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ESR and Fluorescence Polarization Investigation of Molecular Motions in Poly(vinylidene fluoride) and Some Related Copolymers†

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ABSTRACT: Molecular motions in poly(vinylidene fluoride) (PVDF) and some related copolymers are investigated by ESR spin-probe technique and fluorescence polarization. For amorphous copolymers containing 30 and 50 wt % chlorotrifluoroethylene units, two well-defined relaxation processes are apparent. At lower temperatures, the local mode γ process is observed. The activation energy for motion in this region is 6.5 kcal·mol^{-1}. At higher temperatures the T_g relaxation or β process is observed. In this region, both ESR and FP data fit an expression of the WLF type. The transition behavior of PVDF appears more complicated. In addition to the local mode γ process, two β relaxations are observed. A careful analysis of the spectra shows that at T_{50G}, the probes respond to $T < T_g$, T_{g_L}, or T_{g_U} relaxation depending on their molecular volume. With the bulkier probes, the molecular volumes of the polymer segments undergoing β_L and β_U relaxations are estimated by using the relationship derived by Kusumoto et al. between T_g (1 Hz) and T_{50G}.

Introduction

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer that exhibits piezoelectric properties when crystallized in polar β form. Its amorphous phase gives rise to various relaxation processes including local mode relaxations and T_{g_L} and T_{g_U} glass transitions.[1-4] The transition behavior of PVDF was investigated over the frequency range 10^{-1}–10^5 Hz from dynamic mechanical and dielectric experiments. A comprehensive survey of the corresponding results and of additional pulsed NMR data was given by McBrierty et al.[2] in the form of Arrhenius plots.

Electron spin resonance (ESR)[5-6] and fluorescence polarization (FP)[7-8] have proved to be powerful tools for studying the high-frequency phenomena in polymers. Because they need dispersion of suitable probes in the polymer matrix, these two techniques have the inherent advantage of focusing on the relaxation processes associated with the amorphous regions of the material, where the probes are located. Accordingly, any difficulty in discriminating between amorphous and crystalline relaxations occurring in the same temperature range is removed.

In this paper we report ESR and FP data on PVDF and some related copolymers with the aim of defining the high-frequency relaxational behavior of these materials. Taking into account all the data of the different ESR spin-probe experiments and comparing experimental spectra to those calculated under certain assumptions, we want to derive some conclusions concerning the origin of the various relaxation processes.

Experimental Section

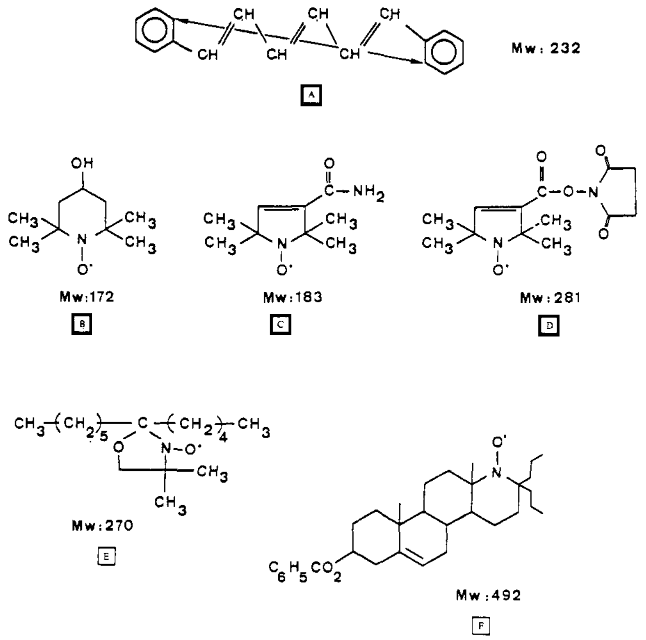
Materials. PVDF was supplied by Kureha Chemical Industry Co. (batch KF 1000). Three random copolymers were additionally investigated: one semicrystalline VDF–TFE copolymer containing 30 wt % of tetrafluoroethylene units from Pennwalt Chemical Corp. (Kynar grade 7201) and two VDF–CTRFE amorphous copolymers provided by ATOCHEM (France) under the trade names Voltalef 3700 and Voltalef 5500, which contained 30 and 50 wt % of chlorotrifluoroethylene units, respectively.

Glass-transition temperatures of these materials, as measured by DSC,[4] are given in Table I.

Table I
Glass-Transition Temperatures of the Materials under Study As Previously Determined by DSC[4]

polymer	T_g, K	T_{g_L}, K	T_{g_U}, K
Voltalef 3700	260		
Voltalef 5500	271		
PVDF		233	318
VDF–TFE copolymer		238	318

Chart I
Structure and Molecular Weight of the Probes Used in This Study[a]



[a] A (DPHT): fluorescent probe (the double arrow indicates the transition moment). B (Tempol), C, D, E, F: nitroxide spin probes.

ESR Measurements. The spin probe chosen for most of this study was 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl. Larger probes were also used, especially in PVDF (Chart I).

Crystalline probe was added to the molten polymer at 483 K with rapid stirring. Doped PVDF samples were then rapidly quenched in an ice–water mixture. In contrast, doped Voltalef samples were gradually cooled to room temperature. In order to avoid spin-exchange contributions to line widths, the probe concentration in bulk samples was kept less than 4 × 10^{-7} mol/g of polymer.

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† This paper is dedicated to Dr. Thirion on the occasion of his retirement in 1985.

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All the samples were prepared in evacuated Pyrex tubes, and the ESR spectra were recorded by using a Varian E-4 spectrometer. An E-257 Varian variable-temperature controller was used to thermostat the cavity, and the temperature was measured by a copper–constantan thermocouple lowered into the cavity before and after each series of measurements. Samples were allowed to equilibrate for a minimum of 5 min for each 10 °C change in temperature. In the case of doped PVDF, a unique sample was used from 113 K up to the temperature at which PVDF crystallization occurs. At higher temperatures, such a method should be equivalent to successive heat treatments of the original sample. Thus, in order to avoid contribution to ESR spectra from annealing effects, a freshly prepared sample was used at each temperature above 333 K.

Field measurements were made with a direct-reading frequency meter (Radiall). The upper temperature reached was limited by either decomposition of the probe or very fast rotation of the probe ($\tau_c < 5.\times 10^{-11}$ s).

FP Measurements. The fluorescent probe chosen for this work was 1,6-diphenylhexatriene (DPHT) (Chart I), the usefulness of which has been previously demonstrated in the fluorescence polarization study of the glass–rubber relaxation.[9]

The polymer samples were swollen for 48 h at 298 K with solutions of DPHT in benzene and then dried in vacuo. The bulk samples were then molded at temperatures close to the melting point and rapidly quenched at room temperature. In the case of Voltalef copolymers toluene was used instead of benzene as the swelling agent and the latter step of sample preparation was omitted in the absence of any liability of the materials to crystallize. The fluorescent probe concentration in bulk samples was less than 10^{-7} DPHT mol/g of polymer.

FP measurements consisted of the determination of the mean fluorescence anisotropy $\bar{r}(T)$, of the lifetime τ, and of the limit anisotropy r_0, as discussed later in this paper. $\bar{r}(T)$ was accurately measured under continuous illumination by using a Nachet NS 400 microscope, which had been modified in order to perform FP experiments.[10] Measurements were carried out from 300 to 475 K by putting the sample in a Mettler FP 4 hot stage. The heating rate was 10 K·min^{-1}. Both τ and r_0 were obtained from fluorescence anisotropy decay experiments at room temperature, using equipment and methods described in a previous paper.[11]

Data Analysis

ESR Line-Shape Analysis. For a given orientation in space the ESR spectrum of a nitroxide consists of a triplet with the splitting determined by the hyperfine **A** tensor, and the position in the field of its center by the **g** tensor.[12] A general solution of the ESR line-shape problem covering both the fast- and slow-tumbling regions has been presented by Freed and co-workers.[13,14]

In order to quantify the effects of an anisotropic rotational motion of the probe, experimental spectra of probe B dispersed in PVDF and copolymers were analyzed by comparing them with simulated line shapes. The computer program used for line-shape simulation was that given in Appendix B of ref 14. The simulated spectra were computed for a Brownian rotational diffusion of spin probe B with the magnetic parameters where $A_z = 5.8$, $A_x = 5.5$, $A_y = 5.7$ G, $g_z = 2.0022$, $g_x = 2.0084$, and $g_y = 2.0060$,[15,16] in agreement with the experimental A_0 and $A_\parallel$ values determined in this work. The magnetic x axis was taken as being along the N–O bond, the z axis along the $2p\pi$ orbital of the nitrogen, and the y axis perpendicular to the other two. The principal axes of the diffusion tensor were labeled x', y', and z'. As well as for PD-tempone[15,16] agreement between calculated and experimental spectra was obtained for $z' = y$. The rotationally invariant lorentzian peak-to-peak first derivative line width T_2IN was estimated from extrapolation of high-temperature data. In the case of Voltalef 3700 and Voltalef 5500, the best fit was obtained with $T_2IN = 1$ G over the whole temperature range. In contrast, for probe B mixed with PVDF, T_2IN was found to be 1.2 G at high temperature but to increase with decreasing temperature.

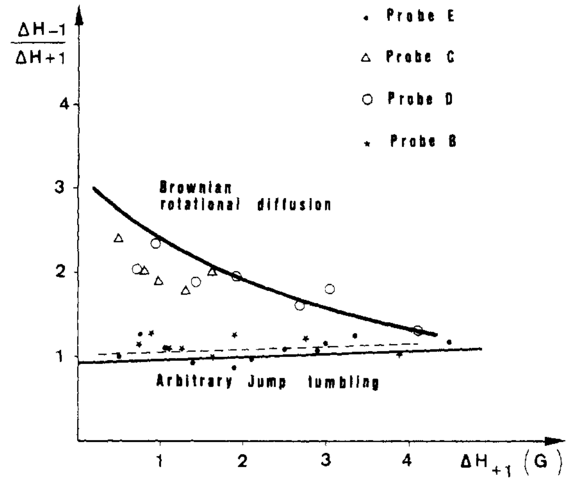

Figure 1. Dependence of the ratio $\Delta H_{-1}/\Delta H_{+1}$ on ΔH_{+1} for PVDF: (★) for probe B; (△) for probe C; (○) for probe D; (•) for probe E.

In the absence of precise data relative to the anisotropic components of the **A** and **g** tensors, simplified methods for estimating the rotational correlation time τ_c have been developed.

(a) Motional Narrowing Spectra. For the particular case of isotropic motional rotation coupled with near-axial symmetry of the hyperfine interaction tensor, τ_c can be calculated from the expression[6]

$$R_+ + R_- - 2 = \frac{b^2}{4}T_2(0)\tau_c \qquad (1)$$

with $R_\pm = T_2(0)/T_2(\pm 1)$, $b = {}^2/_3[A_\parallel - A_\perp]$, and ${T_{2_{(-1)}}}^{-1}$, ${T_{2_{(0)}}}^{-1}$, and ${T_{2_{(+1)}}}^{-1}$ are the widths of the lines corresponding to each value $M = -1, 0, +1$ of the ^{14}N nuclear projection quantum number. As pointed out by different authors,[17-19] the values of τ_c calculated from the isotropic diffusion model are close to the average $\tau_{\bar{D}}$ for anisotropic motion that Freed defines as $\tau_{\bar{D}} = (6\bar{D})^{-1}$ with $\bar{D} = (D_\parallel D_\perp)^{1/2}$ where $D_\parallel$ and $D_\perp$ are the diffusion constants in the case of an axially symmetric molecule. Thus, as a working assumption for the probes C–F, it will be considered that τ_c calculated by assuming isotropic motion gives a satisfactory solution.

(b) Slow-Tumbling Spectra. Several approaches have been used to calculate ESR spectra in the slow-motion region.[6] In particular, one needs only to measure $S = A'_z/A_z$, where A'_z is one-half the separation of the outer hyperfine extrema and A_z is the rigid-limit value for the same quantity. Goldman et al.[20] have found that values of τ_c could be fitted to the equation

$$\tau_c = a(1 - S)^b \qquad (7 \times 10^{-9}\ \mathrm{s} < \tau_c < 10^{-7}\ \mathrm{s}) \qquad (2)$$

The a and b coefficients are sensitive to the diffusion model adopted and the intrinsic line width. From an analysis of the rigid-limit spectra for PVDF and copolymers, it can be seen that the values of a and b given by Goldman et al.[20] for an intrinsic line width of 3 G have to be used for estimating τ_c. The rotational diffusion character was analyzed by using the ratio of the high- to low-field $\Delta H_{-1}/\Delta H_{+1}$ extrema shifts.[21] In agreement with previous studies[19,22] for probes B and E the experimental results closely correspond to the theoretical values for an arbitrary jump-tumbling model. Note that for probe E, only the size of the ring seems to be of importance in the definition of the motion: the flexible aliphatic chain does not seem to intervene. However, increasing the size of the

Table II
Limit Anisotropies r_0 and Lifetimes τ Relative to DPHT Dispersed in Various Polymer Matrices

polymer matrix	r_0	τ, ns
Voltalef 3700	0.32 ± 0.01	9 ± 0.5
Voltalef 5500	0.35 ± 0.02	10 ± 0.5
PVDF	0.32 ± 0.01	12 ± 0.8
VDF–TFE copolymer	0.32 ± 0.01	12 ± 0.8
polyisoprene (from ref 9)	0.32 ± 0.01	7 ± 0.5
polypropylene (from ref 10)	0.32 ± 0.02	
polystyrene (from ref 13)	0.33 ± 0.01	
polybutadiene (from ref 14)	0.33 ± 0.01	6.5 ± 0.5

probe increases the probability of continuous Brownian rotational diffusion (Figure 1).

FP Data Analysis. As detailed elsewhere,[23] FP measurements under continuous excitation yield the quantity

$$\bar{M}(\tau) = \int_0^\infty M(t) \exp(-t/\tau) \, d(t/\tau) \qquad (3)$$

where τ is the mean fluorescence lifetime and $M(t)$ is the orientational autocorrelation function. If $\theta(t)$ means the angle through which the transition emission moment of the probe rotates between time 0 and time t, $M(t)$ obeys the equation

$$M(t) = \langle (3 \cos^2 \theta(t) - 1)/2 \rangle \qquad (4)$$

where the brackets mean an average over the probes emitting at time t. Experimentally, $\bar{M}(\tau)$ is obtained at each temperature T from the mean fluorescence anisotropy

$$\bar{r}(T) = (I_\parallel - I_\perp)/(I_\parallel + 2I_\perp) \qquad (5)$$

by the relation

$$\bar{M}(\tau) = \bar{r}(T)/r_0 \qquad (6)$$

In eq 5, $I_\parallel$ and $I_\perp$ represent the fluorescence intensity components for analyzer directions parallel and perpendicular to the excitation light polarization, respectively.

Also we can define the mobility parameter $m(T)$ by

$$m(T) = (\bar{M}_{(\tau)})^{-1} - 1 \qquad (7)$$

At sufficiently low temperature, when the rotational motion of the probe is completely frozen, $\bar{r}(T)$ and $m(T)$ tend to r_0 and 0, respectively. In contrast, at high temperature, $\bar{r}(T)$ and $m(T)$ tend to 0 and infinity, respectively.

As previously reported for studies on semicrystalline materials,[10] any significant scattering of the incident beam by the crystallites results in a drop of anisotropy values. In the present study, however, measurements on thin samples (less than 15 μm) of PVDF or VDF–TFE copolymer can be analyzed without any correction. In any case, amorphous Voltalef samples were also investigated as proof of the suitability of the experiments.

Limit anisotropies of the materials under study are given in Table II. As appears from these results, r_0 values are roughly independent of the nature of the polymers. In addition, they are very close to previous data relative to other polymers (Table II).

Probe fluorescence lifetimes τ, measured at 298 K, are also given in Table II. Contrary to r_0 values, τ values markedly depend on the nature of the polymer matrix. One may notice that the lifetime is especially large in fluorinated polymers compared to other polymers mentioned in the literature. Owing to the fact that the overall fluorescence intensity $I_{(T)} = I_\parallel + 2I_\perp$ varies directly as the lifetime at the same temperature T, the temperature dependence of τ may be easily deduced from plots of $I(T)/I$ (298 K) as a function of temperature. As shown in Figure 2, both PVDF and VDF–TFE copolymer do not behave like the Voltalef copolymers. Their lifetimes are the longest at low temperature but the smallest at temperatures above 360 K.

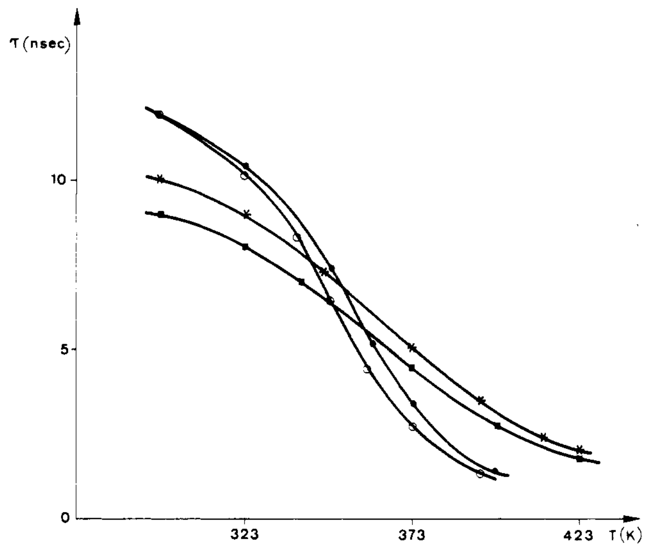

Figure 2. Temperature dependence of the fluorescence lifetime of DPHT: (■) Voltalef 3700; (*) Voltalef 5500; (•) PVDF; (O) VDF–TFE copolymer.

More quantitative information can be obtained from both m and τ, on condition that a suitable model of Brownian motion is used to derive the correlation time of the molecular movement. The simplest model is the Einstein–Stokes model for a spherical body, which has proved convenient in the case of DPHT-doped polyisoprene,[9] polybutadiene,[24] and various styrene–butadiene copolymers.[24] It yields a monoexponential autocorrelation function

$$M(t) = \exp(-t/\tau_R) \qquad (8)$$

where τ_R is the correlation time related to m and τ by the equation

$$\log \tau_R = \log \tau_{(T)} - \log m_{(T)} \qquad (9)$$

The validity of eq 8 and 9 in the case of DPHT-doped PVDF and related copolymers has been checked from fluorescence anisotropy decay experiments. As in the previous studies, $M(t)$ is unambiguously proving monoexponential, which justifies further use of the Einstein–Stokes model and of the correlation time τ_R.

Results and Discussion

In the first part of this section, we will consider ESR and FP data relative to Voltalef copolymers that show two well-established relaxations normally ascribed to amorphous polymers: the T_g relaxation (β) and local process (γ). The second part will be devoted to the dynamics of semicrystalline PVDF polymer and VDF–TFE copolymer.

Voltalef Copolymers. From the representative ESR spectra of the probe-B-doped Voltalef 5500 in Figure 3, it can be seen that the motion of the probe varies from near the rigid limit to the fast region over the temperature range 133–425 K. At low temperature, the ESR spectra consist of broad hyperfine lines, whose overall line shape is that expected from a single type of probe B undergoing slow-tumbling motions. The separation between extrema of the high- and low-field lines of spectra gradually decreases as the temperature increases. Above approximately 284 K, the spectrum narrows more rapidly, which is indicative of a less restrictive environment, and at about 315 K, the observed spectra exhibit three motionally narrowed hy-

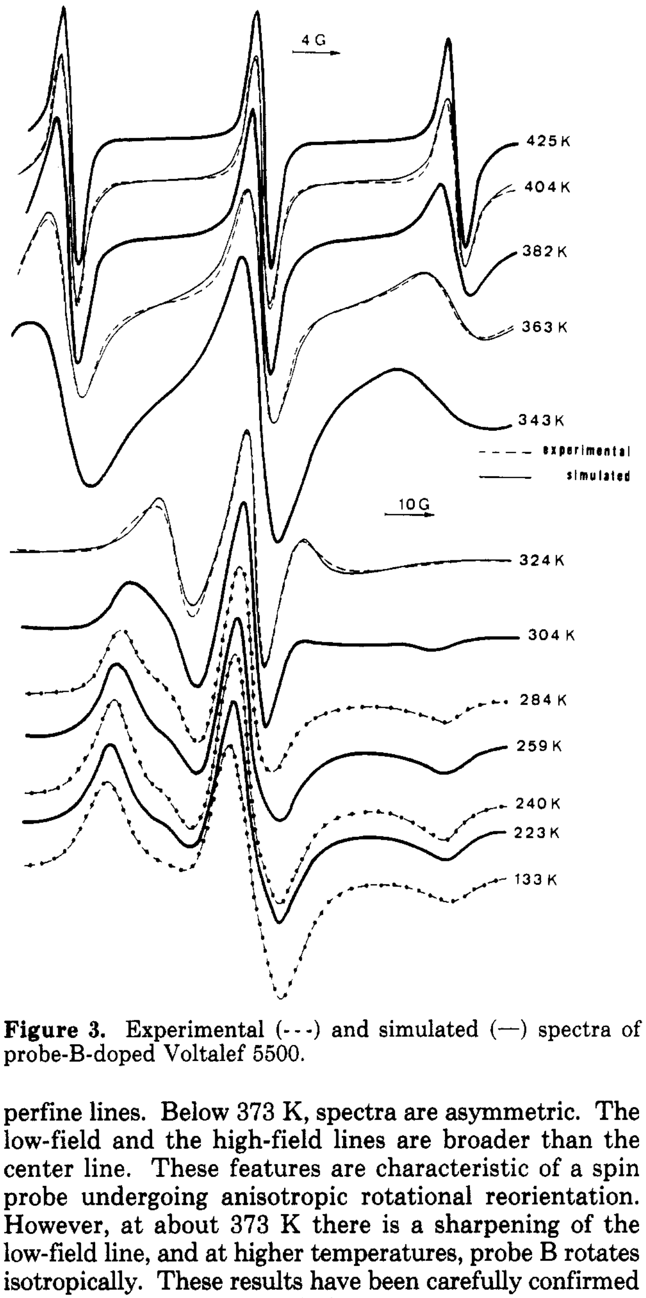

Figure 3. Experimental (---) and simulated (—) spectra of probe-B-doped Voltalef 5500.

perfine lines. Below 373 K, spectra are asymmetric. The low-field and the high-field lines are broader than the center line. These features are characteristic of a spin probe undergoing anisotropic rotational reorientation. However, at about 373 K there is a sharpening of the low-field line, and at higher temperatures, probe B rotates isotropically. These results have been carefully confirmed by computer simulations. At lower temperatures, rotation about the symmetry axis of the rotational diffusion tensor represented by the molecular fixed axis of probe B is about 2–4 times faster than rotation about the remaining axes, while the higher temperature spectra show $N = D_{\parallel}/D_{\perp} = 1$ for the diffusion parameter, corresponding to isotropic rotation. Similar results hold for Voltalef 3700.

Temperature changes in the ESR spectra can yield information on the way in which the rotational reorientation of spin probe is affected by the polymer. The rate of rotation of the nitroxide is quantitatively described by the rotational correlation time.

Below 274–284 K the essential shape of the ESR spectra remains unaltered, but some subtle changes in the separation of the outer hyperfine extrema occur and make it possible to obtain information about the molecular dynamics in this region. The correlation times estimated from eq 2 are surprisingly short, and the activation energy for probe B tumbling is very low (1–1.65 kcal·mol^{-1}). In this temperature range, probe motion seems largely independent of macromolecular motions. Such a behavior has been observed for different probes in other polymers.[5] It has been suggested[6] that the nitroxide radicals experience fairly unhindered motion in "holes" in the polymer matrix.

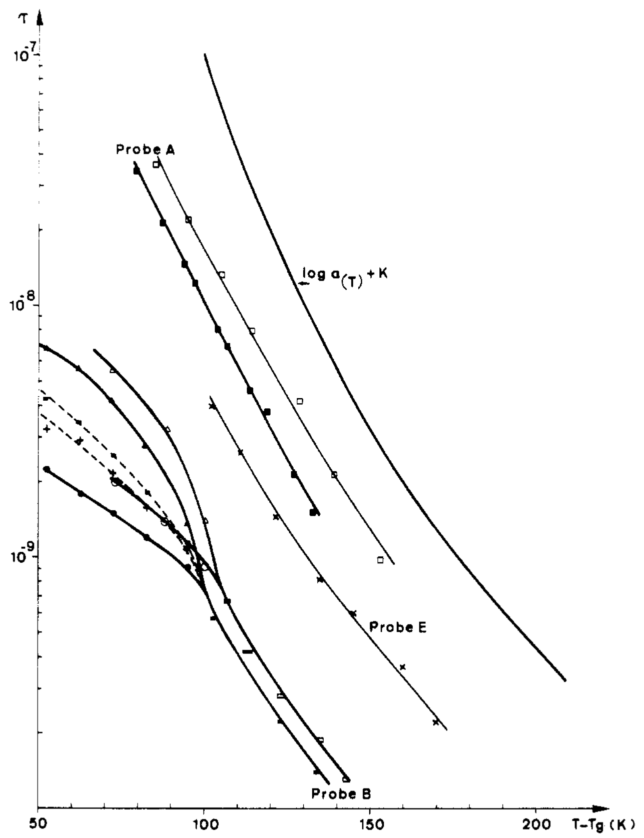

Figure 4. ESR and FP data for Voltalefs. Plots of log τ_c vs. $(T - T_g)$ for probe B in Voltalef 3700 [(▭) $\tau_{\rm iso}$, (△) $\tau_0 = (6D_{\perp})^{-1}$, (○) $\tau_2 = (2D_{\perp} + 4D_{\parallel})^{-1}$] and Voltalef 5500 [(▬) $\tau_{\rm iso}$, (▲) $\tau_0 = (6D_{\perp})^{-1}$, (●)$\tau_2 = (2D_{\perp} + 4D_{\parallel})^{-1}$, (+) $\tau_{\bar{D}} = (6\bar{D})^{-1}$]. Probe-E-doped Voltalef 5500: (×) $\tau_{\rm iso}$. Fluorescent probe-A-doped Voltalefs 3700 (□) and 5500 (■).

The log τ_c vs. $(T - T_g)$ dependences for rapidly tumbling probes B in Voltalef 3700 and Voltalef 5500 are shown in Figure 4, which includes a curve computed from the WLF equation[25]

$$\log a_{(T)} = \log \frac{\tau_c(T)}{\tau_c(T_g)} = -[A(T - T_g)]/[B + T - T_g] \quad (10)$$

where $\tau_c(T)$ is the correlation time at a temperature T and $\tau_c(T_g)$ the correlation time at the reference temperature chosen as the glass-transition temperature determined by DSC. $\tau_c(T_g)$ is the fitting parameter leading to vertical shift of the WLF curve. A and B are the "universal" constants: $A = 17.44$ and $B = 51.6$. These plots are indicative of two relaxation processes. At high temperatures ($T \geq T_{g_{\rm DSC}} + 100$), τ_c has the temperature dependence expected from the WLF theory: it seems likely that the T_g relaxation or β process[26] is being observed. Because of the relatively high frequency of the ESR measurements, the T_g process of Voltalefs 3700 and 5500 appears at a temperature considerably above that determined by DSC. For $T < T_{g_{\rm DSC}} + 100$ there is a noticeable curvature in the plots of log τ_c vs $(T - T_g)$. The calculated $\tau_{\rm iso}$, $\tau_{\bar{D}} = (6\bar{D})^{-1}$, $\tau_0 = (6D_{\perp})^{-1}$, and $\tau_2 = (2D_{\perp} + 4D_{\parallel})^{-1}$ have a temperature dependence smaller than that expected from the WLF theory. It seems likely that in this temperature range the γ process is being observed. The apparent activation energy for this γ-relaxation process was calculated from the slope of log $\tau_{\bar{D}}$ against reciprocal temperature. This activation energy is 6.5 kcal·mol^{-1}, which is similar in magnitude to the activation energies determined for the local mode relaxation in other polymers.[5] Thus, the γ relaxation

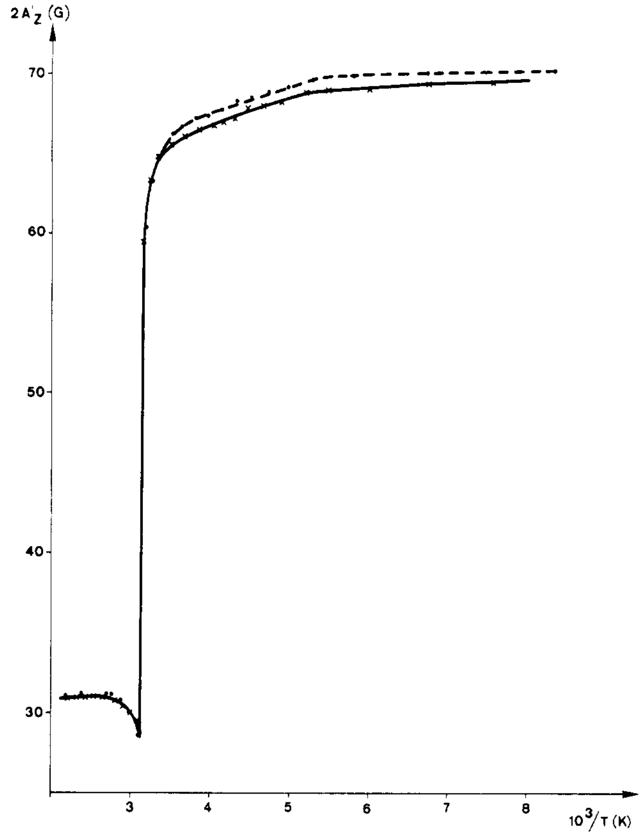

Figure 5. Plots of $2A'_z$ vs. reciprocal temperature in the ESR spectra of probe-B-doped Voltalefs 3700 (•) and 5500 (×).

may be attributed to the local oscillations of the frozen main chains. An important point to emphasize at this stage is that a correlation between T_{50G} ($3 \pm 1 \times 10^7$ Hz), the temperature at which the separation of the outer hyperfine extrema $2A'_z = 50$ G, and the glass-transition temperature T_g ($\simeq 1$ Hz) has been constructed for a series of polymers having well-established and noncontroversial glass temperatures in a study involving a probe that had been carefully calibrated with polymers.[27] However, it is clear that for Voltalefs 3700 and 5500, $T_{50G} = 316$–317 K (Figure 5) does not reflect the glass transition. Small probes such as probe B acquire increased mobility as soon as their rotational frequencies approach the rotational frequencies for the local mode relaxation of the polymer under investigation.

The size of the probe is expected to strongly influence T_{50G} in a given polymer, and usually the T_{50G} value increases as the molecular volume of the probe increases.[5] Kumler and Boyer[27] have suggested that if the volume of the probe is large compared to the activation volume of the glass transition, it will respond to this transition. The validity of the spin-probe method for studying T_g was verified for probe E dissolved in Voltalef 5500. From plots of extrema separation $2A'_z$ vs. temperature, an estimated $T_{50G} = 363$ K is found. At temperatures exceeding T_{50G} ($T_{g_{DSC}} + 92$ K), the experimental data agree with the temperature dependence of the WLF equation (Figure 4). Hence, above 363 K, spin probe E appears to respond to the T_g relaxation. Kusumoto et al.,[28] using a free-volume theory from Bueche,[29] have derived a quantitative relationship between T_{50G} and T_g

$$T_{50G} - T_g = 52[2.9f(\ln 1/f + 1) - 1] \qquad (11)$$

where $f = V_p/V_s$, V_p being the molar volume of the probe and V_s being the volume of the polymer segment relaxing at T_g. Application of this theory to Voltalef 5500 doped with probe E yields $f \simeq 0.715$. In other words, the polymer-segment volume is approximately 1.4 times that of the probe, which seems a wholly reasonable result for a flexible polymer.

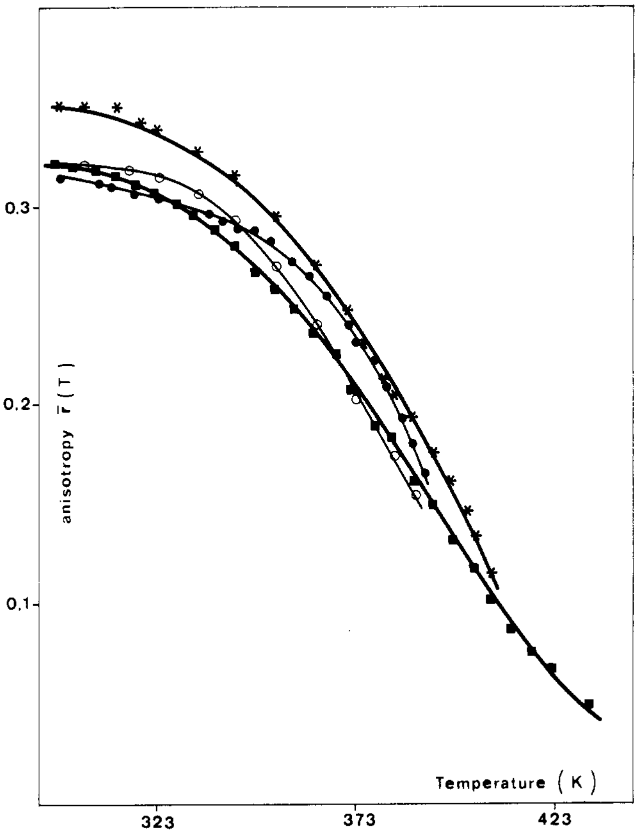

Figure 6. Temperature dependence of the mean fluorescence anisotropy $\bar{r}(T)$: (■) Voltalef 3700; (*) Voltalef 5500; (●) PVDF; (○) VDF–TFE copolymer.

The temperature dependences of the mean fluorescence anisotropy $\bar{r}(T)$ and of the mobility parameter $m(T)$ determined from FP experiments for probe-A-doped Voltalefs 3700 and 5500 are shown in Figures 6 and 7. At low temperature, the mean fluorescence anisotropy $\bar{r}(T)$ is experimentally indistinguishable from the rigid-limit value r_0. At 310–315 K, $\bar{r}(T)$ gradually decreases with increasing temperature, indicating the onset of mobility. However, in this temperature region, values of $m(T)$ calculated from eq 7 are subject to large errors. The smallest value of $m(T)$ that may be obtained with confidence is 0.05, which corresponds to a temperature of 345–350 K. To discover if the molecular motions observed above this temperature belong or not to the glass transition, a convincing check[9,30] consists in a comparison between the temperature dependence of log τ_R, calculated from eq 9 and that of log $a_{(T)}$ predicted by the WLF equation (eq 10).[25] From the plots of log τ vs. $(T - T_g)$ presented in Figure 4, it can be seen that within the temperature range 345 K ($T_{g_{DSC}} + 80$ K) to 410 K ($T_{g_{DSC}} + 150$ K), experimental data fit an expression of the WLF type. Hence, the rotational motion of probe A mixed with either Voltalef 3700 or Voltalef 5500 is controlled by the diffusional segmental motions of the macromolecular chains and reflects the T_g relaxation.

From Figure 4 it is immediately apparent that for Voltalef 5500, the ESR probe E and the FP probe A respond to the T_g relaxation and yield correlation times which appear similar in magnitude when calculated under the same assumption, i.e., an isotropic motional rotation of the probes. The values of correlation times derived from FP experiments are only twice those obtained over the

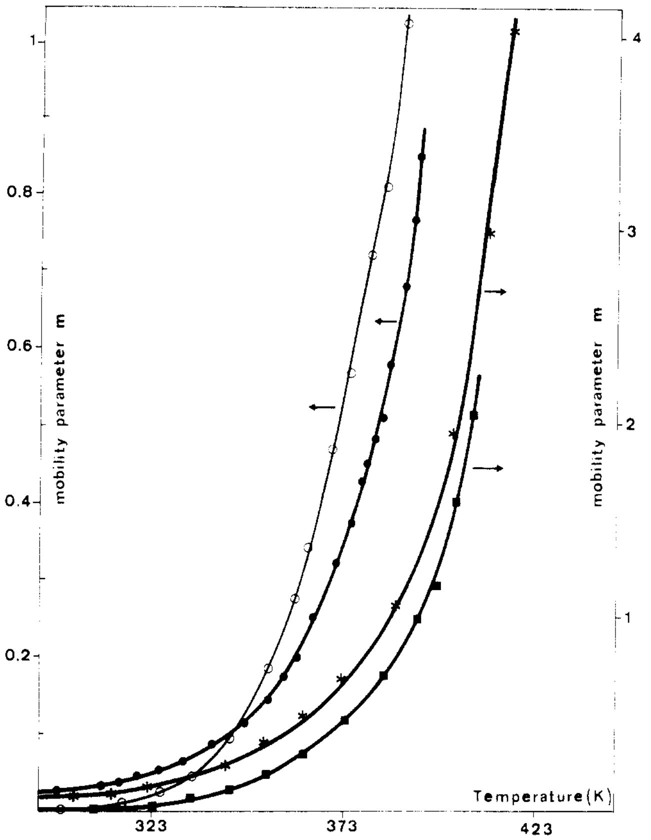

Figure 7. Temperature dependence of the mobility parameter $m(T)$: (■) Voltalef 3700; (*) Voltalef 5500; (●) PVDF; (○) VDF–TFE copolymer.

same temperature range by ESR. Thus, the molecular volumes of probes A and E appear approximately the same. However, it is clear from Figure 4 that the time scales of motions probed by these two techniques are slightly different: ESR probes more rapid motions ($10^{-10} < \tau_c < 5 \times 10^{-9}$ s) than FP ($10^{-9} < \tau_c < 5 \times 10^{-8}$ s), which deals with motions occurring during the fluorescence lifetime (Table II).

A prominent feature of the data derived from both ESR and FP experiments is that at a given $T - T_g$ difference the correlation times calculated for Voltalef 5500 are shorter than those determined for Voltalef 3700 by a factor varying from 1.3 to 2. In other words, $\tau_c(T_g)$, the fitting parameter leading to the vertical shift of the WLF curve, eq 10, is not the same for the two Voltalef copolymers. For Voltalef 5500, the experimental values of $\tau_c(T_g)$ are smaller than those for Voltalef 3700. Such a result would indicate that at the glass-transition temperature the free volume is larger for Voltalef 5500, which contains more chlorotrifluoroethylene units. Recently, differences in $\tau_c(T_g)$ have been also evidenced for elastomers by excimer fluorescence.[30,31] This emphasizes the importance of the chemical structure of the polymer matrix on mobility.

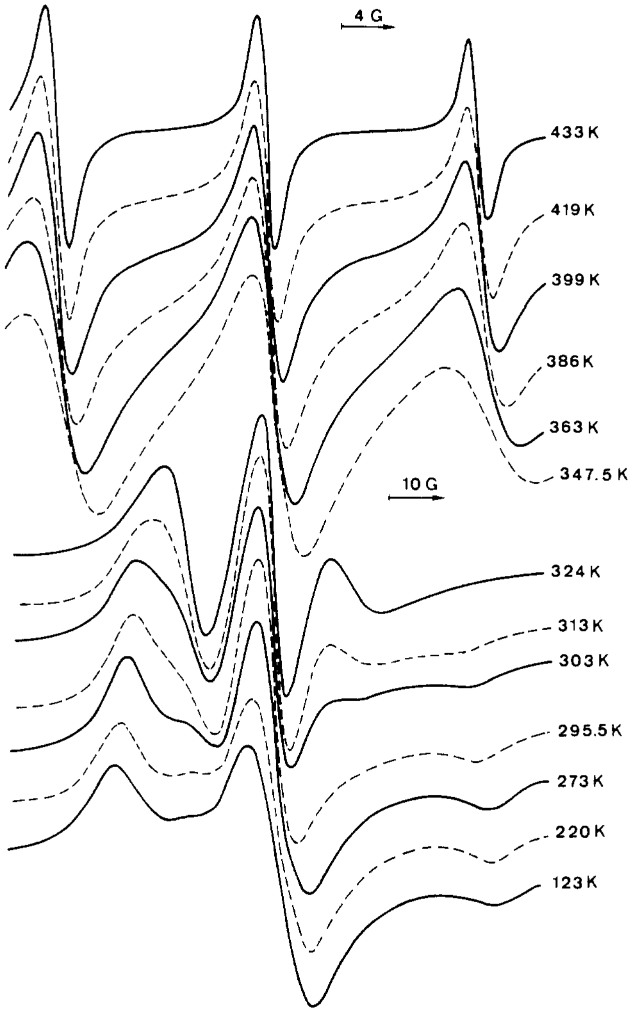

Figure 8. ESR spectra of probe B in PVDF.

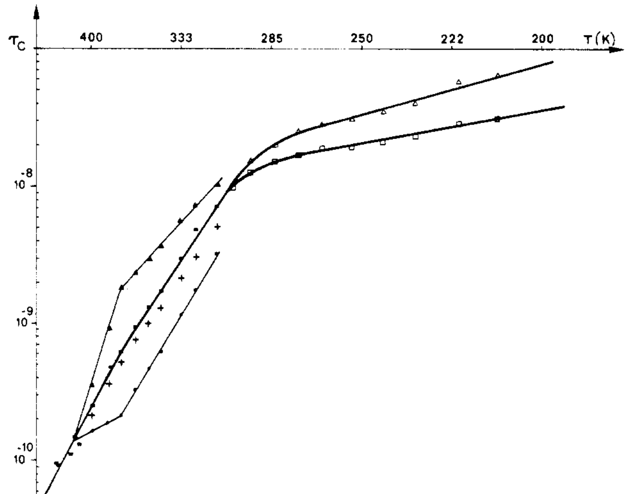

Figure 9. Rotational correlation times calculated from the spectra of probe B mixed with PVDF. Slow-motion region: (△) moderate and (□) large jump diffusion model. Fast-motion region: (■) isotropic, (+) $\tau_{\bar{D}} = (6\bar{D})^{-1}$, (▲) $\tau_0 = (6D_\perp)^{-1}$, and (•) $\tau_2 = (2D_\perp + 4D_\parallel)^{-1}$ anisotropic rotational diffusion model.

Poly(vinylidene fluoride) and VDF–TFE Copolymer. Representative ESR spectra of probe-B-doped PVDF are presented in Figure 8. In the slow-tumbling region, if correlation times estimated from eq 2 are plotted against reciprocal temperature in Arrhenius fashion (Figure 9), transition is revealed at about 273 K. Below this temperature, the behavior of probe B mixed with PVDF is very similar to that observed for probe-B-doped Voltalefs. Again, the activation energy for probe B tumbling is very low (1–1.9 kcal·mol^{-1}), which can be explained by nitroxide radicals undergoing fairly unhindered motion in "holes" in the polymer matrix. Alternatively, modulation of the line widths of the ESR spectra by a δ process might offer an equally plausible explanation. Indeed, the activation energy value is in agreement with the activation energies determined for δ processes in other polymers.[5] However, it can be seen from Figure 10 that no δ process has been evidenced for PVDF in this frequency–temperature range.

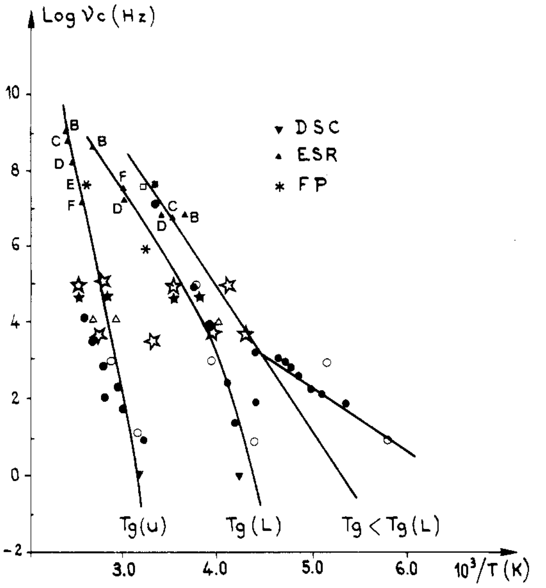

Figure 10. Relaxation map for PVDF (☆), (★), (△), (■, □) data taken from ref 2; (●) (32); (○) (33).

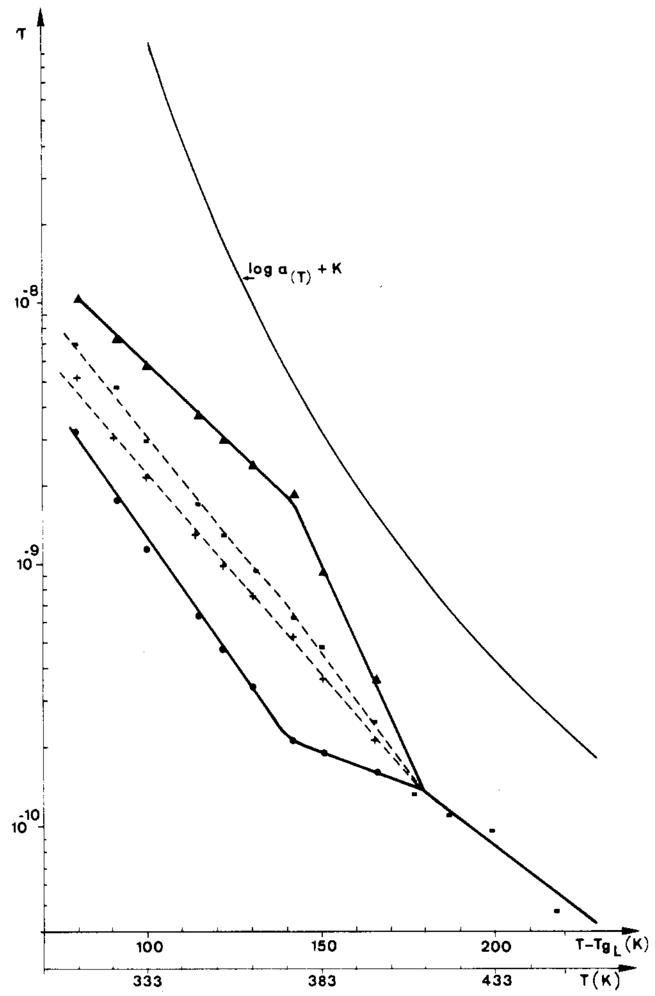

Figure 11. Plot of log τ_c vs. $(T - T_{g_L})$ for probe B in PVDF: (■)τ_{iso}; (+) $\tau_{\bar{D}} = (6\bar{D})^{-1}$; (▲) $\tau_0 = (6D_\perp)^{-1}$; (●) $\tau_2 = (2D_\perp + 4D_\parallel)^{-1}$.

The frequencies of other relaxations are still so slow that they do not have an effect on the ESR spectra.

Above 273 K, the separation of the low- and high-field extrema decreases more rapidly, and at 316 K, the peak-to-peak separation is equal to 50 G. These changes indicate the onset of a rapid motion of the spin probe, which averages the anisotropic terms of the spin Hamiltonian to produce, at about 324 K, spectra characteristic of rapid nitroxide rotation, i.e., spectra exhibiting three motionally narrowed hyperfine lines (Figure 8).

In the fast-motion region, the behavior of probe B dissolved in PVDF, a semicrystalline polymer, is more complicated than that in amorphous Voltalefs. In the temperature range 324–399 K, spectra are asymmetric. The low-field and the high-field lines are broader than the center line (Figure 8). These features are characteristic of a spin probe undergoing anisotropic rotational reorientation. However, at about 373 K there is a sharpening of the low-field line, and at and above 413 K probe B rotates isotropically. These results have been carefully confirmed by computer simulations. Between 324 and 373 K, the anisotropic diffusion parameter $N = D_\parallel/D_\perp$ lies in the range 5–10. For higher temperatures, a sharp decrease in the value of N is observed, and at and above 413 K $N = 1$: the system rotates isotropically (within experimental error).

It is clear from Figure 11 that below 373 K, the temperature dependence of the correlation times deviates from the WLF equation. As observed for probe-B-doped Voltalefs, T_{50G} = 316 K does not reflect the glass transition. Again, it seems likely that in the temperature range 273–373 K the γ process is being observed. Indeed, it is worthwhile to note that at 273 K, when the jump-diffusion model is used to describe the motion of the probe, the rotational frequency calculated from the relation $\nu = (2\pi\tau_c)^{-1}$ is in linear correlation with the NMR, dielectric, and dynamic mechanical γ relaxation frequencies (Figure 10). In addition, the apparent activation energy calculated from the slope of log $\tau_{\bar{D}} = (6\bar{D})^{-1}$ or log τ_{iso} against reciprocal temperature is found to be about 8.7 kcal·mol^{-1}, which is similar in magnitude to the activation energies determined by other techniques for the local mode relaxation in PVDF.[2,33-35] At 373 K, the ESR data lie on the same curve of log ν_c vs. reciprocal temperature as data obtained for the β_L process by NMR, dielectric, and dynamic mechanical relaxation (Figure 10). Above this temperature, the correlation times calculated for both isotropic diffusion and $\tau_{\bar{D}} = (6\bar{D})^{-1}$ have the temperature dependence expected from the WLF theory for the T_{g_L} relaxation. It is to be noted, however, that, while probe B dissolved in Voltalef copolymers undergoes isotropic rotational reorientation as soon as it responds to the T_g relaxation or β process, the probe B motion in PVDF becomes isotropic only at about 413 K, the temperature at which its rotational frequency is in correlation with β_U relaxation frequencies (Figure 10). This observation and the results obtained for bulkier probes E and F, which will be discussed later, would indicate that in the temperature range 373–413 K the observed spectra are the superposition of an isotropic spectrum and an anisotropic spectrum. The isotropic spectrum would correspond to the spin probes located in rubbery isolated amorphous regions, and the anisotropic spectrum would be identified with spin probes located in amorphous regions under restraint by crystallites.

A fundamental problem concerns the accuracy with which the rotating spin probes reflect motions of the polymer matrix. This was highlighted by work on PVDF using five different probes.

Representative ESR spectra of the bulkiest probe, F, dissolved in PVDF are given in Figure 12. They show significant differences in line shape from those obtained for the smallest probe, B (Figure 8). In particular, in the slow-motion region, (T < 394 K), the spectra obtained for the probe-F-doped PVDF appear to be the superposition

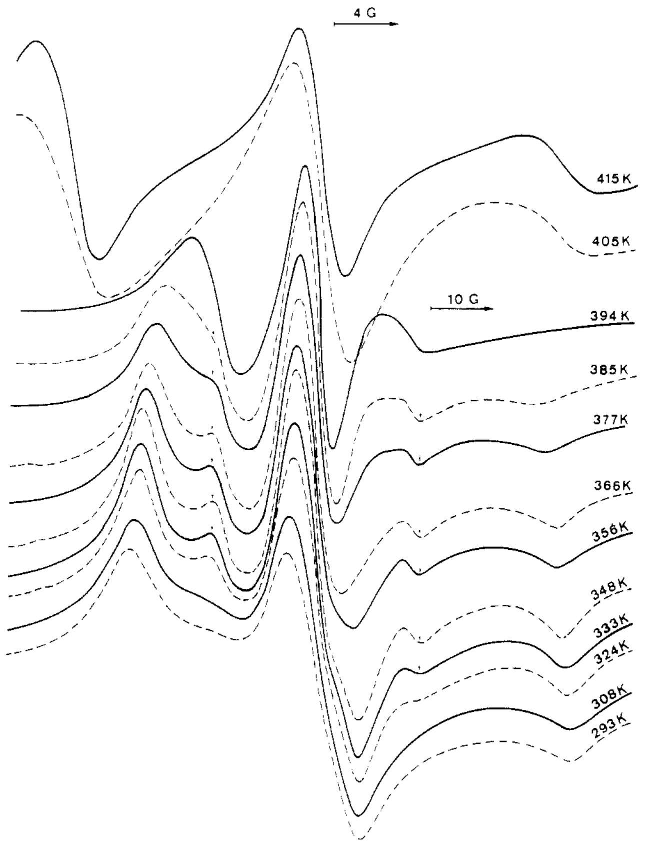

Figure 12. ESR spectra of probe F in PVDF.

of the broad line and narrow line spectra, in sharp contrast to a relatively well-resolved single line observed for the smallest probe, B. The narrow component shows insignificant dependence of its outer peak resonance positions on temperature (Figure 13) in contrast to the inward shift of the outer peaks of the broad-line spectrum with increasing temperature. As a result, at about 394 K, the broad-line and narrow-line spectra coalesce, and at higher temperatures the spectra show the motionally narrowed three-line pattern. The superimposed spectral feature is believed to arise from two different environments for probe F, that is to say, both rigid and rubbery regions are present in the PVDF system between 323 and 393 K. Such an assumption is consistent with a system exhibiting a double glass transition with the T_{g_L} transition occurring approximately 70–80 K below the T_{g_U} transition. It is to be noted that Boyer and Kumler[36] have also observed two sets of extrema separation in anionic polystyrene, polycarbonate, polyisobutylene, and poly(2,6-dimethylphenylene oxide). Data obtained by other techniques led them to postulate the existence of ordered and disordered regions in these polymers. One should also consider the possibility that the ESR spectra of Figure 12 arise from a single radical phase that undergoes very anisotropic motion, resulting in an incomplete averaging of the hyperfine and **g** anisotropy.[14,19,37] However, it can be seen from Figure 13 that the separation between the high- and low-field lines of the narrow component is in linear correlation with the splitting between the outermost lines observed at and above 393 K, and hence with the isotropic component of the hyperfine interaction, which leads us to assign the narrow component to highly mobile nitroxides. For nitroxides, the limit between fast tumbling and slow tumbling has been estimated to an effective correlation time of $4 \pm 1 \times 10^{-9}$ s. From these τ_c limits a practical mean frequency of $4 \pm 1 \times 10^7$ Hz can be calculated. From Figure 10, it seems likely that the fast phase which appears at about 323–333 K is associated with the β_L process. In contrast, the rotational frequency (1.6×10^7 Hz) determined at T_{50G} (392 K) lies on the same curve of log ν_c vs. reciprocal temperature as data obtained for the β_U process by other techniques. Application of the theory of Kusumoto et al.[28] yields f = 0.485, indicating that the volume of the polymer segment involved in the β_U process is approximately 2 times that of the probe.

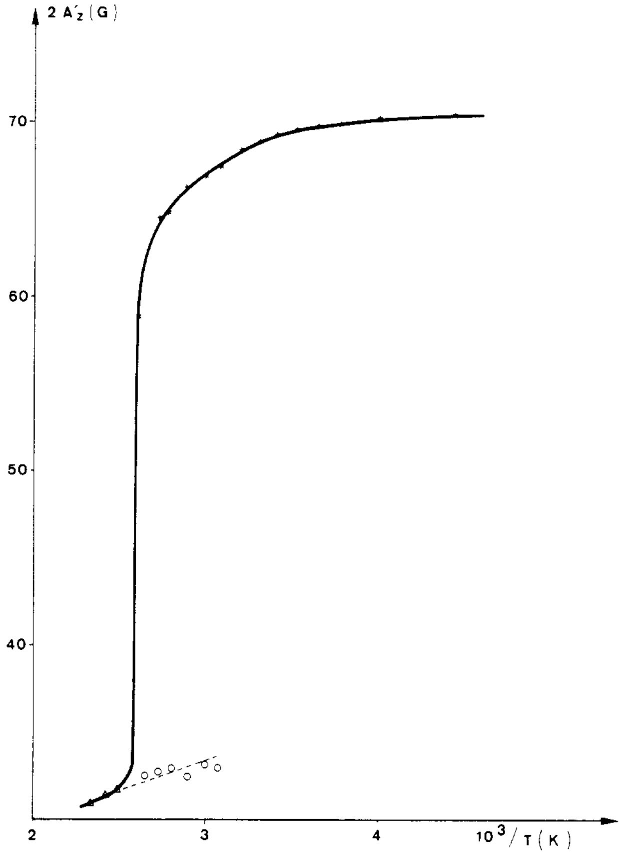

Figure 13. Plot of $2A'_z$ vs. reciprocal temperature in the ESR spectra of probe-F-doped PVDF: (O) narrow and (X) broad line spectra.

Similar behavior results for probe E. From approximately 320 K up to 365 K, the observed spectra appear to be the superposition of two spectra—one characteristic of a highly immobilized nitroxide (extrema separation $2A'_z$ 63.4–40 G), the other of a rapidly tumbling radical (extrema separation 32–30 G). Application of the theory of Kusumoto et al.[28] to PVDF doped with probe E yields f = 0.27 (T_{50G} = 360 K). As expected from the molecular volumes of the probes, this value of f is consistently smaller than the one for probe F in the same polymer. The molecular volume of the relaxing segment for the β_U process is approximately 3–4 times that of probe E.

In agreement with the experimental findings that the molecular volumes of the ESR probe E and the FP probe A are similar, it can be seen from the plots of log τ vs. ($T - T_g$) presented in Figure 14 that the FP probe A is also sensitive to the β_L and β_U processes. The onset of mobility occurs at about 317 K, i.e., 84 K above the T_{g_L} temperature determined by DSC (Table I). Between 317 and 356 K, the correlation time has the temperature dependence expected from the WLF theory, (eq 10) provided that T_{g_L} is chosen as the reference temperature. In contrast, above 356 K, the experimental data agree with the temperature dependence of the WLF equation on condition that T_{g_U} is chosen as the reference temperature. Consistency of the above data may be checked by comparison with the relaxation map (Figure 10). The rotational frequencies

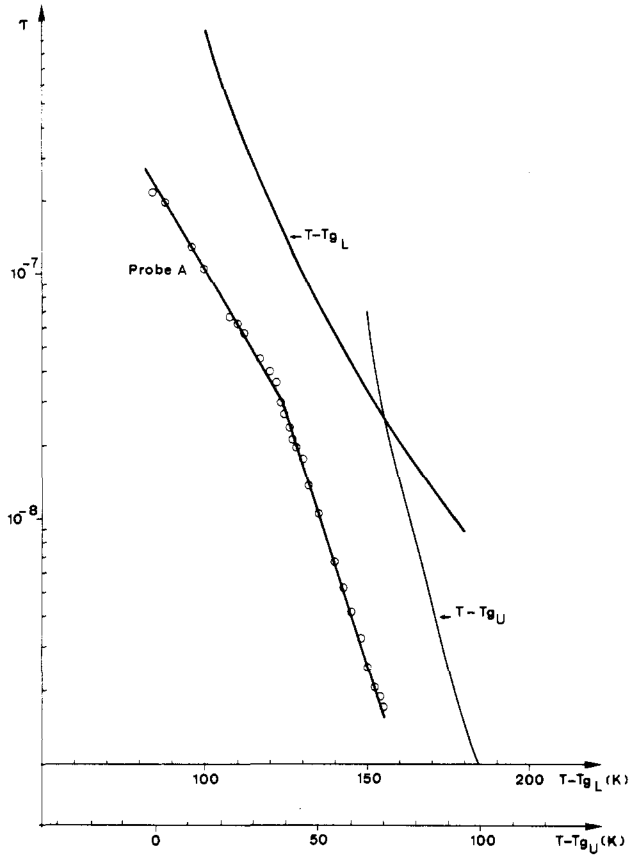

Figure 14. Plots of log τ_R vs. $T - T_{g_L}$ or $T - T_{gU}$ for probe-A-doped PVDF.

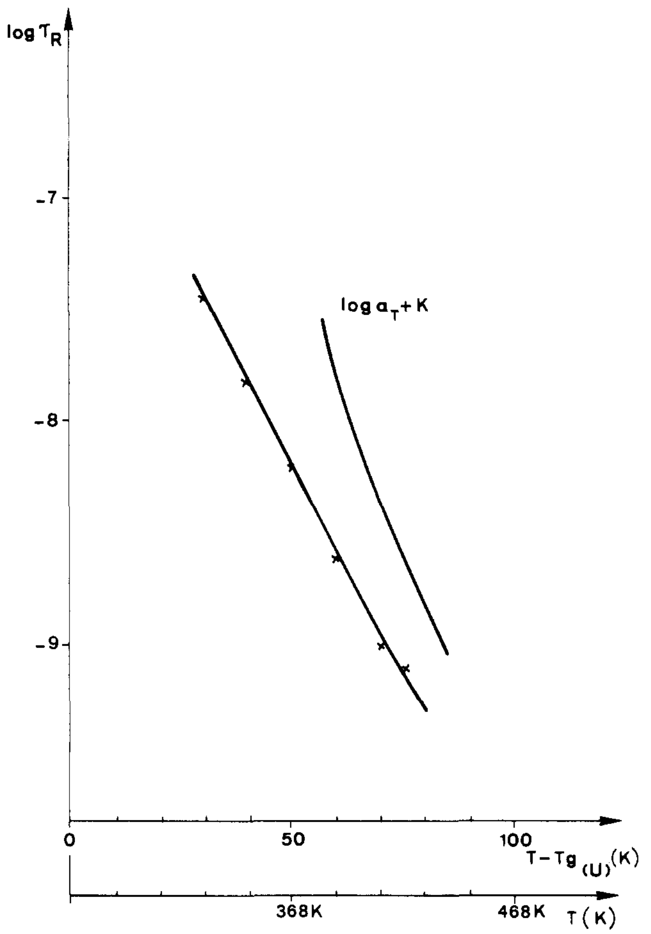

Figure 15. Plot of log τ_R vs. $T - T_{g_U}$ for probe-A-doped copolymer VDF-TFE.

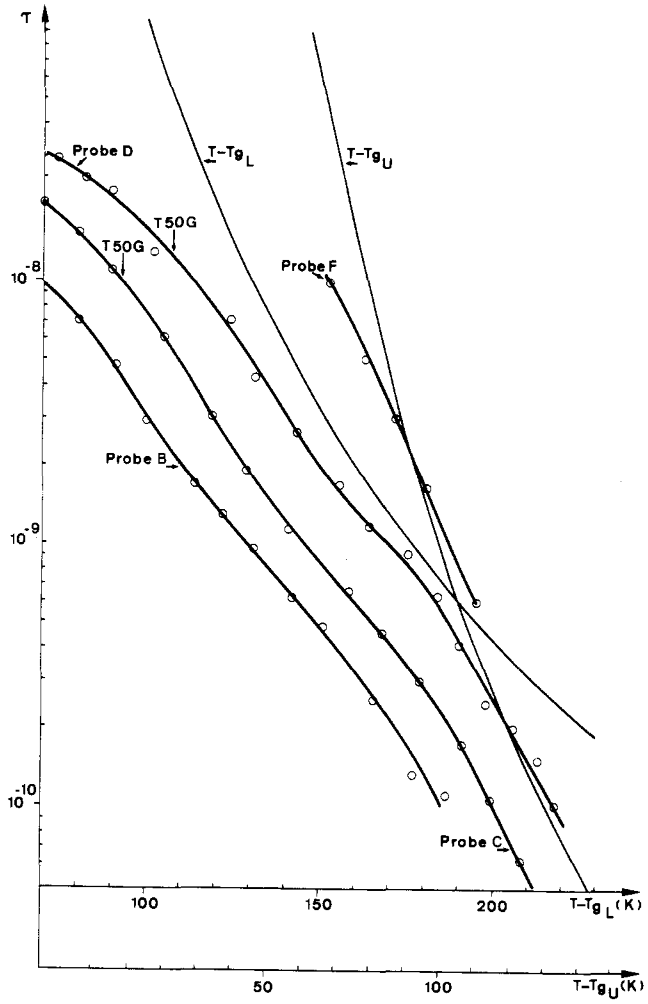

Figure 16. Plots of log τ_c vs. $T - T_g$ for probes B, C, D, and F in PVDF. In the slow-motion region, τ_c was calculated by assuming a Brownian rotational diffusion model for probe D and a moderate jump diffusion model for probe C.

calculated at 317 and 380 K from the relation $\nu = (2\pi\tau)^{-1}$ lie on the same curves of log ν vs. reciprocal temperature as data obtained by other techniques for the β_L and the β_U processes, respectively.

It is immediately apparent from Figure 15 that the FP probe A dissolved in VDF-TFE copolymer containing 30 wt % of tetrafluoroethylene units responds to the T_{g_U} - relaxation at high temperature. Unfortunately, below 340 K, the mobility parameter $m(T)$ is smaller than 0.05 and values of τ_R are subject to large errors, so that no reliable proof of T_{g_L} evidence can be obtained by FP measurements.

Finally, it is of interest to mention that the behavior of the ESR probes C and D is intermediate between that of the small probe B and that of the bulky probes E and F. In the slow-motion region, the replacement of probe B by either probe C or probe D does not affect significantly the temperature changes in the ESR line shapes. More precisely, it was found that above 273 K, the ESR spectra show a noticeable narrowing, which reflects an increase in the rotational reorientation of the probes due to the onset of the γ process. In contrast, T_{50G} increases from 316 K (probe B, $M_w = 172$) to 326 K (probe C, $M_w = 183$) and 340 K (probe D, $M_w = 281$). A similar type of behavior has been observed by Kumler et al.[37] These authors have evidenced only minor variation in the experimental T_{50G} values as the molecular weight of the probe is varied from 170 up to 281. Bearing in mind that the value of τ_c obtained by assuming an isotropic rotational diffusion of the probe accurately reflects the value of the average τ_D for anisotropic motion, plots of log τ_c vs. $(T - T_g)$, as shown in Figure 16, were constructed. These diagrams show that the bulkier probe D can be considered to reflect the glass transition at T_{50G}. However, it is obvious from Figures 10 and 16 that this T_{50G} value is correlated with the T_{g_L}-relaxation process and not with the T_{g_U} relaxation, as concluded by Kumler and Boyer.[27] When the theory of Kusumoto et al.[28] is used, a value of $f \simeq 1$, eq 11, is found, indicating that the volume of the polymer segments undergoing β_L relaxation is approximately that of probe D. At about 418 and 408 K for probes C and D, respectively, the experimental ratio $(R_+ + R_- - 2)/(R_+ - R_-)$ approaches the theoretical values calculated for radicals undergoing isotropic reorientation.[6] Figures 10 and 16 show that both probes C and D respond to the T_{g_U}-relaxation process.

Registry No. PVDF (homopolymer), 24937-79-9; (VDF)·(TFE) (copolymer), 25684-76-8; (VDF)·(CTRFE) (copolymer), 9010-75-7.

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Two-Dimensional Nuclear Magnetic Resonance Analysis of Poly(vinyl chloride) Microstructure

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ABSTRACT: One- and two-dimensional heteronuclear ^{1}H–^{13}C and homonuclear ^{1}H NMR experiments have been examined for their usefulness in establishing stereochemical sequence assignments in poly(vinyl chloride). Correlation via the ^{1}H–^{13}C coupling leads to increased resolution in both the proton and carbon spectra, and stereosequence assignments may be made by inspection of the 2D map. Homonuclear correlation via three-bond scalar coupling (COSY) may be used to make some of the stereochemical assignments based on the proton data alone. Differences in the magnitudes of the coupling constants may be exploited to uniquely define some of the stereochemical spin systems by utilizing the correlations via double-quantum coherences. Longer range correlations (relayed coherence transfer) define larger segments of the polymer backbone. These studies show that many of the techniques developed for small molecules are applicable to polymer systems and the complete stereochemical resonance assignments may be obtained by the utilization of a number of 2D experiments.

Introduction

The physical properties of synthetic polymers depend on their microstructure and conformational properties, and methods for elucidation of the structure are an important part of polymer research. NMR is a powerful tool for polymer characterization since the NMR parameters (chemical shift, coupling constants, and relaxation rates) depend on the local environment and dynamics of the nuclei.[1,2] High resolution ^{1}H NMR is a particularly attractive tool due to its high observing sensitivity, but it is somewhat limited due to relatively broad lines and peak overlap. One way to overcome these limitations is to use

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