$$\mathrm{SD}_{\mathrm{P1}} = (I_{\mathrm{CH_3\text{-}EPE}})/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \qquad (17)$$

$$\mathrm{SD}_{\mathrm{P2}} = (I_{\alpha\alpha\text{-}\mathrm{EPPE}})/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \qquad (18)$$

The values of the monomer distribution and sequence distribution are given in Table III. These values combined with the distributional information can be used to deduce the copolymerization mechanism.

Conclusions

It is possible, using carbon-13 NMR, to determine all n-ad distributions thru triads in ethylene–propylene copolymers using eq 1 thru 10. In the structurally more simple copolymers reported here, we were able to derive partial tetrad and pentad distributions. Since the spectral regions used to obtain this information show considerably less resolution in rubbers it is unlikely that this information can be derived from spectra of these polymers.

Finally, we have shown that it is possible to obtain information concerning both the monomer and sequence distributions. It will be shown in a subsequent paper how this information can be used to examine the mechanism of the polymerization process.

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An NMR Relaxation Study of a Hexafluoroisobutylene/Vinylidene Fluoride Copolymer (HFIB/VF$_2$)

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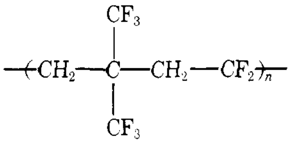
ABSTRACT: Fluorine and proton NMR relaxation data of HFIB/VF$_2$ have revealed an α relaxation associated with the glass transition. This relaxation is characterized by an activation energy of approximately 73 kcal/mol. The transition is observed in both the proton and fluorine data and the proton spin–spin relaxation times can be deconvoluted into crystalline and amorphous components above the glass transition temperature. A local mode relaxation with activation energy of ~9 kcal/mol is observed in the proton data. Reorientation of the CF$_3$ groups is observed in the fluorine data with an activation energy of approximately 5 kcal/mol. What begins as two separate reorientational processes at low temperature probably becomes a complicated reorientational process in the high-temperature limit involving these two processes and the glass transition.

Poly(3,3,3-trifluoro-2-trifluoromethylpropene/1,1-difluoroethylene) (HFIB/VF$_2$) is a copolymer made from a 50/50 molar composition of hexafluoroisobutylene (HFIB) and vinylidene fluoride (VF$_2$).[1,2] The polymer is believed to assume a configuration in which the monomer units add in a head-to-tail fashion giving rise to a copolymer structure of[1]



$$-\!\!\left(\mathrm{CH_2}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CF_2}\right)_{\!n}\!\!-$$

The copolymer is highly crystalline with a melting point of 600 K.[2] It is reported to have more desirable physical properties at elevated temperatures than other fluoropolymers.[2] For example, HFIB/VF$_2$ has a high modulus and tensile strength retention at high temperatures; its heat distortion temperature is 493 K at 264 psi of stress.[2] It is superior to other fluoropolymers in surface hardness, abrasion, and scratch resistance.[2] Its good resistance to attack by organic and inorganic solvents, low water vapor permeability, and excellent nonsticking and nonwetting properties make it a very attractive material to replace other fluoropolymers in many applications.

A recent dielectric and dynamic mechanical relaxation study of HFIB/VF$_2$ has shown two relaxations in the temperature range 100 to 460 K.[3] The low-temperature relaxation exhibits a maximum in tan δ at 210 K with an activation energy of 9 kcal/mol. The relaxation is ascribed to a local mode motion of low amplitude in the backbone of the polymer. The high-temperature relaxation, which was assigned to the glass transition, has a high activation energy and does not exhibit the characteristic WFL type curve over the frequency range studied. HFIB/VF$_2$ is such a highly crystalline material that preliminary attempts to determine the glass transition by differential scanning calorimetry on quenched low molecular weight materials were unsuccessful.[4]

Nuclear magnetic resonance provides a unique tool for probing molecular motions in polymeric systems. This particular system offers the added advantage of possessing fluorine and hydrogen atoms, both of which have magnetic moments. Protons are found only in the main chain and, as such, a comparison of the relaxation processes for the two magnetic nuclei should throw some light on the nature of the molecular processes taking place.

Experimental Section

The samples of HFIB/VF used in this study were obtained from Dr. S. Chandrasekaran of Allied Chemical Corp. Sample A is a powdered material with a melt flow index of 0.8 g/10 mins for a 5 kg load. Sample B is a film of suspension polymerized material which was compression molded at 350 °C. The melt flow index was 13 g/10 min for a 2.16 kg load. Because HFIB/VF$_2$ is insoluble in all known solvents, molecular weights could not be measured by solution methods. Evacuated samples were obtained by pumping the samples to 10^{-5} mm Hg at 100 °C for 4 h prior to sealing the NMR tube.

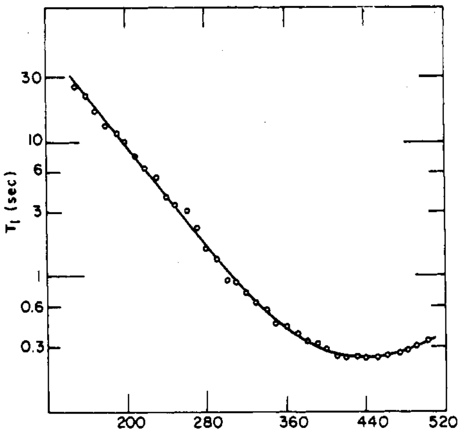


Figure 1. Plot of fluorine spin-lattice relaxation time vs. temperature for HFIB/VF, sample A.

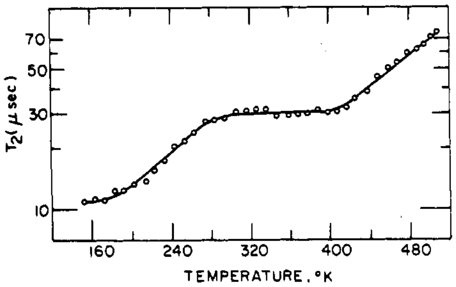


Figure 2. Plot of fluorine spin-spin relaxation time vs. temperature for HFIB/VF, sample A.

The NMR spin-lattice (T_1) and spin-spin (T_2) relaxation times were obtained on a Bruker SXP spectrometer operating at 90 mHz for protons and 84.7 mHz for fluorine. The 90° pulse width was 2.5 μs, with a recovery time of 6 μs. The temperature was controlled by a gas-flow system thermostated with a copper-constantan thermocouple and controlled to an accuracy of ±1°. T_1 was measured by the $180-\tau-90°$ pulse technique while T_2 was taken as $t_{1/2}/\ln 2$ where $t_{1/2}$ is the time for the free induction decay (FID) to fall to one-half its original value.

Results and Discussion

A plot of fluorine T_1 vs. temperature for sample A is given in Figure 1. A broad minimum of 250 ms is observed at 440 K. The corresponding T_2 plot (Figure 2) exhibits a low-temperature transition at 180 K and another of greater intensity at 400 K. Proton T_1 data of sample A are given in Figure 3. A relatively weak minimum is observed at 380 K while a broader minimum is centered at 450 K. Below 330 K the magnetization recovery is exponential and the proton spin-lattice relaxation is described by a single time constant. Between 330 and 400 K, however, the recovery is nonexponential and two T_1's are obtained. Above 400 K, the magnetization recovery reverts to its single exponential form and all through the high-temperature flat minimum only one T_1 is observed. In the proton T_2 plot (Figure 4) a low-temperature transition is observed at 260 K. This is a fairly small transition; T_2 changes by about 3 μs through the transition. At 390 K T_2 again increases rapidly. At 430 K a second T_2 component (T_{2a}) some four times larger in magnitude than the smaller T_2 component (T_{2c}) is observed. Both T_2's continue to increase with increasing temperature. The proton T_1 plot of sample B is given in Figure 5. The low-temperature minimum occurs at 380 K, while the high-temperature minimum is centered at 500 K. For this sample, two T_1's are observed for temperatures up to 400 K, above which only one T_1 component is found. T_2 plots of this sample are similar to the proton T_2 plot of sample A.

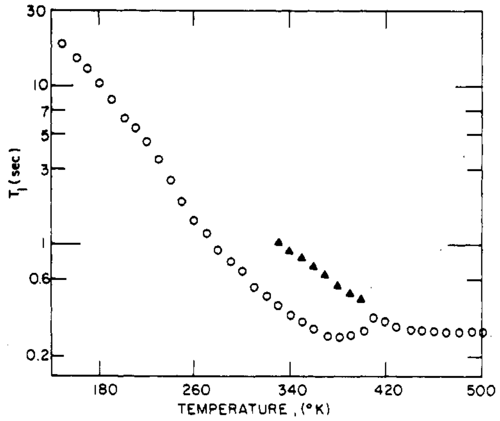


Figure 3. Plot of proton spin-lattice relaxation time vs. temperature for HFIB/VF, sample A: (▲) second T_1 component.

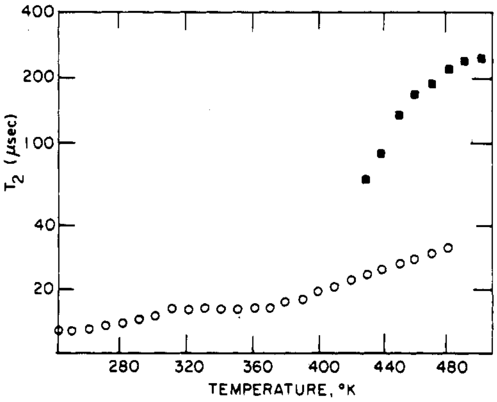


Figure 4. Plot of proton spin-spin relaxation time vs. temperature for HFIB/VF, sample A: (○) T_{2c}; (■) T_{2a}.

The high-temperature transitions in T_1 and T_2 from both the proton and fluorine relaxation data of sample A are similiar in position and intensity to that observed in the proton data of sample B. The ^{19}F T_1 minimum and T_2 transition at 440 and 400 K, respectively, and the proton T_2 transition and T_1 minimum at 400 and 450 K, are all related to the same molecular process. There is good correlation between the frequency points determined by NMR and those of dielectric and dynamic mechanical measurements on the transition map of Figure 6. This high-temperature process has an activation energy of approximately 73 kcal/mol.

The T_1 minima associated with this relaxation are fairly broad and the corresponding T_2's undergo relatively large changes compared to the other relaxations, indicating a somewhat efficient relaxation process. The proton T_2 data reveal the added feature of a second T_2 component (T_{2a}) due to the amorphous regions. This component increases a lot more rapidly than that of the crystalline component (T_{2c}). At temperatures below 400 K the magnetization recovery is described by one T_2. This is the region of the rigid glass in which the micro-Brownian motions accessible to the amorphous regions are frozen out and T_{2a} ant T_{2c} are indistinguishable. On approaching the glass transition, however, the extensive motions of the amorphous phase are not accessible to the rigid crystalline regions. The motions in these phases become sufficiently different in intensity to permit differentiation of the reorientational processes in each phase. As a result, the high temperature or α relaxation is assigned to the glass transition. The high activation energy associated with this process and the efficient relaxation mechanisms available to the amorphous polymer chains are indicative of the more generalized motions experienced by the chains at this transition.

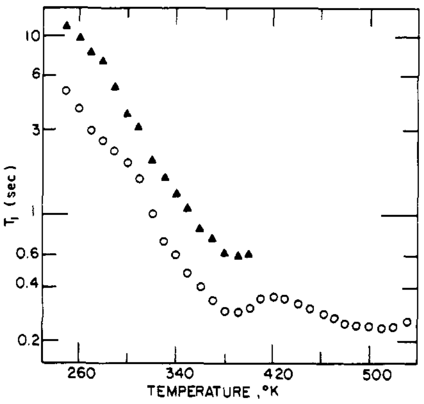


Figure 5. Plot of proton spin–lattice relaxation time vs. HFIB/VF, sample B: (▲) second T_1 component.

Despite the relatively large increase in molecular reorientation above T_g as compared to that in the rigid glass, differential scanning calorimetry shows no signs of a glass transition even in low molecular weight samples of this polymer. If it assumed that the quantity of rigid phase determined by T_2 is a rough approximation of the amount of crystalline material present (despite the limitations in determining crystallinity by T_2), then the question arises, why does a material containing 70% amorphous material not show a T_g calorimetrically. The answer to this question probably lies in the nature of the polymer chains in the amorphous regions. Conventionally the amorphous regions are thought to consist of chains which assume a random coil conformation. However, it is known that chains which exist in defect regions of crystals, on crystalline surfaces as defects or as chain folds, and as tie molecules between crystallites are much more constrained than the truly amorphous regions. Since the observation of the glass transition by calorimetry is based on an increase in the number of degrees of freedom above T_g as compared to the rigid glass, it is conceivable that for such constrained regions of an intrinsically stiff chain the net increase in degrees of freedom is small. If these regions constitute a large fraction of the overall amorphous phase, the result is an almost unobservable calorimetric T_g. The change in heat capacity at T_g for a large body of semicrystalline polymers does not follow the expected linear behavior of an ideal two-phase system. As a matter of fact within the middle range of crystallinities the deviations from linearity are so severe that a much lower fraction of amorphous phase is obtained, based on the ratio of measured heat capacity change to that of the totally amorphous material.[5] In addition, it has recently been shown that the constrained anisotropic motions of chain ends or cilia and chain folds give rise to less intense transitions than one may expect for the glass transition of the truly amorphous regions.[16] If the amorphous regions consist, to a large degree, of this intermediate phase the changes in T_2 at T_g may reflect the restraint imposed on the motion of these entities by the crystalline phase.

As mentioned above, at the glass transition, two T_2 components are observed in the proton plot, with T_{2a} increasing much more rapidly than T_{2c}. No second T_2 component is observed at the same transition in the fluorine data. Since there are only two fluorine atoms in the backbone of the chains compared to six in the two trifluoromethyl groups, the fluorine T_2 data are governed to a large extent by the motion of the CF_3 groups. At the glass transition temperatures, the motions of the CF_3 groups are already fairly extensive in both the crystalline and amorphous regions. The glass transition is associated with large scale main chain motion in the amorphous regions and it becomes a little more difficult to separate the motions in each of these phases, especially when these motions are dominated by side groups which are very active in each phase.

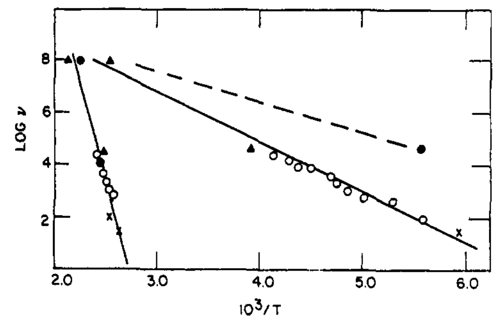


Figure 6. Transition map of HFIB/VF: (●) fluorine NMR data; (▲) proton NMR data; (○) dielectric data, ref 3; (×) dynamic mechanical data, ref 3.

The low-temperature fluorine T_2 transition at 180 K does not appear to exhibit a corresponding T_1 minimum nor does it exhibit a counterpart in the proton T_2 data. Perhaps the corresponding high-frequency components of this motion which would be reflected in a T_1 minimum are masked by the minimum due to the glass transition. That is, the activation energy for this process is so small that before a separate T_1 relaxation can be realized, the motions due to the glass transition become so extensive as to dominate the whole relaxation process. If one assumes that the T_1 minimum corresponding to this low-temperature fluorine relaxation overlaps that of the α relaxation, one obtains an activation energy of approximately 5 kcal/mol. Such a small activation energy accompanied by the absence of any corresponding transition in the proton T_1 and T_2 data or dielectric data establishes the origin of this transition as due to reorientation of the trifluoromethyl groups pendant to the backbone. Methyl groups require very small energies of activation and relatively little free volume to reorient. As a result, they reorient as readily in the crystalline as in the amorphous state. The trifluoromethyl group requires only a slightly larger free volume and activation energy than methyl, but not enough to make the reorientation preferential to the amorphous or crystalline phases. As a matter of fact, it occurs fairly readily in each phase despite the fact that molecular models show the polymer chain to be fairly stiff. Previously reported NMR data on copolymers of tetrafluoroethylene–hexafluoropropylene (FEP) indicate that the perfluoromethyl groups are locked in and do not rotate.[6] However, there is dielectric evidence of a low-temperature relaxation in FEP which has an activation energy of 4 kcal/mol and has been ascribed to reorientation of CF_2H impurity groups.[7] Motion of the CF_3 group might conceivably be hindered by neighboring fluorine atoms on either side on the backbone of FEP. However, in the case of $HFIB/VF_2$, the steric size of the hydrogen atoms on adjacent methylene groups is not large enough to prevent this motion especially when this motion occurs in cooperation with the local mode process discussed below.

The low-temperature β relaxation exhibits its T_2 transition at 260 K and its T_1 minimum at 380 K and is observed only in the proton relaxation data. The relaxations in samples A and B agree with each other in both intensity and position on the temperature scale. The transitions in both samples, although well defined, are only moderately intense. Observation of the relaxation in the proton data only and an activation energy of approximately 9 kcal/mol lends support to its assignment as a low amplitude local mode motion in the backbone of the polymer.[3] What begins therefore as two separate processes corresponding to reorientation of $-CF_3-$ and a local mode backbone motion probably becomes a complicated correlated motion at higher frequencies in which the two processes are indistinguishable.

It has been suggested that the local mode motion involves very short segments of the intermediate $-CH_2CF_2CH_2-$ groups in the amorphous regions of the polymer and results in slight changes in the localized conformation of the polymer chain.[3] Low-temperature γ relaxations have been observed in other polymers and have been assigned to chain rotation in the amorphous regions and rotation at defects in the crystalline chain.[8–10] Calculations of T_2 for polyethylene based on two models ((1) in which some of the crystalline chains experience flip–flop motion while a large proportion of the amorphous chains undergo rotation, and (2) in which the crystalline regions are rigid while all the amorphous chains undergo rotation) have been carried out.[11] The calculations provide good agreement with experimental data in which T_2 changes for this process are very small.[9] A γ relaxation with an activation energy of 12 kcal/mol has also been observed in vinylidene fluoride–hexafluoropropylene copolymers. This relaxation has been ascribed to local motion in the amorphous regions.[12] A similiar reorientational process occurs in PVF$_2$ with $\Delta E = 7.1$ kcal/mol. This process is thought to be due to rotation of the amorphous chains.[13] Based on these reported observations and the NMR transitions in the proton relaxation data, we conclude that the reorientation process is of the local mode type but the specific nature of the reorientational process is unclear. The relaxation process is probably confined to the amorphous regions. However, the NMR, dielectric, and mechanical results on samples which were quenched to alter the degree of crystallinity were indistinguishable from their slowly cooled counterparts.

The presence of two T_1's at temperatures below the β relaxation in samples A and B can be manipulated by sample preparation and is indicative of two morphologically different environments. When $T_2 \ll T_1$, the magnetic nuclei in the rigid regions can transfer their energy via the spin–diffusion process[14] to the more mobile regions before it is dissipated into the thermal motion of the molecules via the T_1 processes. Above 430 K, two T_2 components are observed. The crystalline (rigid) fraction gives rise to a component which constitutes approximately 25% of the overall decay. However, the T_1 data show that the more rigid fraction, as represented by the longer T_1, represents 75% of the sample. The intensities of the T_2 components are proportional to the number of spins in each phase. Douglass and McBrierty[13] have demonstrated that for samples containing morphologically different regions which are not coupled (i.e., which relax independently), the relaxation curves will result in two slopes with intensities representitive of the number of spins in each region. They have also shown that when the coupling between regions is comparable to the intrinsic relaxation rates of each region, the intensities associated with the two relaxation processes are not simply given by the true relative intensities of each phase. As a matter of fact, in such cases, the greater intensity is associated with the longer relaxation time. The present anomaly in the T_1 intensities, therefore, can be explained in terms of the model of Douglass and McBriety.[15] From the spin-diffusion contribution to the relaxation process one estimates a path length of approximately 172 Å for diffusion of the spin energy out of the crystalline regions to the more efficiently relaxing amorphous region.

Conclusions

Fluorine and proton NMR relaxation data of HFIB/VF$_2$ have revealed an α relaxation associated with the glass transition. This relaxation is characterized by an activation energy of approximately 73 kcal/mol. The transition is observed in both the proton and fluorine data and the proton spin–spin relaxation times can be deconvoluted into crystalline and amorphous components above the glass transition temperature. A local mode relaxation with activation energy of $\sim$9 kcal/mol is observed in the proton data. Reorientation of the CF$_3$ groups is only observed in the fluorine data with an activation energy of approximately 5 kcal/mol. What begins as two separate reorientational processes at low temperature probably becomes a complicated reorientational process in the high-frequency limit involving these two processes and the glass transition. There is good correspondence between the points of dielectric, dynamic mechanical, and NMR relaxation in the transition map of the various relaxations of the polymer.

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