4188 *Macromolecules* **1991,** *24,* 4188-4194

EPR Study of Chain Rotational Dynamics in Dilute Aqeuous Solutions of Spin-Labeled Poly(methacrylic acid) at Different Degrees of Neutralization

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Received July 18, 1990; Revised Manuscript Received December 3, 1990

ABSTRACT: Spin-labeled poly(methacrylic acid) (SL-PMA) was synthesized and EPR spectra of its dilute aqueous solutions were measured at different degrees of neutralization over the temperature range 272-333 K and analyzed. The temperature dependence of parameters characterizing the segmental rotational mobility of SL-PMA and the internal rotation of the spin-label relative to the polymer chain were determined by fitting line shapes of the experimental EPR spectra to the simulated ones. The simulated EPR spectra were calculated by use of axially symmetric Brownian rotational diffusion for modeling the rotational diffusion of the spin-label. The determined apparent activation energies of SL-PMA segmental rotational diffusion are discussed in connection with both its conformation in dilute aqueous solution and the activation energy of the viscous flow of the solvent used.

Introduction

An EPR study of dilute solutions of spin-labeled polymers is able to supply data characterizing local segmental rotational motions. The nitroxide spin-label is supposed to be bound to chain segments of the spin-labeled polymer at randomly distributed sites. A contribution of the reorientation of the whole polymer molecule to the spin-label rotational diffusion may be neglected in the case of high molecular weight polymers.[1] We assume that the spin-label rotational diffusion comprises an approximately isotropic rotational diffusion of the polymer chain segment to which the spin-label is bound, characterized by the rotational diffusion parameter R_S, and an internal rotation of the spin-label about the chemical bond through which it is bound to the polymer chain segment, characterized by the rotational diffusion parameter R_I. The resulting axially symmetric rotational diffusion of the spin-label is then characterized by two components of the rotational tensor, $R_\perp = R_S$ and $R_\parallel = R_S + R_I$, and by an angle ϑ at which the axis of internal rotation, identical with the rotational diffusion symmetry axis, is tilted in the xz plane from the z axis of the nitroxide axis system.[2] It is generally possible to determine all three parameters mentioned above by analyzing each of the experimental spectra by comparing its line shape with the simulated spectrum. Temperature dependences of the rotational diffusion parameters may be obtained by an analysis of the EPR spectra taken at different temperatures.

Helfand[3] has presented results of Brownian dynamics computer simulations of polymer chains and of the kinetic analysis of passage over barriers. He showed that the single-bond rotations followed by compensating rearrangements of the neighboring units or by cooperative counterrotations of second-neighbor bonds are predominantly responsible for local motions of the polymer chain and that the activation energy of segmental rotational mobility should be close to the height of one potential barrier for the single-bond rotation in the polymer chain. The temperature and viscosity dependence of a correlation time τ_c characterizing the rotational diffusion of a polymer chain segment in dilute solution, which is supposed to be inversely proportional to the rate constant for isomerization, is then predicted by Kramers' theory[4] in the high-friction limit as

$$\tau_c = A\eta \exp(E_a/RT) \tag{1}$$

where A is a constant independent of temperature and viscosity, R is the gas constant, T is the absolute temperature, and E_a is the height of a potential energy barrier for the single-bond rotation in the polymer chain. By use of the Arrhenius form in a description of the viscosity temperature dependence

$$\eta = \eta_0 \exp(E_\eta/RT) \tag{2}$$

expression 1 leads to

$$\tau_c = A' \exp[(E_a + E_\eta)/RT] \tag{3}$$

where A' is a constant and the apparent activation energy, E_{appar}, obtained from $\ln \tau_c$ vs $1/T$ plot is therefore predicted as

$$E_{\mathrm{appar}} = E_a + E_\eta \tag{4}$$

where E_η is the activation energy of the viscous flow of the solvent. These expressions were suggested and experimentally verified by Monnerie and collaborators[5,6] and were also foreseen in Helfand's analysis.[7]

Approximately the same barrier heights for local segmental motions in the polymer chain, $E_a \doteq 25$ kJ/mol, were calculated by use of expression 4 from the experimental apparent activation energies of the segmental rotational mobility, which we determined[2,8] in dilute solutions of spin-labeled poly(methyl methacrylates) (SL-PMMA) in two different solvents, dibutyl phthalate in the temperature range 273-373 K and ethyl acetate in the range 193-303 K. It was also found, however, that the apparent activation energy of segmental rotational diffusion in SL-PMMA in ethyl acetate decreases considerably at temperatures above 310 K due to the conformational transition, characterized by a sudden increase in the flexibility of the PMMA chain,[9] to which PMMA is subjected in the temperature range 318-328 K in this solvent. This finding confirms the expected existence of the dependence of apparent activation energy of the segmental rotational mobility on the polymer chain conformation mentioned also by Monnerie.[5]

Polyelectrolytes offer an excellent opportunity for a more detailed study of the effect of polymer chain conformation

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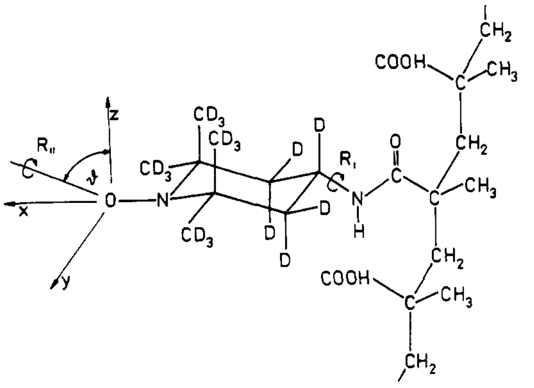
Chart I



on the character of local segmental motions. A polyelectrolyte molecule in an aqueous solution may be greatly expanded by electrostatic repulsion between polar groups, and this effect manifests itself in a very high intrinsic viscosity. The size of the polyelectrolyte random coil is, among other things, a function of the degree of neutralization α. The reduced viscosity of a typical polyelectrolyte in an aqueous solution (e.g., poly(acrylic acid)) increases with α increasing up to $\alpha \doteq 0.4$ and then slowly decreases due to the saturation effect.[10]

This paper reports an EPR study of dilute aqueous solutions of spin-labeled poly(methacrylic acid) (SL-PMA) at different degrees of neutralization α. Poly(methacrylic acid) (PMA) is a simple polyelectrolyte, which is however known to undergo a conformational transition in an aqueous solution upon ionization; consequently, its properties in this solvent deviate from the normal polyelectrolyte behavior described above. It exists in a very compact conformation stabilized by short-range interactions at low α values, whereas at $\alpha > 0.3$, long-range electrostatic interactions become predominant and the very compact structure is converted into an extended one, which then shows a normal polyelectrolyte behavior upon further increase of α. This conformational transition, which may be characterized by the fact[11] that at 293 K 50% of the very compact conformation disappears at about $\alpha = 0.17$, is responsible for the steep increase of reduced viscosity[10] at $\alpha \doteq 0.15$.

The segmental dynamics of PMA in dilute aqueous solutions at different degrees of neutralization were studied by Mulder et al.,[12,13] who measured the ^{2}H NMR relaxation rates of methyl and methylene deuterons in the methyl- and methylene-deuterated forms of PMA at 301 K at five magnetic field strengths ranging from 0.4 to 6.3 T. They determined the rotational diffusion parameters by fitting the experimental frequency dependences of methyl and methylene deuteron relaxation rates with theoretical values calculated by using a rotational diffusion model characterized by an overall axial symmetry and unrestricted internal rotation of the methyl group. Data obtained by the two magnetic resonance methods are compared.

Experimental Section

Synthesis of SL-PMA. Two spin-labeled polymers of substantially different molecular weights were prepared by copolymerization and by polymer analogous reaction, respectively. The chemical structure of the chain unit carrying the spin-label is the same in both polymers and is given in Chart I.

a. Copolymerization. Methacrylic acid (10 g) was heated with 4-(methacryloylamino)perdeuterio-2,2,6,6-tetramethylpiperidine (1 g), azobis(isobutyronitrile) (0.05 g), and methanol (40 mL) to 333 K for 14 h under argon atmosphere in a sealed ampule. By oxidation of this reaction mixture in 30% H_2O_2 with disodium tungstate (0.5 g) and ethylenediaminetetraacetic acid (0.5 g) proceeding for 7 days, nitroxide was formed in position 1 of the piperidine ring. The rest of the free nitroxide was removed by dialysis (tube Serva, 20-mm diameter) against quartz-bidistilled water (specific resistance 1 MΩ cm). The dialysis was continued until the EPR spectrum of free nitroxide had disappeared completely, and the polymer was then dried. 4-(Methacryloylamino)perdeuterio-2,2,6,6-tetramethylpiperidine was synthesized similarly to the proton derivative.[14]

b. Polymer Analogous Reaction. PMA (M_w = 400 000; 3 g) was dissolved in dimethylformamide (400 mL) and reacted with dicyclohexylcarbodiimide (0.07 g) and 4-aminoperdeuterio-2,2,6,6-tetramethylpiperidine-*N*-oxyl[15] (0.06 g) for 24 h. The polymer was then dialyzed against quartz bidistilled water similarly as before and dried.

c. Polymer Characterization. Water content of ~10% was determined in both dried polymers by Fischer's method. No ash content was found after their mineralization. The concentrations of the spin-labeled chain units, $\sim 1.5 \times 10^{20}$ g^{-1}, were found by EPR in both polymers; each of the spin-labeled chain units thus corresponds to ~50 methacrylic acid chain units. The concentrations of COOH groups in both polymers were determined by adding excess NaOH (0.1 N) to their aqueous solutions and titrating with 0.1 N HCl (phenolphthalein). More than 90% of theoretical was found in each polymer.

The molecular weight of SL-PMA prepared by copolymerization, M_η = 30 000, was calculated from the intrinsic viscosity measurement in aqueous 2 N NaOH at 298 K. The $[\eta]$–M relationship reported by Katschalsky and Eisenberg[16] was used. The intrinsic viscosity was obtained from the Huggins plot. The molecular weight of PMA used in the polymer analogous reaction, M_w = 400 000, was determined by static light scattering using a modified Sofica 42 000 apparatus (633 nm, 298 K) in the 2-methoxyethanol solvent. The refractive index increment was determined as 0.109 cm^3 g^{-1} (Brice-Phoenix BP-2000 V differential refractometer; 633 nm, 298 K).

Sample Preparation. Dilute solutions of SL-PMA neutralized to the required degree were prepared by mixing a polyacid stock solution (α = 0.0) in either D_2O or quartz bidistilled H_2O with an appropriate amount of 0.4 N NaOH or of a polysalt stock solution (α = 1.0). The degree of neutralization α achieved was checked by using the concentration of COOH groups remaining in the sample determined by titration. The resulting sample concentrations were ~10 mg of polymer/mL of solvent. Liquid aqueous samples were filled into a JES-LC-01 quartz aqueous solution sample tube (active volume 0.02 mL) and the spectra were recorded over the temperature range 273–333 K. Rigid-limit EPR spectra were obtained by recording EPR spectra of frozen solutions in quartz sample tubes of 5-mm o.d. at 113 K. Before measurement, all samples were deoxygenated by purging with nitrogen at room temperature.

EPR Measurements. EPR spectra were recorded with a JEOL-PE-3X spectrometer equipped with an EC-100 computer. The measurements were performed with 100-kHz magnetic modulation at a microwave output 2 mW in the case of liquid aqueous samples and at lower outputs (0.4–1.0 mW) in the case of frozen polycrystalline samples. The cavity temperature was stabilized with the JES-VT-3A temperature controller to ±0.5 K and measured with a platinum resistance thermometer. The magnetic field was measured with a MJ-110R NMR magnetometer Radiopan Poznán. All g factors were measured relative to the fourth line of Mn^{2+} in MgO EPR marker, assuming $g = 1.981$ for this line. The spin-label concentrations in the samples were calculated by comparing the second integral of the spectrum of the sample with the second integral of the spectrum of the standard (benzene solution of diphenylpicrylhydrazyl).

Simulations of EPR Spectra. At first the simulated slow motional and motionally narrowed EPR spectra were calculated by using the corrected version[2] of the Polnaszek–Freed program for tilting the principal axes of the magnetic tensors of a nitroxide radical with respect to the principal axis of diffusion.[17] In the end we used the Schneider–Freed set of programs,[18] which has been implemented into our computer recently. The Brownian rotational diffusion as a model of rotational diffusion of the spin-label and a Lorentzian line shape characterized by a rotationally invariant first-derivative peak-to-peak line width ΔH_{pp} were used in both cases. Rigid-limit EPR spectra were simulated

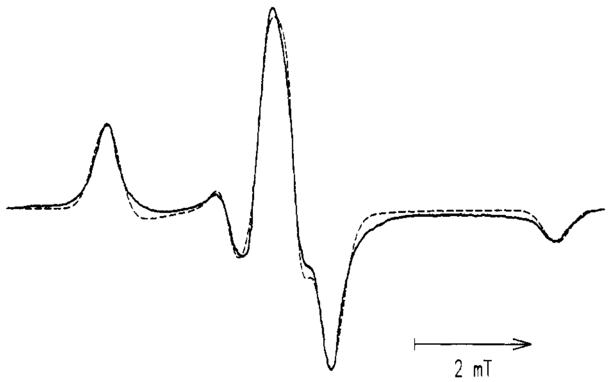


Figure 1. Rigid-limit EPR spectrum of SL-PMA in dilute aqueous solution at $\alpha = 0.0$ measured at 113 K (—) and the simulated spectrum calculated by use of the parameters given in the text (- - -).

by use of the corrected version of the Rigid Limit Nitroxide Program,[17] assuming Gaussian line shapes with the orientationally dependent line width $T_2^{-1}(\varphi) = a + b\cos^2\varphi$, where φ is the polar angle between the nitroxide axis system z axis and the direction of the external magnetic field. The terms correct to the second order in hyperfine interaction and g-tensor anisotropy[19] and the $1/g$ correction[20] were included in the resonance condition for allowed EPR transitions. All programs were run on a Siemens 7536 computer.

Results

Magnetic Tensor Components of the Spin-Label. Components of the **A** and **g** tensors of the spin-label in the system under study were determined from the rigid-limit EPR spectra of frozen aqueous solutions of SL-PMA measured in D_2O at 113 K (Figure 1). Solutions in D_2O provided narrower lines and better resolved spectra than H_2O solutions. It was found that the line shapes of these spectra are independent of the degree of neutralization α within the limit of experimental error. The simulated rigid-limit spectrum calculated by using the **A**-tensor components, $A_x = 0.65$ mT, $A_y = 0.52$ mT, $A_z = 3.86$ mT, the **g**-tensor components, $g_x = 2.0087$, $g_y = 2.0058$, $g_z = 2.0020$, and the line-width parameters, $a = 0.30$ mT and $b = 0.15$ mT, fits the experimental rigid-limit EPR spectra best (Figure 1).

EPR Spectra of SL-PMA in Liquid Aqueous Solutions. The line shapes of experimental spectra demonstrate a pronounced dependence of the spin-label rotational mobility on both the degree of neutralization α and temperature. Polymers of both molecular weights (30 000 and 400 000) supplied identical line shapes within the limit of experimental error in both solvents used (D_2O and quartz-bidistilled H_2O). Typical motionally narrowed EPR spectra were observed at 293, 313, and 333 K for $\alpha = 0.4$, 0.5, and 1.00. The remaining experimental EPR spectra measured (for their list see Table I) were slow motional spectra. A spectrum of the free spin-label at a very low concentration (below 1% of the concentration of the bound one) was found to be superimposed on most of the experimental slow motional spectra recorded. This spectrum was numerically subtracted from the experimental spectra before their analysis when it was necessary and possible. This procedure could not be applied to the experimental motionally narrowed spectra because the spectrum of the free spin-label was not resolved in them. The concentration of the free spin-label in the samples was found to increase slowly with time, probably due to the splitting off of the spin-label from the polymer chain.

The value of the isotropic splitting constant, $a^N = 1.72 \pm 0.01$ mT, determined from the motionally narrowed spectra, is somewhat higher than one-third of the trace of the **A** tensor determined from the rigid-limit EPR spectra. The temperature dependence of the **A**-tensor components or various effects of the environment polarity when polycrystalline sample and liquid aqueous solution were compared are probably responsible for this discrepancy. Hence, the values of the **A**-tensor components used in the calculation of the simulated spectra were somewhat increased to match the determined isotropic nitrogen splitting constant.

Table I
Components (in Units of 10^8 s^{-1}) of the Axially Symmetric Tensor of the Spin-Label Rotational Diffusion Determined by Analyzing Experimental EPR Spectra of SL-PMA[a]

	273 K		293 K		313 K		333 K	
α[b]	$R_\perp$	$R_\parallel$	$R_\perp$	$R_\parallel$	$R_\perp$	$R_\parallel$	$R_\perp$	$R_\parallel$
0.0	0.0048[c]	0.33[c]	0.0080[c]	0.35[c]	0.013[c]	0.45[c]	0.019[c]	0.48[c]
0.2	0.0080[c]	0.35[c]	0.016[c]	0.48[c]	0.024[c]	0.64[c]	0.19	1.6
0.4	0.018	0.64	0.048	0.80	0.11	1.1	0.24	1.6
0.5	0.029	0.64	0.064	1.1	0.19	1.6	0.43	1.6
1.0	0.016	0.64	0.032	1.1	0.070	1.6	0.19	1.9

[a] The symmetry axis of this tensor was found to be tilted in the xz plane by 40° with respect to the z axis of the nitroxide axis system. [b] Degree of neutralization α = [base]/[COOH]. [c] The components of the rotational diffusion tensor characterizing the rotational mobility of the spin-label bound to the very compact part of the PMA chain.

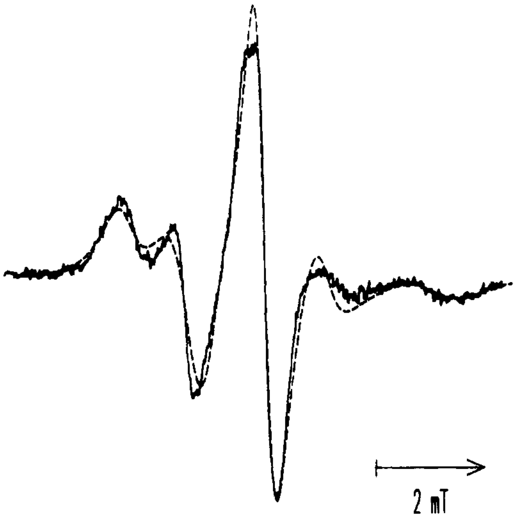


Figure 2. EPR spectrum of SL-PMA in dilute aqueous solution at $\alpha = 0.0$ measured at 273 K (—) and the simulated spectrum calculated by use of the parameters $R_\perp = 0.0048 \times 10^8$ s^{-1}, $R_\parallel = 0.33 \times 10^8$ s^{-1}, $\vartheta = 40°$, and $\Delta H_{pp} = 0.08$ mT (- - -).

Experimental slow motional spectra measured at 273 K and the spectrum measured at 293 K for $\alpha = 0.0$ were successfully simulated by using A_x and A_y components of the **A** tensor increased to $A_x = 0.75$ mT and $A_y = 0.60$ mT as well as the orientation of the rotational tensor symmetry axis characterized by an angle $\vartheta = 40°$. Examples of the experimental EPR spectra and of the simulated ones fitting them best are given in Figures 2 and 3. The remaining discrepancies between line shapes of the experimental and simulated spectra could probably be eliminated by using a better set of corrected values of the **A** and **g** tensors of the spin-label bound to PMA in an aqueous solution. As there is no way of determining more reliable values experimentally with continuous-wave X-band EPR, we made no such effort. The simulated spectra calculated by use of a jump or free diffusion models for the spin-label rotational diffusion do not fit the experimental spectra better. Motionally narrowed EPR spectra were analyzed by using the same values of the **A**- and **g**-tensor components and the method described in one of our previous papers,[2]

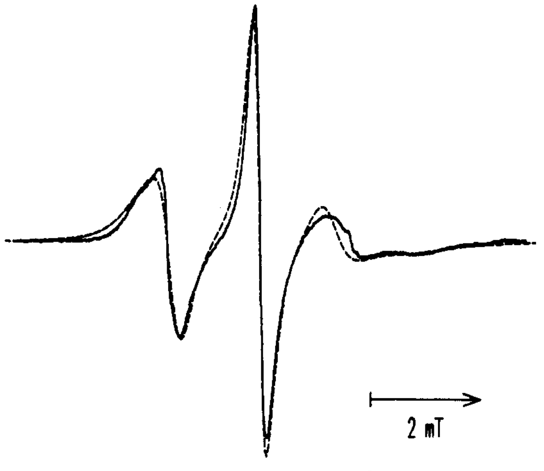


Figure 3. EPR spectrum of SL-PMA in dilute aqueous solution at $\alpha = 0.5$ measured at 273 K (—) and the simulated spectrum calculated by use of the parameters $R_\perp = 0.029 \times 10^8\ \mathrm{s}^{-1}$, $R_\parallel = 0.64 \times 10^8\ \mathrm{s}^{-1}$, $\vartheta = 40°$, and $\Delta H_{\mathrm{pp}} = 0.02$ mT (- - -).

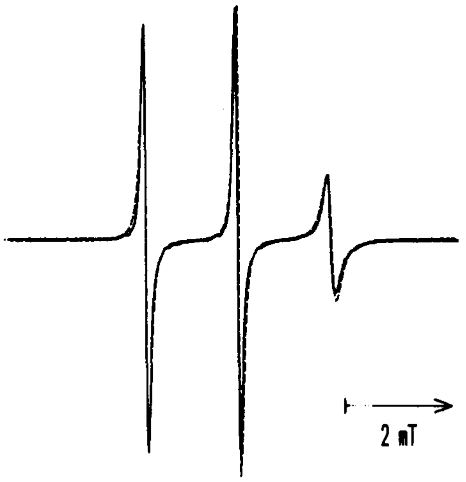


Figure 4. EPR spectrum of SL-PMA in dilute aqueous solution at $\alpha = 0.5$ measured at 333 K (—) and the simulated spectrum calculated by use of the parameters $R_\perp = 0.43 \times 10^8\ \mathrm{s}^{-1}$, $R_\parallel = 1.6 \times 10^8\ \mathrm{s}^{-1}$, $\vartheta = 40°$, and $\Delta H_{\mathrm{pp}} = 0.02$ mT (- - -).

assuming ϑ to be independent of temperature; an example of both the experimental and simulated spectra is given in Figure 4.

As far as the five remaining slow motional spectra measured at 313 and 333 K for $\alpha = 0.0$ and at 293, 313, and 333 K for $\alpha = 0.2$ are concerned, it was quite impossible to simulate satisfactorily the intensity ratio and the splitting of their low- and high-field extrema components simultaneously. With respect to the predicted coexistence of the very compact and of the extended conformation of PMA in aqueous solutions at $\alpha < 0.3$, each of these spectra was analyzed in terms of a two-site model as a superposition of the slow motional spectrum of the spin-labels bound to the very compact parts of the PMA coil and of the motionally narrowed spectrum of the spin-labels bound to the extended parts. The motionally narrowed components of these spectra were simulated with use of the rotational diffusion parameters roughly similar to values determined by analyzing the experimental spectra measured at $\alpha = 0.4$ and 0.5 at the same temperature. The rotational diffusion parameters characterizing rotational mobility of the spin-label bound to the very compact parts of the polymer coil were then determined by simulation so as to fit the positions and intensities of the outer extrema of these two-site spectra. Roughly 5% and 20% of the spin-labels bound to the extended parts of the PMA coil were determined for $\alpha = 0.0$ at 313 and 333 K, respectively, and 10% and 30% for $\alpha = 0.2$ at 293 and 313 K, respectively. Practically no fraction of the spin-labels bound to the extended parts of the PMA coil was found for $\alpha = 0.0$ at 273 and 293 K and for $\alpha = 0.2$ at 273 K. On the other hand, spin-labels bound to the extended parts of the PMA coil clearly prevail in the spectrum measured at 333 K for $\alpha = 0.2$. Hence, the determined fractions of the spin-label bound to the extended parts of the PMA coil increase not only with the degree of neutralization α but also with temperature. The fractions determined by EPR are generally lower then those calculated[11] from the data obtained by spectrophotometric and potentiometric titrations at 298 K. The complexity of the two-site spectral analysis precludes a more accurate determination of these fractions and also the determination of α dependence of the parameters characterizing rotational diffusion of the spin-label bound to the extended part of the PMA coil in this α range. An example of the two-site experimental and simulated spectrum is given in Figure 5. An attempt to simulate these spectra by assuming the existence of a distribution of the rotational diffusion parameters did not result in a better agreement between the experimental and simulated spectra.

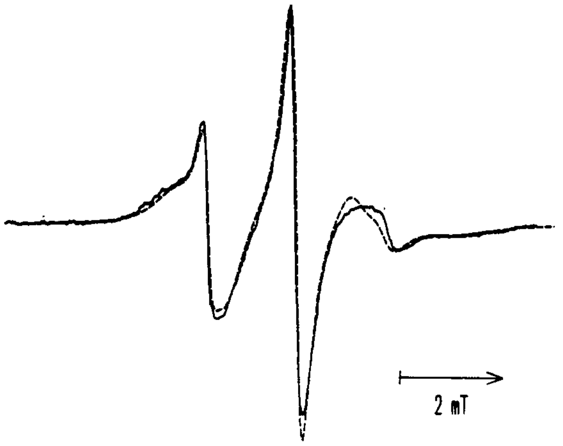


Figure 5. EPR spectrum of SL-PMA in dilute aqueous solution at $\alpha = 0.0$ measured at 333 K (—) and the sum of a simulated slow motional spectrum calculated by use of the parameters $R_\perp = 0.019 \times 10^8\ \mathrm{s}^{-1}$, $R_\parallel = 0.48 \times 10^8\ \mathrm{s}^{-1}$, $\vartheta = 40°$, and $\Delta H_{\mathrm{pp}} = 0.04$ mT and of a simulated motionally narrowed spectrum calculated by use of the parameters $R_\perp = 0.13 \times 10^8\ \mathrm{s}^{-1}$, $R_\parallel = 0.80 \times 10^8\ \mathrm{s}^{-1}$, $\vartheta = 40°$, and $\Delta H_{\mathrm{pp}} = 0.01$ mT. The share of the motionally narrowed spectrum represents ~20% of the total spin-label concentration in the sample (- - -).

All rotational diffusion parameters determined in this study are summarized in Table I. The values characterizing rotational mobility of the spin-label bound to the very compact parts of the PMA coil are given there for $\alpha = 0.0$ and 0.2 except for data given for $\alpha = 0.2$ at 333 K, which like the rest of the data characterize the rotational mobility of the spin-label bound to the extended parts of the PMA coil. The value $\vartheta = 40°$ characterizing the orientation of the rotational tensor symmetry axis determined in the fitting process is somewhat lower than $\vartheta = 51°$ determined for SL-PMMA.[2,8] It indicates that the conformation of the spin-label bound to SL-PMA dissolved in aqueous solution differs from the conformation of the same spin-label bound to SL-PMMA dissolved in the ethyl acetate or dibutyl phthalate solvent.

The α dependence of the parameter $R_{\mathrm{S}} = R_\perp$ characterizing the approximately isotropic rotational diffusion of the polymer chain segment is plotted in Figure 6, and the Arrhenius plots of R_{S} and $R_{\mathrm{I}} = R_\parallel - R_\perp$ are given in Figures 7 and 8, respectively. Estimated errors of deter-

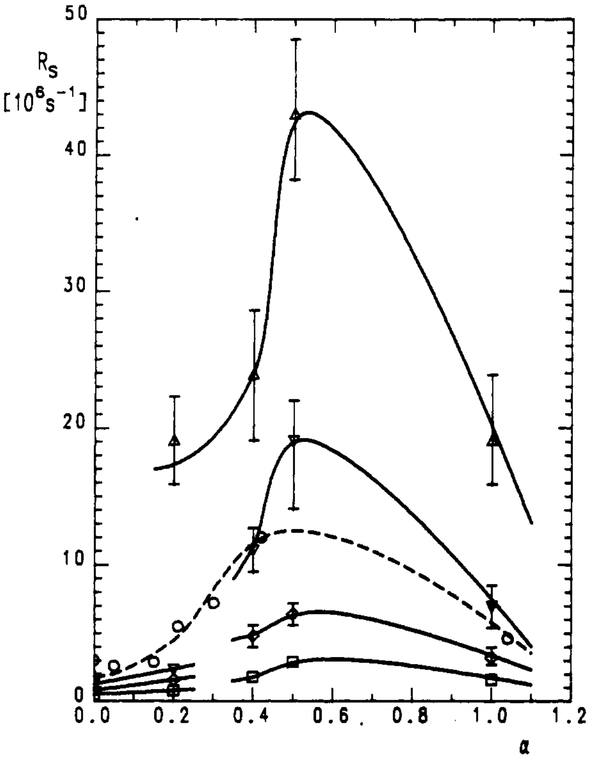


Figure 6. Dependences on the degree of neutralization α of the parameter R_S characterizing segmental rotational mobility determined by EPR for SL-PMA in dilute aqueous solutions at 273 (□), 293 (◇), 313 (▽), and 333 K (△), respectively, and of the parameter $D_\perp$ characterizing segmental rotational mobility determined by NMR study[12] for deuterated PMA in dilute aqueous solution at 301 K (○).

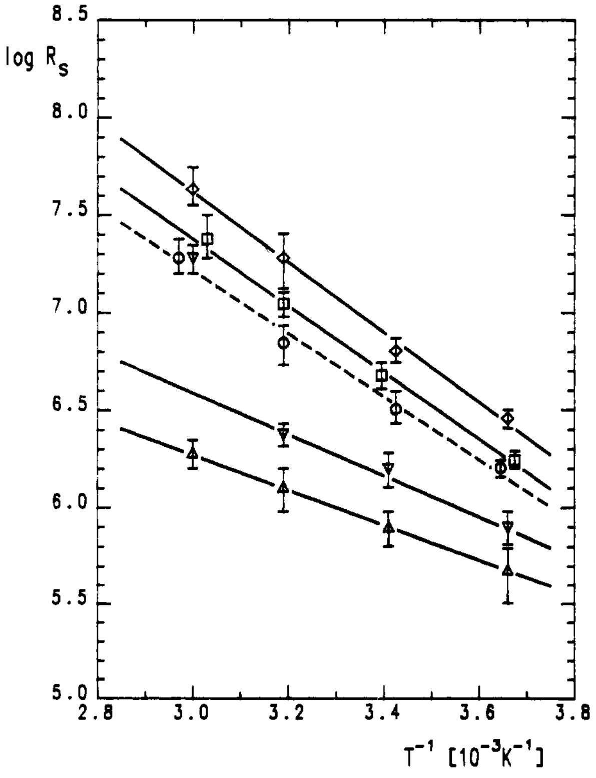


Figure 7. Arrhenius plot of the parameter R_S characterizing the segmental rotational mobility of SL-PMA in dilute aqueous solutions. $\alpha = 0.0$ (△), $\alpha = 0.2$ (▽), $\alpha = 0.4$ (□), $\alpha = 0.5$ (◇), and $\alpha = 1.0$ (○).

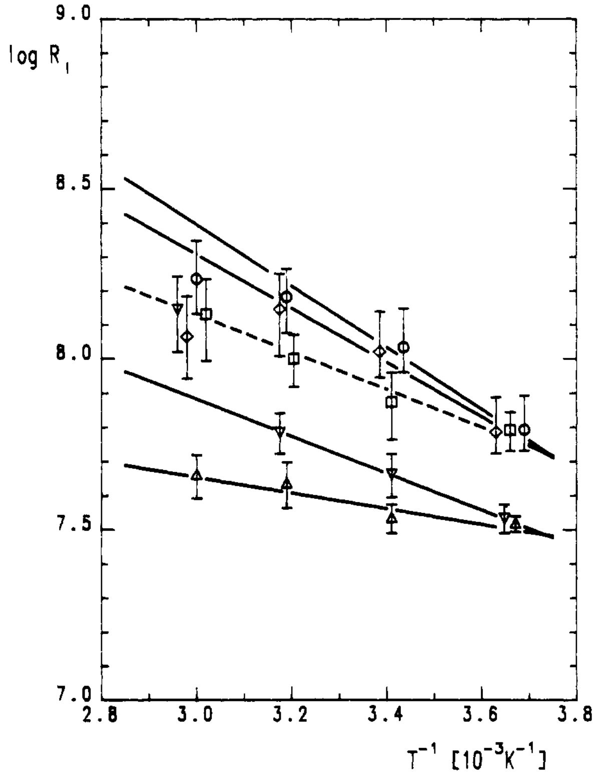


Figure 8. Arrhenius plot of the parameter R_I characterizing the internal rotation of the spin-label bound to PMA in dilute aqueous solutions. $\alpha = 0.0$ (△), $\alpha = 0.2$ (▽), $\alpha = 0.4$ (◇), $\alpha = 0.5$ (○), and $\alpha = 1.0$ (□).

mination are given in the figures only when they exceed the size of the symbols used. It should be kept in mind that $R_\perp$ and $R_\parallel$ are mutually dependent within error limits determined by analyzing a particular experimental spectrum.

It follows from the experimental data presented above that an adequate representation of the α dependence of PMA segmental rotational mobility at each temperature from the range studied (given in Figure 6) should consist of two curves characterizing its very compact and extended conformation, respectively. The spin-label bound to the very compact parts of the PMA coil was not identified in any of the experimental spectra for $\alpha > 0.2$; at 333 K a significant share of it was identified only for $\alpha = 0.0$. Parameters characterizing rotational diffusion of the spin-label bound to the extended parts of PMA coil at low α cannot be determined reliably due to the complexity of the two-site spectral analysis. The values of the parameter $D_\perp$ determined by Mulder et al.[12] in the NMR studies of the ^{2}H relaxation data in dilute aqueous solutions of deuterated PMA at 301 K (Table V of the quoted paper), which characterize the PMA segmental rotation mobility similarly to $R_\perp$, are also presented in Figure 6. We find these NMR data to be in a good agreement with our EPR ones. To our knowledge, such quantitative agreement between data of two different magnetic resonance methods characterizing polymer dynamics has not been reported yet.

Linearity of the Arrhenius dependences of R_S in Figure 7 is not very surprising, considering the narrow temperature range studied. The apparent activation energies, E_{appar}, equal to 17 and 20 kJ/mol, were determined from data characterizing the very compact PMA conformation at $\alpha = 0.0$ and 0.2, respectively, and values 33, 34, and 31 kJ/mol were obtained from data characterizing the extended conformation at $\alpha = 0.4, 0.5,$ and 1.0, respectively, using expression 3 written in terms of the rotational diffusion parameter $R_S \sim \tau_c^{-1}$

$$R_S = R_S^0 \exp[-(E_{\text{appar}})/RT] \qquad (5)$$

The simultaneously determined preexponential factors R_S^0, which should be independent of both the solvent viscosity and temperature, ranged from 1×10^9 s^{-1} for $\alpha = 0.0$ to 1×10^{13} s^{-1} for $\alpha = 0.5$. The lower values of the apparent activation energies of the internal rotation, 4, 10, 15, 17, and 10 kJ/mol for α = 0.0, 0.2, 0.4, 0.5, and 1.0, respectively, were determined from the data presented in Figure 8, using an expression similar to (5) written for the rotational diffusion parameter R_I.

Implementation of the Lanczos algorithm into the new Schneider–Freed set of programs[18] and a reliable determination of the sufficient basis set and of the number of Lanczos steps necessary to obtain a fully convergent EPR spectrum in dependence on the character of spin-label rotational diffusion result in significant savings of computer time in comparison with the old Polnaszek–Freed program.[17] Inclusion of the L odd terms in the calculation is probably responsible for minor differences found between the EPR spectra simulated by use of this new set and the spectra simulated with the old program. The spectra discussed in this paper were calculated by using the basis set defined by $L^e_{\max} = 24$, $L^o_{\max} = 15$, $K_{\max} = 4$ and $M_{\max} = 2$, or smaller. Full convergence was reached after 128 Lanczos steps at most and required ~260 s of computer time.

Discussion

Substantially higher segmental rotational mobilities and their apparent activation energies characterizing the extended PMA conformation at α = 0.4, 0.5, and 1.0 when compared with the data characterizing the compact one at α = 0.0 and 0.2 follow from the experimental data presented in Table I and Figures 6–8. An assumption that the apparent activation energy of segmental rotational mobility is given by expression 4 has led to surprisingly low heights of potential barriers, E_a = 1, 4, 17, 18, and 15 kJ/mol at α = 0.0, 0.2, 0.4, 0.5, and 1.0, respectively, using $E_\eta \doteq 16$ kJ/mol for an aqueous solvent in the temperature range in question. The apparent activation energies of internal rotation found were lower than the activation energy of viscous flow of the solvent used or approximately equal to it, similarly as found for SL-PMMA in the ethyl acetate and dibutyl phthalate solvents.[2,8] Both latter findings cast doubts on the adequacy of expression 3 to describe the observed temperature and viscosity dependence of the PMA segmental rotational diffusion.

Just after the original version of this paper had been submitted for publication, Glowinkowski et al.[21] published results of ^{13}C NMR studies of poly(isoprene) local segmental dynamics in solvents covering a wide range of viscosities in a broad temperature region. They concluded that the Kramers' theory[4] and resulting expression 3 might be inappropriate for describing the local dynamics of many synthetic polymers and could lead to serious errors when the potential energy barriers for conformational transitions were calculated from temperature-dependent data. They quantitatively explained their experimental data using the equation

$$\tau_c = A\eta^\beta \exp(E_a/RT) \qquad (6)$$

A theoretical background for this equation supplies the Grote–Hynes theory,[22] which rationalizes why the correlation time scales as η^β instead of the first-power dependence (3) predicted by Kramers' theory.[4] The exponent $\beta < 1$ depends on the moment of inertia and size of the isomerizing unit and on the curvature of the potential energy surface at the top of the barrier. Hence, no universal value of β is expected and the potential energy barrier, E_a, cannot be determined from the temperature dependence of the dynamics in a single solvent. Glowinkowski et al.[21] determined the value $\beta = 0.41$ for poly(isoprene) in dilute solutions utilizing data obtained in 10 solvents covering a factor of 70 in viscosity. Providing β has been determined, E_a can be calculated from

$$E_{\text{appar}} = E_a + \beta E_\eta \qquad (7)$$

Introduction of the exponent $\beta < 1$ into expression 4, which results in (7), makes it possible to explain qualitatively the generally low values of E_{appar}, which characterize the temperature dependences of both segmental and internal rotational diffusion in PMA, with regard to E_η. One may speculate that the dependence of E_{appar} on the degree of PMA neutralization found might be explained in terms of the Grote–Hynes theory[22] by a modification of the height and shape of the top of the potential energy barrier as a consequence particularly of the mentioned conformational transition from the compact to extended conformation at low α and, to a lesser extent, as a consequence of the PMA coil expansion due to the long-range electrostatic repulsion of the charged groups at higher α. Unfortunately, no data characterizing such a modification of this barrier are available at present. A qualitative explanation of the observed increase of segmental rotational mobility with increasing expansion of the PMA coil may be found in a paper published recently by Bahar, Erman, and Monnerie.[23] They presented some new results of their studies of local orientational motions in flexible polymer chains performed with dynamic extension of the rotational isomer state (DRIS) model. Among other things, they concluded that the preexponential factor in type 1 expression may depend on the size of the moving sequence of bonds in the polymer chain and that the correlation time characterizing reorientation of the label connected with one of the segments in the moving sequence decreases with increasing number of segments in this sequence. This dependence of correlation time on the length of the moving sequence may nevertheless be counterbalanced by the effect of size of the moving sequence when the latter is taken into account. The observed increase of segmental rotational mobility in the PMA chain with α increasing from 0.0 to 0.5 may be qualitatively explained by a generally accepted increase of the persistence length in polyelectrolytes, which is closely related to the number of segments in the moving sequence of the polymer chain, with increasing degree of their neutralization α, provided that the effect of the size of the moving sequence is of smaller importance.

Results of EPR studies of spin-labeled PMA in dilute aqueous solutions have been recently published by Wielema and Engberts.[24] They briefly reported the dependence of EPR spectral line shapes on the degree of neutralization α at room temperature, in a general agreement with data presented in this paper, but did not attempt any adequate analysis of the experimental EPR spectra. They concluded that the slow motional component of the spectrum measured at α = 0.01 is due to the spin-label attached to those parts of the polymer for which the backbone segmental motion is slowed down as a result of the formation of hydrophobic microdomains made possible by the neutralization of carboxylic groups and leading to the formation of a compact coil. With respect to the experimental data available, including their own, it seems confusing to try to explain the existence of PMA in a compact coiled conformation and the occurence of the slow motional spectra as a consequence of the neutralization of carboxylic groups.

Conclusions

EPR has proved that the rotational mobility of the spin-label bound to PMA chain segments at randomly distributed sites depends on the degree of its neutralization α in dilute aqueous solutions and on temperature in the range from 273 to 333 K. All experimental EPR spectra were successfully simulated by using the axially symmetric Brownian rotational diffusion as a model of the rotational diffusion of the spin-label. The temperature dependences of the parameters characterizing both the segmental rotational mobility and the internal rotation of the spin-label relative to the PMA chain were determined by this process. The results are in a surprisingly good agreement with the published NMR data. The segmental rotational mobilities and their activation energies characterizing the very compact PMA conformation, which prevails in the aqueous solutions at low degrees of neutralization α, are much lower than the values characterizing the extended PMA conformation, which prevails at higher α. Both conformations were found to exist simultaneously in the α range from 0.0 to 0.2 at higher temperatures in agreement with the spectrophotometric data.[11] The segmental rotational mobility of PMA was found to increase with coil expansion when α increases from 0.0 to approximately 0.5. This increase may be qualitatively explained with respect to the results presented by Bahar and collaborators[23] by increasing the number of segments in the moving sequence of the PMA chain when α increases in this range.

Acknowledgment. We are very grateful to Dr. M. Bohdanecký, Dr. J. Stejskal, Dr. J. Šomvárský, and Mrs. E. Plachetková from this Institute for the determination of the molecular weight of SL-PMA, for the determination of the molecular weight of PMA, for valuable assistance in the implementation of computer programs, and for a number of analytical determinations.

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Registry No. PMA, 54193-36-1.