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# Study of Slow Molecular Motion of Spin Probes in Polymers by the Double-Modulation ESR Method

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ABSTRACT: The slow molecular motion of a spin probe dispersed in a polystyrene (PS), poly($\alpha$-methylstyrene) (P$\alpha$MS), poly(4-vinylpyridine) (P4VP), and poly(methyl methacrylate) (PMMA) matrix has been studied by the double-modulation ESR (DMESR) method. The rotational correlation times determined as a function of temperature reveal two (PS, P$\alpha$MS, and P4VP) and three (PMMA) discrete motional regions. The position of crossover points between 190 and 200 K is affected very little by the structure and molecular weight of the polymer and is attributed to the temperature at which rotational motion of the spin probe skeleton takes place. Above this internal probe transition the DMESR spectra undergo a rapid line broadening in accordance with increase of temperature. Discrete molecular motions above 200 K and the corresponding effective activation energies reflect a considerable influence of the host polymer on the spin probe motion. It was concluded that the probe rotational motion responds to the side-chain motion and that the effect of these local motions is more pronounced in the matrix of higher local density. It was also shown that the DMESR method can depict a coupling of end or side-chain methyl group motions with the methyl groups of the perdeuterated spin probe below the internal probe transition.

## Introduction

The ESR spin probe and spin-labeling techniques have proved to be a powerful tool for studying relaxation processes in synthetic polymers.[1,2] The ESR spectrum of a stable nitroxide radical is sensitive to changes in rotational motion characterized by the rotational correlation time, $\tau_R$, over the range $10^{-11} < \tau_R < 10^{-7}$ s. However, the conventional inhomogeneously broadened ESR spectrum of a nitroxide is insensitive to slow motions of $\tau_R \geqslant 10^{-6}$ s. In this case, rigorous spectral simulations are required to obtain $\tau_R$.[3] Therefore, there is considerable interest in using methods for measuring rotational correlation times longer than $10^{-6}$ s, which are characteristic of polymers in the glassy state. The experimental techniques available for detection of slow motions are based on the elimination of inhomogeneous broadening of the ESR spectra.

The most complete information on homogeneously broadened lines can be obtained by the electron spin echo technique.[4] There are several alternative methods based on continuous wave (CW) techniques, such as the well-known saturation transfer spectroscopy.[5] However, this method does not directly give the homogeneous line width, and detailed spectral simulations are required in order to obtain the rotational correlation time. Recently, another simple (CW) technique—double-modulation ESR (DMESR)—has been employed.[6-9] The potential of the DMESR technique has already been demonstrated on some polymers to study the dynamics of spin labels or spin probes in the slow-motional region.[10,11]

The main problem in the study of slow molecular motions of spin probes dispersed in a polymer matrix is the relationship between the probe motion and its environment. Some conventional ESR measurements have shown that in the low-temperature region the spin probe motions are mainly determined by the micropore dimensions of the polymer matrix.[12,13] On the other hand, ESR line-shape analysis of spin-labeled and spin-probed poly(methyl methacrylate) has revealed a strong correlation of the nitroxide motion with side-chain motions of the host polymer.[14]

The objective of this paper is to measure how and to what extent the homogeneously broadened DMESR line of unbound nitroxide is coupled with the side-chain or local motions and/or with the free volume size in the polymer matrix below the glass transition temperature, $T_g$. The sensitivity of the homogeneously broadened DMESR line even to small changes in the probe motion provides direct experimental evidence about the relation between the probe motion and the host polymer. For this reason four polymers—poly(methyl methacrylate) (PMMA), polystyrene (PS), poly($\alpha$-methylstyrene) (P$\alpha$MS), and poly(4-vinylpyridine) (P4VP)—differing in chain structure, side-chain relaxation modes, and molecular weight have been selected. The influence of polymer structure on the transition of the spin probe skeleton has been also examined. In this study the DMESR line widths of both the perdeuterated and undeuterated spin probes were analyzed and correlated with the specific motions in the host polymer.

## Experimental Section

**Sample Preparation.** Polystyrene (PS), poly($\alpha$-methylstyrene) (P$\alpha$MS), poly(4-vinylpyridine) (P4VP), and poly(methyl methacrylate (PMMA) samples were synthesized by anionic polymerization at the Charles Sadron Institute. The polymers were characterized either by light scattering or by size exclusion chromatography (SEC) using a Waters Associates 150C chromatograph coupled with three detectors.[15] The molecular weights of the polymers are listed in Table I.

All of the polymers have a narrow molecular weight distribution. The samples were doped with nondeuterated (Aldrich) and deuterated 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (MSD Isotopes) probe in benzene or DMF solution (P4VP) at ambient temperature. The spin probe concentration was 0.01 wt %. The solvent was slowly evaporated and the samples were dried under reduced pressure at 373 K.

**ESR Measurements.** Double-modulation ESR (DMESR) spectra were recorded on a Varian E-109 X-band spectrometer equipped with an additional modulation coil and a Wavetek radio-

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Table I
Weight-Average Molecular Weights of Polymers

| PS | P$\alpha$MS | P4VP$^a$ | PMMA |
|---|---|---|---|
| $3 \times 10^4$ | $4.1 \times 10^4$ | $1 \times 10^4$ | $2 \times 10^4$ |
| $1.26 \times 10^6$ | $1.11 \times 10^5$ | $1.85 \times 10^5$ | $4.4 \times 10^5$ |

[a] Characterized only by light scattering.

frequency generator as a second frequency source. The first modulation frequency was the fixed spectrometer frequency of $\nu_m$ = 100 kHz; the second modulation frequency was swept in the range from 250 to 350 kHz, while the magnetic field was fixed at the position of the maximum (CW) ESR absorption signal. The DMESR line centered at 300 kHz was monitored and accumulated in a Hewlett-Packard 5480B signal analyzer. The line width, $\Delta_{obs}$, of the DMESR spectra can be related to the correlation time of the standard sample. Thus one can obtain the proportionality constant of the correlation time and the line width of the DMESR spectra, $\Delta_{obs}$. In the present study a similar procedure was carried out by using perdeuterated spin probe in a glycerol–water matrix as a more reliable standard sample than the undeuterated spin probe, where the line width, $\Delta_{obs}$, is significantly broadened due to the unresolved intramolecular proton interactions.[16]

In this approach the DMESR line width can be written in the form of three contributions[8]

$$\Delta_{obs} = \Delta_D + \Delta_T + \Delta_R \tag{1}$$

where the concentration contribution to the homogeneous broadening caused by static dipolar interactions is $\Delta_D$. $\Delta_T$ corresponds to the $T_1$ and $T_2$ relaxation mechanisms for a rigid probe, and $\Delta_R$ is an effective motional contribution. At very low spin probe concentration $\Delta_D$ can be neglected. Considering the fact that the second term in eq 1 has very little influence at higher temperatures, the homogeneous contribution to the line width is mainly determined by the slow-motional dynamics of the spin probe in the matrix. An effective correlation time, $\tau_R^*$, in this case is given by

$$\tau_R^* = (2\pi\Delta_{obs})^{-1} \tag{2}$$

which is in close agreement with the jump diffusion model.[8]

## Results and Discussion

**Rotational Correlation Times.** Measurements of double-modulation ESR spectra are performed in the slow-tumbling region of the spin probe well below the glass transition temperature of the polymer measured. The range of temperature did not exceed 270 K since at higher temperatures the observed DMESR line width has become comparable with the distance between the two signals. The estimation of the rotational correlation time is demonstrated on poly(4-vinylpyridine). The temperature dependence of the spectral line widths of P4VP doped with the perdeuterated and undeuterated spin probe, respectively, paralleling the line widths of the spin probe in the glycerol–water matrix, is shown in Figure 1.

The determination of the rotational correlation times, $\tau_R$, from the DMESR spectra relies on a comparison with the glycerol–water model[8] rather than on the theoretical description and simulation of line shapes. Recently, two theoretical explanations of the double-modulation line shapes have been discussed.[17-19] Therefore, the calibration of double-modulation line width according to the model system seems to be appropriate so as to avoid theoretical divergences of the proposed line shape origin.

The dashed line in Figure 1 represents the extrapolation of the Arrhenius plot of HMHF (Hwang–Mason–Hwang–Freed) results[20] of the spin probe in the glycerol–water matrix to the slow-motional regime ($\tau_R \sim 10^{-4}$–$10^{-5}$ s) studied in the present work. A similar approach is used for the comparison of the $\tau_R$'s obtained by two-dimensional spin-echo spectroscopy with the extrapolated $\tau_R$'s from HMHF.[4] Our experimental DMESR $\tau_R^*$'s obtained for the same model sample show a parallel Arrhenius plot at ca. 200 K. Thus for the given temperature interval it can be assumed, in the first approximation, that the experimental values of $(2\pi\Delta_{obs})^{-1}$ are proportional to the $\tau_R$ from HMHF with the proportionality constant expressed by the following relation:

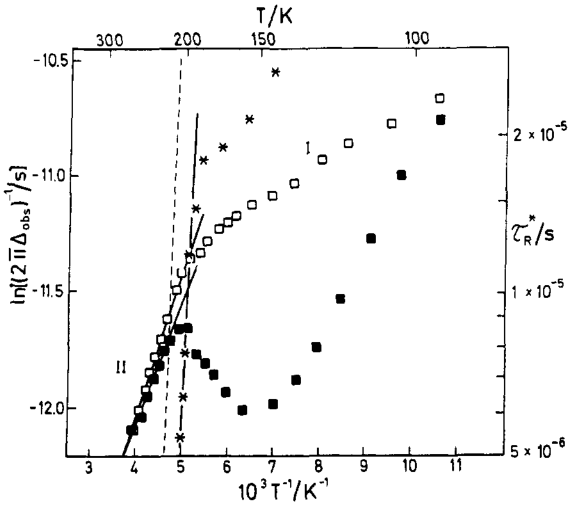

**Figure 1.** Temperature dependence of the DMESR line widths of spin probe dispersed in P4VP: (■) undeuterated spin probe; (□) perdeuterated spin probe; (*) perdeuterated spin probe in model glycerol–water system. The dashed line represents the rotational correlation time, $\tau_R$, extrapolated from the results of HMHF. The extrapolated line and the solid fitted line corresponding to the DMESR line widths of the same model system are shown to demonstrate the calibration of the DMESR line widths. The error of the line-width measurements does not exceed 5%.

$$\tau_R \approx 9(2\pi\Delta_{obs})^{-1} \tag{3}$$

It should be noted that the activation energies estimated from the Arrhenius plots of $\tau_R$ (relation 3) are accurate under the given approximation. The present knowledge of the DMESR line shapes does not permit us to define a motional model based upon theoretical consideration of the line-width broadening, as, for example, in the case of spin-echo measurements.[21] The absolute values of the activation energies are expected to vary depending on the motional model. However, their relative changes determined by the polymer matrix will retain the same trend.

**Spin Probe Motion in P4VP, PS, and P$\alpha$MS.** Two distinct regions are observed for both the undeuterated and deuterated spin probes in the P4VP matrix and the glycerol–water matrix, respectively (Figure 1). The crossover points of both probes in the P4VP matrix appear at approximately the same temperature. However, there is a considerable difference in the $\tau_R$ vs temperature behavior between the two spin probes in the lower temperature regime (region I). At ca. 150 K the curve of the undeuterated probe exhibits a well-defined minimum, also observable by pulse ESR measurements.[22,23] This minimum is attributed to the internal free rotation of the $CH_3$ groups of the piperidine ring. Such behavior of the undeuterated spin probe can be related to the proton dynamics and quantitatively described as follows. One would expect that an average anisotropic superhyperfine interaction $|A(\theta)|$ between the electron and protons of the piperidine ring will contribute to the homogeneous broadening with an effective correlation time of protons, $\tau_p$, being $\tau_p \sim |A(\theta)|^{-1}$. The slow motions of protons for $\tau_p > |A(\theta)|^{-1}$ bring about broadening of the homogeneous

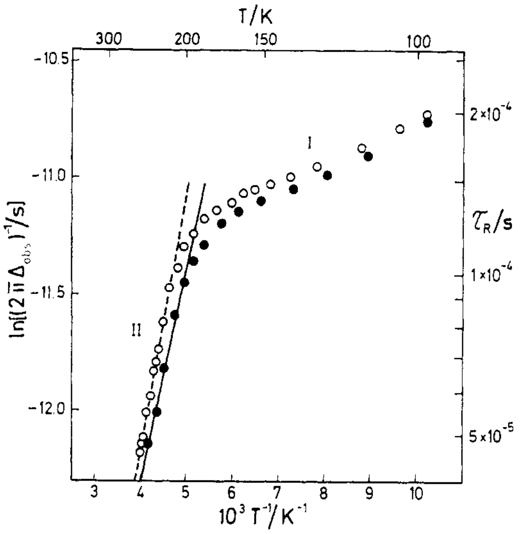

**Figure 2.** Temperature dependence of the DMESR line widths of perdeuterated spin probe doped in PS of different molecular masses: (○) $\bar{M}_w = 3 \times 10^4$; (●) $\bar{M}_w = 1.26 \times 10^6$. $\tau_R$ on the right-hand vertical scale denotes the calibrated values according to relation 3.

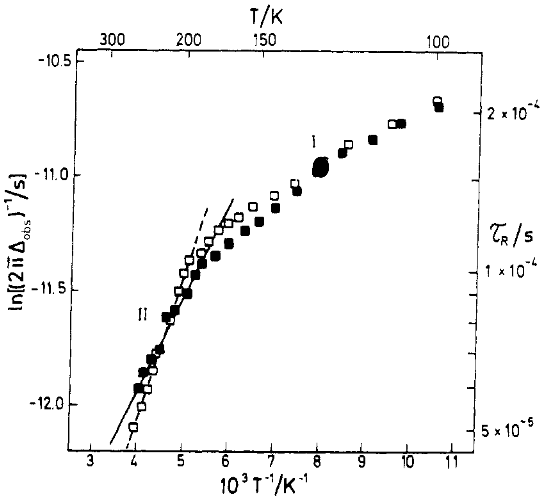

**Figure 3.** Temperature dependence of the DMESR line widths of perdeuterated spin probe doped in P4VP: (□) $\bar{M}_w = 1 \times 10^4$; (■) $\bar{M}_w = 1.85 \times 10^5$. $\tau_R$ on the right-hand vertical scale denotes the calibrated values according to relation 3.

line width or decrease of $|2\tau\Delta_{\text{obs}}|^{-1}$ with increasing temperature. In the opposite case when $\tau_p < |A(\theta)|^{-1}$, an increase of $|2\tau\Delta_{\text{obs}}|^{-1}$ with increasing temperature can be attributed to the narrowing of the homogeneous line width. In the perdeuterated spin probe one can expect a reduced $|A(\theta)|$ of deuterons. This effect and the different internal dynamics of deuterons give an almost monotonic increase of the line width plotted against the reciprocal temperature (Figure 1).

The dynamics of both probes in the P4VP matrix is similar at temperatures above 200 K (region II) and changes noticeably with increasing temperature. The change of the Arrhenius plots of the rotational correlation times (regions I and II) appears between 190 and 200 K irrespective of the polymer matrix in which the spin probe is embedded (Figures 2–4). Evidently, this transition is an intrinsic property of the specific nitroxide molecule and marks the temperature at which the mobility of the spin probe skeleton begins to be evident. Judging from the very narrow temperature interval at which this transition occurs in all the investigated polymers and in the model glycerol–water system, the matrix seems to have little influence on the internal transition of the spin probe.

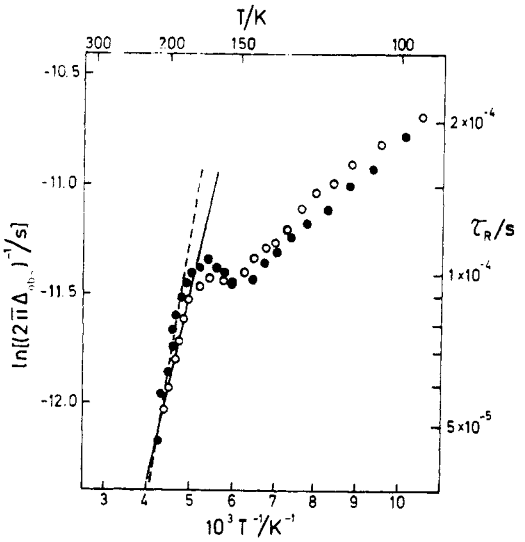

**Figure 4.** Temperature dependence of the DMESR line widths of perdeuterated spin probe doped in PαMS: (○) $\bar{M}_w = 4.1 \times 10^4$; (●) $\bar{M}_w = 1.11 \times 10^5$.

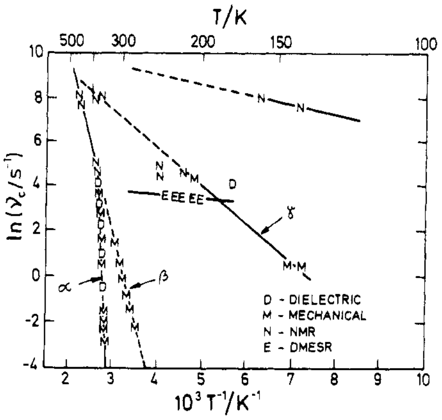

**Figure 5.** Temperature dependence of the correlation frequency determined by DMESR for slow rotational motion of spin probe (this work) and the corresponding relaxation time observed by NMR dielectric and mechanical methods for PS (refs 23–26).

In the case of the undeuterated spin probe, a minimum of the same depth appears at the same temperature for P4VP and the other matrices. This result correlates with the pulse experiments.[22] The minimum depends on the number of methyl groups attached to the carbon atoms neighboring the nitrogen moiety.

P4VP and PS doped with the perdeuterated probe show a similar monotonic increase of the DMESR line width below 190 K as predicted (Figures 2 and 3). However, as the temperature is increased above the internal transition of the nitroxide, the line broadening (region II) is considerably influenced by the polymer structure and molecular weight of the polymer. According to the NMR results, molecular motion in polystyrene above 200 K is dominated by low-amplitude torsional libration of the phenyl groups[24] with an activation energy of ca. 32 kJ mol$^{-1}$ and is ascribed to the $\gamma$-relaxation process.

The frequency points calculated from the DMESR line width in region II are plotted in the transition map (Figure 5) obtained from NMR[24-26] and dielectric and mechanical data.[27] The activation energy calculated from the spin probe motion is considerably lower (Table II) than those obtained by other techniques (Figure 5). Obviously, the spin probe motion is not governed by the same relaxation process. Ring flipping is a highly restricted form of rotation,[28] and it is less probable that this rotation would activate spin probe motion.

Table II
Activation Energies of Spin-Probed Polymers

| sample | $\bar{M}_w$ | $E/(\mathrm{kJ\ mol^{-1}})$ region II | $E/(\mathrm{kJ\ mol^{-1}})$ region III |
|---|---|---|---|
| PS | $3 \times 10^4$ | 9.2 | |
| | $1.26 \times 10^6$ | 7.7 | |
| PαMS | $4.1 \times 10^4$ | 7.4 | |
| | $1.11 \times 10^5$ | 10.1 | |
| P4VP | $1 \times 10^4$ | 6.3 | |
| | $1.85 \times 10^5$ | 3.8 | |
| PMMA | $2 \times 10^4$ | 2.5 | 7.0 |
| | $4.4 \times 10^5$ | 2.6 | 10.4 |

It is known that in some polymers a lowering of concentration of chain ends with increasing molecular weight changes the packing around the chain ends and causes a decrease in free volume.[29] Thus, one can expect a slight restriction of spin probe motion and consequently a slower line broadening of the DMESR spectra. Indeed, this can be seen in Figure 2. These results suggest that the probe motion below $T_g$ is predominantly determined by free volume availability. The corresponding activation energy (Table II), which is lower for PS of higher molecular weight, is consistent with the argument that smaller average "holes" restrict spin probe motion. It has already been concluded that restricted probe rotation results in lower barrier heights for these motions compared to the barrier heights for rotation out of the restricted cone.[30]

It should be kept in mind that the nitroxide molecule is not attached to the polymer chain but dispersed in the matrix. Thus the spin probe distribution will depend on the local free volume in the glassy polymer. The work of Yu et al.[31] with chromophore probes in polystyrene and calculation of the free volume distribution have shown that the probe is distributed in regions with the greatest free volume. If so, the difference in line broadening will reflect the relative free volume distribution. Our previous DMESR concentration dependence measurements on star-shaped polystyrene have demonstrated that the DMESR spectra are very sensitive to the local distribution of the spin probe.[10]

DMESR line broadening of the spin probe doped in the P4VP matrix follows the same pattern with the change of molecular weight as in the PS matrix. However, slower line broadening and consequently lower apparent activation energies for approximately similar molecular weights can be understood in terms of restricted probe motion. This restricted rotational motion may be explained by the polymer–nitroxide interaction due to the polarity of the ring nitrogen in P4VP rather than the change of local free volume, which is similar to the free volume of polystyrene.

The spin probe embedded in the PαMS matrix reveals different motion in both temperature regions as compared with PS and P4VP (Figure 4). Slight minima at the position of the internal methyl group motion of the nitroxide molecule appear in the perdeuterated nitroxide for which a monotonic increase of the line width is predicted. Bearing in mind that PαMS is denser than PS and P4VP, that the hindered motion of the α-$CH_3$ group takes place at 120 K,[32] and that the probe skeleton is immobile below 190 K, it is reasonable to suppose that the $CD_3$ groups of the probe are coupled with the α-$CH_3$ motion. The influence of phenyl ring flipping as a highly restricted form of rotation[28] is excluded since the minimum is absent in polystyrene. In region II the corresponding effective activation energies for spin probe motion increase with increasing molecular weight (Table II). When comparing the line broadening with the molecular weight of the PS and PαMS matrices, one should take into account the complexity of the spin probe motion. The influence of the average hole size on spin probe motion has already been discussed. At the same time the probe motion can be coupled with the high-frequency local motion below $T_g$. Thus, the faster line broadening of the higher molecular weight PαMS can be explained as follows: the spin probe motion distributed in a matrix of higher local density (or lower free volume) can be easily coupled to the side-chain motion (α-$CH_3$ motion) and therefore the probe will report faster motion and consequently higher effective activation energy.

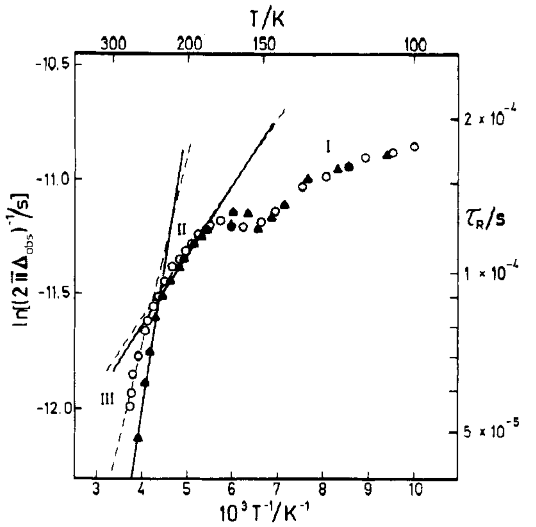

**Figure 6.** Temperature dependence of the DMESR line widths of perdeuterated spin probe doped in PMMA: (○) $\bar{M}_w = 2 \times 10^4$; (▲) $\bar{M}_w = 4.4 \times 10^5$. $\tau_R$ on the right-hand vertical scale denotes the calibrated values according to relation 3.

**Spin Probe Motion in PMMA.** The spin probe motion in the PMMA matrix reveals three relaxation processes over the temperature interval investigated (Figure 6). A marked difference in the slope appears again between 190 and 200 K, as observed in the other polymers. This result confirms the finding that the structure of the polymer chain has a minor influence on a particular spin probe transition. The PMMA matrix shows a similarity with the PαMS matrix in region I below the intrinsic transition of the spin probe. A small minimum at the position of internal methyl group motion of perdeuterated nitroxide is also observed. The existence of this minimum is most probably connected with active low-temperature rotations of the ester side-chain methyl groups coupled with the $CD_3$ motion of the nitroxide molecule. We believe that the low-temperature minimum of the perdeuterated probe in PMMA, PαMS, and some elastomers[33] can only be seen if the spin probe is in closer contact with the side chain or methyl end group being motionally active at temperatures lower than 200 K. The presence of two discrete motions above 200 K indicates that the spin probe tumbling is influenced by the high-frequency motion of the side groups. The third process observed as region III becomes active above 240 K in the temperature region ascribed to the α-$CH_3$ motion.[34] Activation energies (Table II) of 7–10 kJ $mol^{-1}$ determined in the corresponding temperature region are found to be within the range of activation energies for the PMMA main-chain α-$CH_3$ rotation determined by conventional ESR[14] and NMR and dielectric methods.[27] Therefore, the assignment of region III to α-$CH_3$ motion is consistent with all of the presented results. The apparently low activation energy (2.5 kJ $mol^{-1}$) determined for the relaxation process defined as region II suggests that the spin probe motion at these temperatures may be affected by the ester side-chain $CH_3$ rotation, which is in accord with the measurements of Tsay and Gupta.[14] However, the difference between conventional ESR and DMESR measurements is in the order of magnitude of rotational correlation times. The DMESR method depicts only slow-tumbling probes with rotational correlation times of the order of $10^{-4}$–$10^{-6}$ s.

Significantly "closer" contact of the spin probes with the side chains in the PMMA matrix compared with the PS and P4VP matrices demonstrated in region I would also imply that above 200 K the spin probes distributed in a matrix of higher local density or smaller negligible free volume will be coupled to the high-frequency motion of the polymer segments or side chains. In fact, a faster line broadening is observed for higher molecular weight PMMA as in the case of PαMS. Effects of side-chain motions on the spin probe embedded in a matrix of higher local density will be more prominent than in the less dense matrix. Unfortunately, it is not possible to resolve quantitatively the contributions of polymer side-chain motion and free volume changes to the spin probe motion. A more accurate estimate would probably require a complete DMESR line-shape analysis and additional experiments.

## Conclusion

The DMESR spectra of spin probes doped in several polymers have been studied as a function of temperature below the glass transition temperature. Two (PS, PαMS, and P4VP) and three (PMMA) discrete spin probe motions are observed in the measured interval. The marked change of the Arrhenius plots between 190 and 200 K is ascribed to the internal probe transition. The measurement on the four different polymers and the glycerol–water system supports our assertion that this internal transition of the specific spin probe is rather insensitive to the nature of the polymeric matrix.

We conclude that the DMESR line broadening of the spin probe above 190 K is very sensitive to the available free volume and side-chain motions of the host polymer.

The appearance of the minima on the ln $\tau_R$ vs temperature diagram for PMMA and PαMS below 200 K is most probably a result of the coupling between the methyl groups of the perdeuterated spin probe and the polymer side-chain groups motionally active at these temperatures.

The demonstrated sensitivity of the DMESR method opens the possibility of studying small changes of local noncooperative segmental or side-chain motions below $T_g$ and variations in the free volume, which may be affected by physical aging.

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**Registry No.** PS (homopolymer), 9003-53-6; PαMS (homopolymer), 25014-31-7; P4VP (homopolymer), 9003-47-8; PMMA (homopolymer), 9011-14-7; 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, 2896-70-0.