2 symmetric stretching mode.[35] As we will show later these new assignments are consistent with our copolymer poling experiment.

The clearly resolved doublet observed for the copolymer needs a more detailed analysis. In our earlier study we concluded that the 842 and 850 cm^{-1} bands observed in PVDF at liquid nitrogen temperature are associated with crystal field splitting.[9] The 850 cm^{-1} doublet for the copolymer is somewhat complicated by the fact that PTrFE exhibits a relatively weak and broad peak at 851 cm^{-1}.[14] We have summarized the 850 cm^{-1} region for various experiments in Figure 6. The relative intensity of the doublet can differ significantly as a function of annealing, electric field strength and polarity, or sample orientation. The two components at 844 and 849 cm^{-1} (110 K) are found to be polarized perpendicular to the draw direction, as expected. We believe these two components are related to the ordered regions in the copolymer and may also be related to the crystal field splitting found for PVDF. We came to this conclusion because of the enhanced splitting observed for the copolymer film at low temperature (Figure

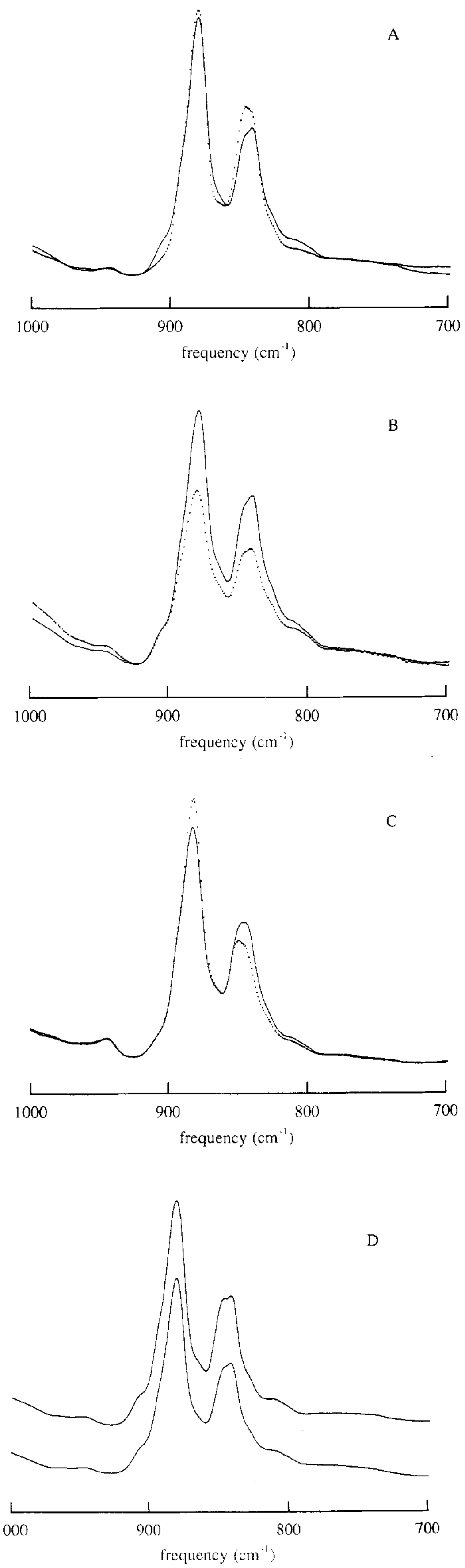

Figure 6. Infrared data in the 1000–700 cm^{-1} region of 75/25 PVDF/TrFE films: (A) (···) annealed; (—) as cast; (B) oriented sample with draw ratio 1.6; (—) perpendicular polarization; (···) parallel polarization; (C) electric field applied, (···) E = 2.2 MV/cm; (—) 0.0 MV/cm; (D) (top) 110 K; (bottom) room temperature.

6D). Generally speaking, vibrations sensitive to the magnitude and specificity of nonbonded intermolecular interactions are sensitive to temperature as these two components are.

This assignment can also be confirmed by preparing a solution cast film that contains both crystalline and amorphous regions. On the basis of previous energy calculations, it is known that the trans conformation of the β unit cell is more stable.[16] Therefore for annealed samples, bands assigned to trans chain conformations or unit cells are seen to rise in intensity while features assigned to gauche structures weaken in intensity. For the PVDF–TrFE copolymer, annealing significantly enhanced the splitting of the doublet in the 850 cm^{-1} region, with an inversion in the relative intensities of the two components, as seen in Figure 6A.

Poling Hysteresis. The infrared spectra obtained for the copolymer film in the presence of a cyclic electric field differ significantly as a function of field strength and polarity. Spectral changes measured in the presence of the field are indicative of the conformation and/or chain orientation changes taking place. It should be emphasized that variations in infrared intensity and frequency due to conformation and packing changes must be separated from those due to orientation change relative to the polarization of the incident electric field in order to understand the field-induced microstructural change.

The bands listed in Table I follow the applied electric field quite closely. The 850 cm^{-1} band intensity change with field strength at different temperatures is shown in Figure 7. As the electric field is increased, the large CF$_2$ dipoles have a tendency to align in the field direction, parallel to the propagation direction of the IR beam in our experimental geometry. Thus vibrational modes with transition dipole moment along the CF$_2$ dipoles show decreased absorbance as the field is increased. Bands assigned to modes with transition moment normal to the CF$_2$ dipole direction, such as the CF$_2$ asymmetric stretch, should show an intensity increase with field. Although the two components near 850 cm^{-1} are both perpendicularly polarized, they show different degrees of intensity change in the presence of the electric field as shown in Figure 6C. This observation is consistent with our assignment that these two bands are associated with the vibrations of the unit cell and have transition dipole moments at an angle with respect to each other. The 883 and 850 cm^{-1} bands both exhibit perpendicular polarization. However, as seen from Figure 6C, upon poling the 883 cm^{-1} band increases in intensity, while the 850 cm^{-1} band weakens in intensity. The polarization and electric field induced behavior of the 883 cm^{-1} band, and the two components of the 850 cm^{-1} band demonstrate that the crystalline units are aligned in the drawing direction and the molecular chains are rotated by the electric field.

Similar to the behavior observed for the 850 cm^{-1} bands, the plot of intensity change with field strength for the 883 cm^{-1} band shown in Figure 8 also demonstrates the dipole reorientation following a cyclic field. Our observations support the notion that the trans sequences for the copolymer, as for the β phase in PVDF, are the molecular units which give rise to the piezoelectric effect. For PVDF the piezoelectric effect is directly associated with the effective dipole moment for the β unit cell containing two nearly planar zigzag chains. In our earlier studies, we found no evidence of coupling to the applied electric field for α phase, unless the applied field exceeded 2 MV/cm. For the copolymer, virtually all bands follow the changing electric field closely, with the exception of the doublet in

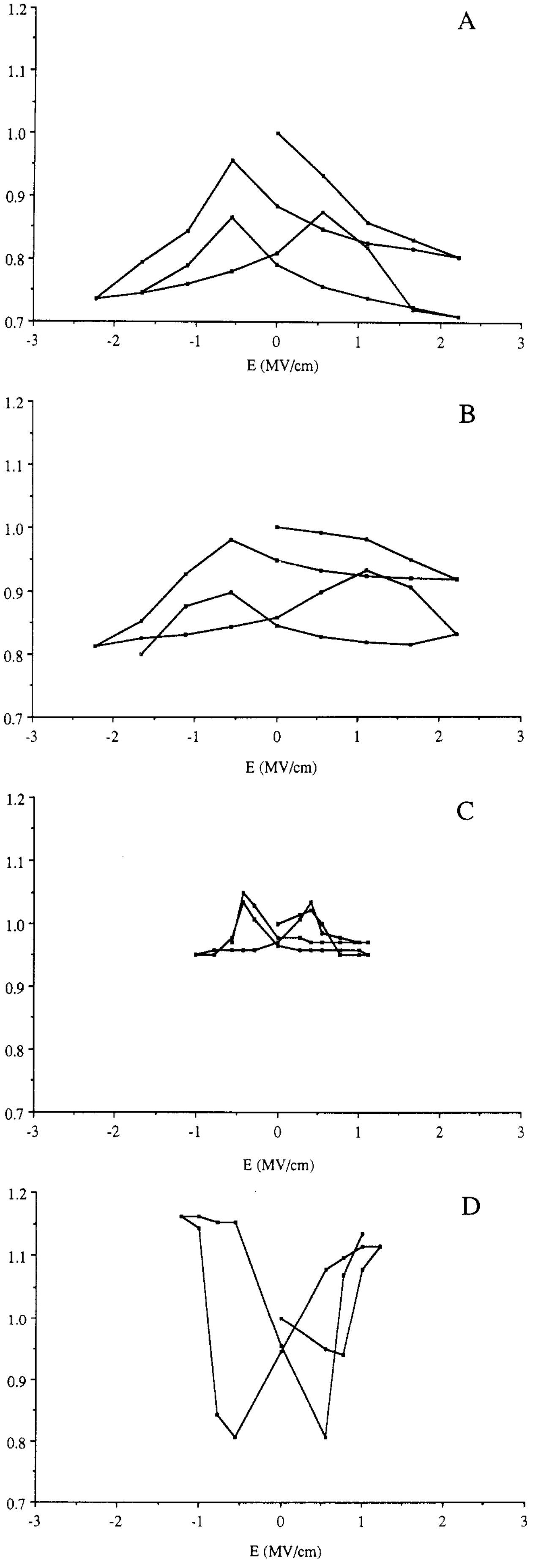

Figure 7. Intensity change of the 850 cm^{-1} band as a function of electric field and temperature: (A) 20 °C; (B) 75 °C; (C) 94 °C; (D) 125 °C.

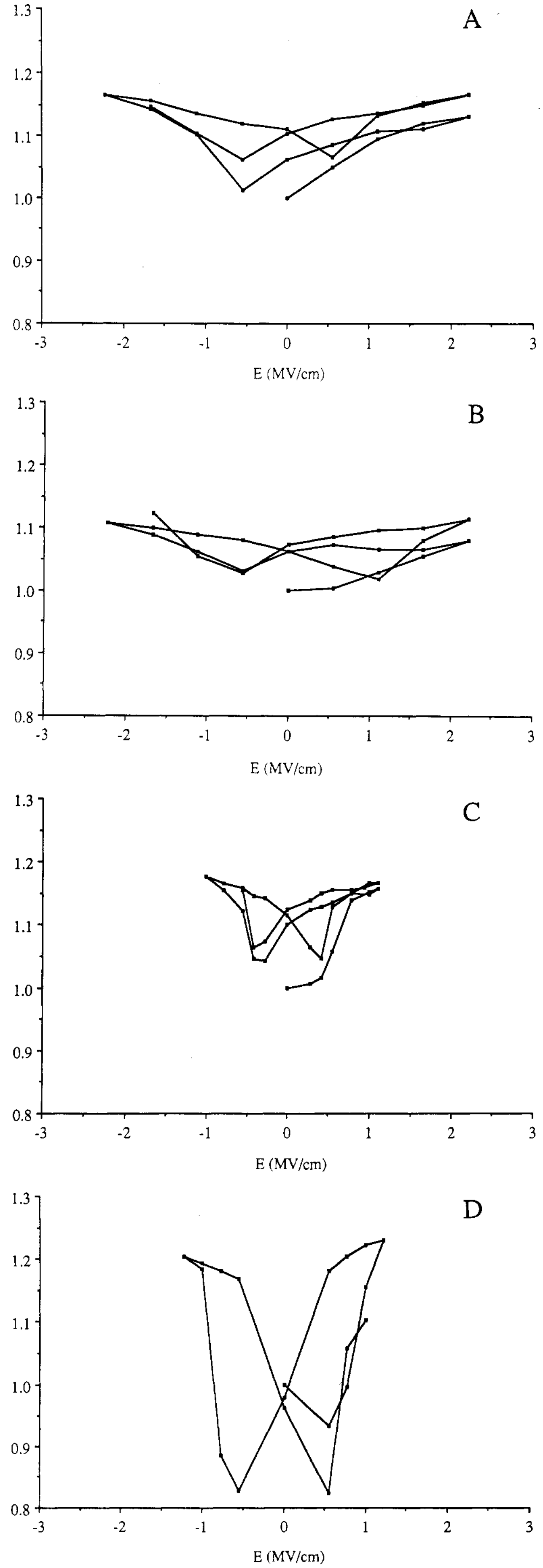

Figure 8. Intensity change of the 883 cm^{-1} band as a function of electric field and temperature: (A) 20 °C; (B) 75 °C; (C) 94 °C; (D) 125 °C.

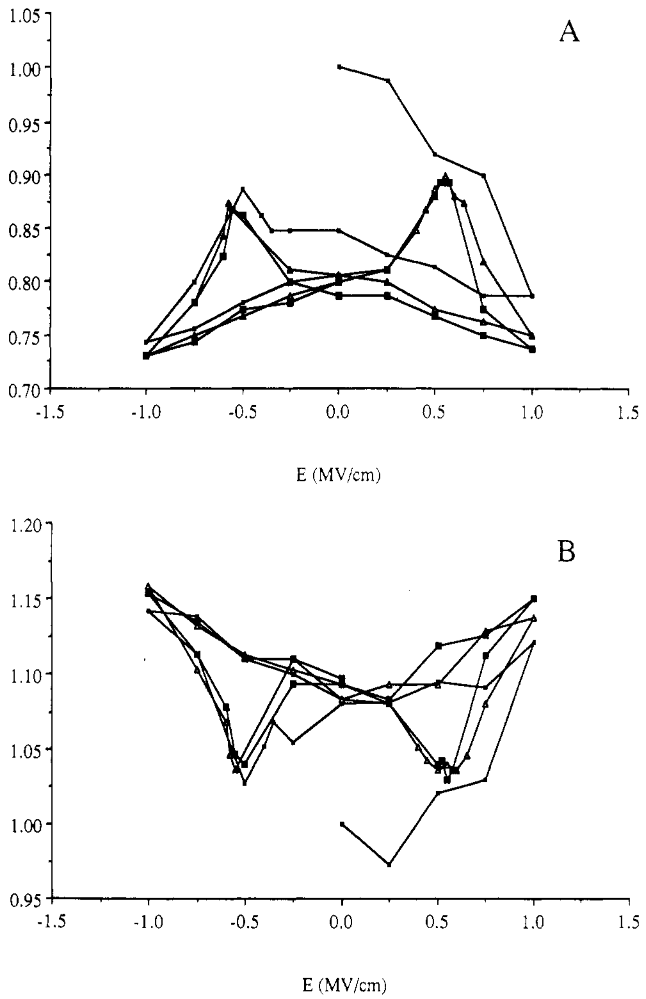

Figure 9. Intensity change as function of electric field for three poling cycles at room temperature: (A) 850 cm^{-1}; (B) 883 cm^{-1}.

the 1350 cm^{-1} region. However it is difficult to conclude that different phases exist and how each would react to the field.

As the electric field strength is reduced back to zero, the infrared band intensity weakens but does not return to its initial value. A negative field must be applied to obtain the initial band intensity. This field, termed the coercive field, effectively removes the remnant polarization induced by the applied electric field.[41] This intensity versus electric field plot forms a hysteresis curve and from it permanent structural modifications due to molecular packing and conformation change can be separated from the reversible orientation of dipoles. Thus it is possible to describe structural changes in terms of the volume fraction of different phases only if the residual chain orientation is considered. This can be accomplished by applying the coercive field and measuring the spectrum in the depolarized state. This technique has been applied to PVDF to monitor the reduction in the volume fraction of the α phase with varying field strength and temperature.[8,10]

In our previous study on PVDF, the hysteresis cycles did not differ substantially. Over three cycles, we did not observe changes larger than the signal to noise ratio unless experiments were carried out at high temperatures. However, a more recent study suggests that the intensity of the trans band increases steadily as a function of cycles.[42] Hysteresis curves for the copolymer show a large change during the first poling cycle, although subsequent cycles are identical, and this can be seen from Figure 9.

For the copolymer, the hysteresis curves change significantly as a function of temperature as shown in Figures

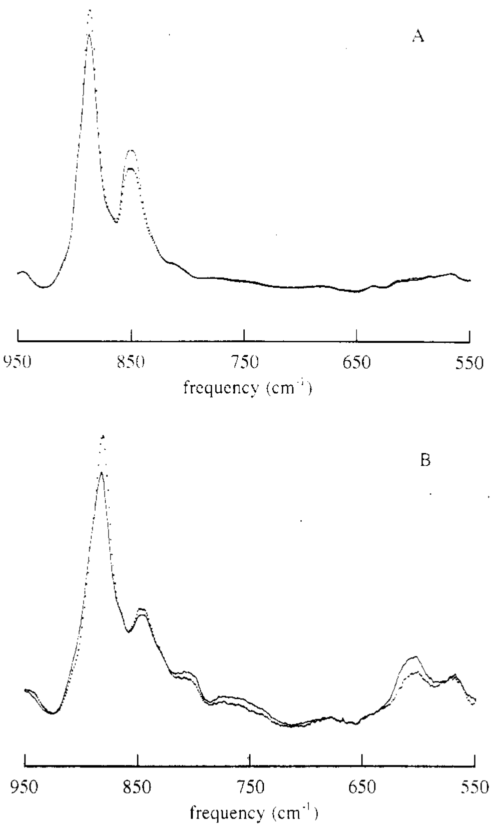

Figure 10. Infrared spectra of 75/25 PVDF/TrFE obtained before and during the application of an electric field as a function of temperature (950–550 cm^{-1}): (—) 0.0 MV/cm; (···) 1.0 MV/cm; (A) 20 °C; (B) 125 °C.

7 and 8. In Figure 8 curves at 20 and 75 °C are quite similar, but at 94 °C intensity change is observed at a much lower field strength, and at 125 °C the intensity change increases dramatically. At this temperature, which is above the 116 °C Curie temperature, the 883 cm^{-1} band intensity initially decreases with field strength and then increases as the field strength rises. Upon lowering the field back to zero, the intensity returns very nearly to its initial value. This behavior is in contrast to that seen at 94 °C, which is below the Curie transition, where an irreversible intensity increase occurs during the first half cycle.

A considerable amount of structural disordering occurs at the Curie transition. This disordering is thought to be primarily conformational; however, dielectric results suggest that thermally activated rotational motions of chain segments in the crystal also play a role.[14] Lattice spacings for a 72 mol % copolymer increase linearly with temperature in both the low- and high-temperature phases.[14,16,17] The lattice expansion and increased chain mobility found at high temperature allow greater rotational freedom of the chains[16] and reduce intermolecular dipole–dipole interactions.

Spectra obtained before and during field application at 25 and 125 °C are shown in Figure 10. The larger degree of spectral change observed at high temperature is indicative of the increased mobility found above the Curie temperature. However, above this temperature thermal energy removes most of the permanent structural change, so that the infrared intensity returns to near its initial value upon removal of the field, as shown in Figure 8. This is analogous to the loss of remnant polarization observed at the Curie temperature measured by D–E hysteresis.[38–40]

A lowering of the coercive field is expected with increasing temperature due to greater chain mobility and is observed in the D–E hysteresis of a 65/35 copolymer.[38] We observe a slight reduction of the coercive field from approximately 0.56 MV/cm at room temperature to 0.42 MV/cm at 94 °C. These values are similar to those obtained from D–E hysteresis which measures a macroscopic polarization,[38,39] while infrared spectroscopy is sensitive to localized dipole reorientation. Thus the agreement in values measured by these different techniques demonstrates the role of dipole orientation as the primary mechanism for polarization in these materials.

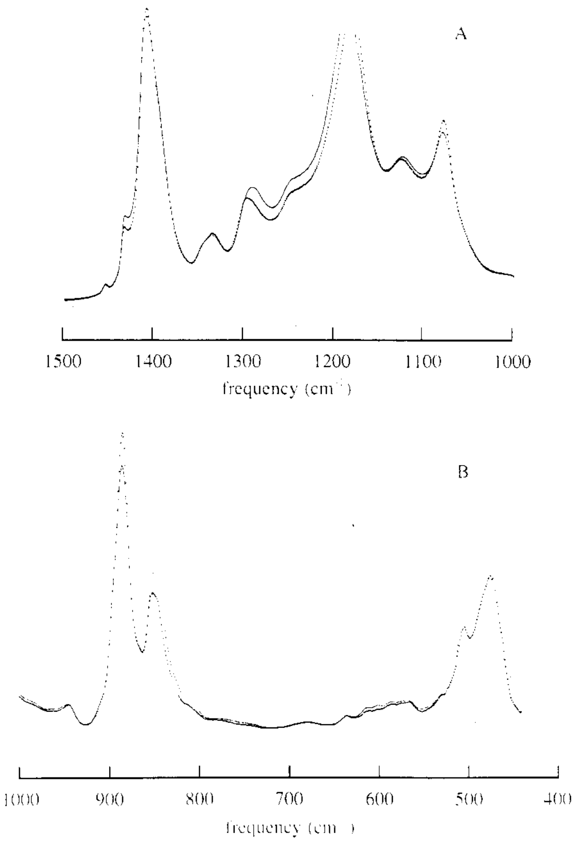

Figure 11. Infrared spectra of 75/25 PVDF/TrFE as a function of electric field. Spectra are obtained in the depolarized state: (—) 0.0 MV/cm; (···) 2.2 MV/cm; (A) 1500–1000 cm^{-1}; (B) 1000–400 cm^{-1}.

Irreversible Structural Change. It is well established that piezoelectric activity can be enhanced significantly by the poling process.[6] We have shown previously that the structure of PVDF can be changed substantially by the application of an electric field at high temperatures.[8,10] It is then interesting to compare the effects of electric field on the chain conformation and packing of the PVDF–TrFE copolymer. Infrared spectra measured before poling and in the depolarized state are shown in Figure 11. When the residual polarization or chain orientation is removed by the application of the coercive field, it may be concluded that an irreversible structural change has taken place because the intensities of both the 850 and 1290 cm^{-1} bands are decreased in the depoled state as compared to the initial measurement.

As previously discussed, the 1290 cm^{-1} band has been assigned to VDF sequences corresponding to sequences of trans isomers four or more units long. In the depolarized state an intensity decrease is observed. This suggests that there is a removal of trans sequences upon poling an oriented film.

The decrease in the trans sequences is indeed surprising when compared to the data we obtained previously for PVDF. In that case we observed a conversion to the β form from the α crystalline unit cell.[8,10] Therefore it is partic-

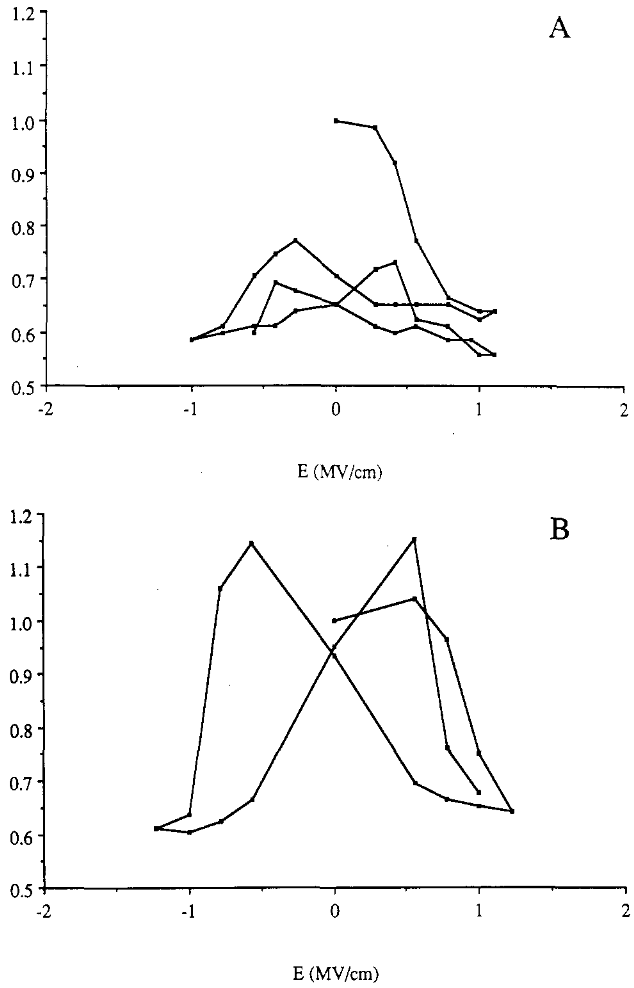

Figure 12. Intensity change of the 612 cm^{-1} band as a function of electric field and temperature: (A) 94 °C; (B) 125 °C.

ularly important to assess the structural changes in the copolymer as a function of field and temperature. Poling and depoling at room temperature result in decreased intensity of the 850 cm^{-1} band, again indicating a reduction in the amount of these trans sequences. As seen in Figure 7, at 75 °C the intensity change is slightly more reversible, and at 94 °C the depoled intensity is greater than the initial intensity. Thus it appears that the number of sequences of three or more trans bonds has decreased by poling at temperatures up through 75 °C but at 94 °C, at which there are less of these sequences to begin with, their number increases with poling. As seen in Figure 11B, the relative intensities of the 850 cm^{-1} components are inverted in the depolarized state. As mentioned previously, these bands are thought to be associated with interchain interactions. Since the relative intensity changes of these bands are similar to those seen upon annealing, it can be concluded that the chain packing may be improved due to the application of the field.

If the trans sequences are increasing in these copolymers at high temperature, then we should expect a corresponding decrease in the gauche content. This indeed is confirmed by observing the vibrations sensitive to the gauche conformation, bands at 612 and 802 cm^{-1}. The broad band near 612 cm^{-1} is observed only at high temperature. The decrease in band intensity upon poling at 94 and 125 °C is shown in Figure 12. As mentioned above, this band is assigned to a tg conformation for a 55/45 copolymer.[12] The large irreversible intensity drop in the first half poling cycle at 94 °C, shown in Figure 7, is indicative of the removal of the tg conformation from the chain upon poling. The hysteresis at 125 °C is similar to that of the 883 cm^{-1} band with nearly reversible intensity change above the Curie temperature. This suggests that the tg conformation reappears once the field is removed above the Curie temperature. The intensity change with field is larger than that of the 883 cm^{-1} band, and both bands show sharp intensity changes at the same field strength. Thus it appears that dipoles in a tg conformation couple to the field as efficiently as those in the trans state, with dipoles in both conformations following the field together.

The reduction of long trans sequences observed in the depoled state is unexpected. It should be noted, however, the film we are studying has been uniaxially drawn. Since we began with an oriented material adopting a predominantly trans conformation, the perturbing effect of a cyclic electric field may be to disrupt the order which we see as a reduction in the amount of trans sequences. That such a conformation change occurs at room temperature is in contrast to PVDF, in which significant conformation change takes place only at elevated temperature. At 94 °C thermal fluctuations reduce interchain interactions and increase dipole vibrational amplitudes. At this temperature there are fewer long trans sequences and poling increases their number. An oriented all trans chain poled at room temperature will disorder. In contrast, poling at higher temperatures a conformationally disordered chain, i.e. containing gauche conformers, results in an increase in the trans content. Cyclic poling at 94 °C produces a slight intensity increase for the 1290 cm^{-1} band, similar to that of the 850 cm^{-1} band. Here thermal energy and the reduction of interchain interactions allow dipole units to flip over to align with the field increasing the amount of trans segments, which are initially fewer in number at this temperature.

Conclusions

The response of a 75 mol %VDF–25 mol % TrFE copolymer in a high strength electric field has been studied by vibrational spectroscopy. Spectra obtained at different temperatures exhibit conformation sensitive bands which characterize the field induced microstructural change. Nearly all vibrational bands are sensitive to the applied field, suggesting that the trans β phase is the predominant structure. Vibrational assignments have been clarified by examining the effects of temperature, annealing, orientation, and electric field on the infrared spectrum. A band at 850 cm^{-1} is found to be sensitive to intermolecular interactions based on its splitting which is enhanced at low temperature. The polarization of the two components of this band and their relative intensity changes seen upon poling suggest that the crystalline units are aligned in the draw direction and the chains within are rotated by the electric field. A cyclic electric field is applied in order to separate the orientation of dipoles from irreversible structural changes. This produces a hysteresis in the IR intensity and the shape of the hysteresis changes significantly as a function of temperature. Bands assigned to both trans and gauche conformations are sensitive to the applied field, indicating that dipoles in both conformations couple to the field. Hysteresis curves show irreversible intensity changes when the field is applied below the Curie temperature but nearly reversible behavior above this temperature. Here greater intensity changes are observed during poling and result from the increased chain mobility found above the Curie temperature. The 1290 and 850 cm^{-1} bands, associated with trans sequences, show an intensity decrease after depolarization. This demonstrates that trans sequences are removed upon poling an oriented film, as the field disrupts the mechanical orientation. At 94 °C there are fewer trans sequences initially, and they are increased by poling, as thermal energy and decreased interchain interactions allow dipoles to align with the applied field. Intensity changes also suggest poling may produce an improvement in packing density.

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An Analysis of Phase Separation Kinetics of Model Polyurethanes

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ABSTRACT: Phase separation kinetics of MDI-PPO model polyurethanes have been characterized by infrared spectroscopy and DSC. The phase separation rate at temperatures between the soft segment T_g and the hard domain dissociation temperature exhibits a functional dependence that is quite similar to the well-known "bell shaped" function pertaining to crystal growth theory. The rate of phase separation was determined to be strongly dependent upon temperature. For one model polyurethane the maximum rate occurred at ~40 deg below the transition from heterogeneous to homogeneous phase. The decrease of phase separation rate at high temperatures is due to the slow initiation time. The non-Gaussian nature of the soft segment conformational distribution appears to be a contributing effect to the slow high-temperature phase separation rate. The two sets of data from infrared spectroscopy and DSC suggest a high correlation between the formation of hydrogen bonds and the overall heat flow measurable during isothermal phase separation.

Introduction

The mechanical properties of polyurethanes can be optimized by carefully choosing the types of hard[1,2] and soft segments,[1,3] molecular weight and molecular weight distribution of the two components,[4–6] synthetic method,[7,8] and the stoichiometric ratio between them.[9,10] The mechanical properties can also be dependent on the size and perfection of the phase separated morphology.[8,11] Due to the incompatibility between the hard and soft segments, polyurethane copolymers undergo microphase separation resulting in hard segment rich hard domains, soft segment rich soft matrix and an interphase between them. It is generally accepted that the strength and the elastic behavior of polyurethanes is directly related to the stability of the hydrogen-bonded hard segment rich domains, acting as junction points in the network. The existence of this heterogeneous, phase-separated structure in polyurethanes was first suggested from the mechanical behavior of the copolymer.[12] In some cases, more direct evidence have also

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