Macromolecules **1994,** *27,* 3977–3981

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

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Received February 8, 1994; Revised Manuscript Received April 12, 1994[⊗]

ABSTRACT: Spin-labeled poly(acrylic acid) (SL-PAA) was synthesized and electron paramagnetic resonance (EPR) spectra of its dilute aqueous solutions were measured at different degrees of neutralization α in the temperature range 273–353 K. The temperature dependence of parameters characterizing the segmental rotational mobility of SL-PAA and the internal rotation of the spin label relative to the polymer chain were determined by simulating the line shapes of the experimental EPR spectra. The segmental rotational dynamics of SL-PAA was found to be nearly independent of its degree of neutralization. The absence of the methyl group is probably responsible for higher segmental rotational mobility of SL-PAA at all degrees of neutralization and in the entire temperature range studied, when comparing with spin-labeled poly(methacrylic acid) (SL-PMA) under the same conditions. SL-PAA forms strong complexes with both poly(ethylene oxide) (PEO) and poly(*N*-vinylpyrrolidone) (PVP) in aqueous solutions at α = 0.0 and 0.1. The complexes immediately precipitate from the solution under our experimental conditions. Complexation of SL-PAA neutralized to higher degrees (α = 0.2–1.0) with PEO or PVP in aqueous solutions was not observed.

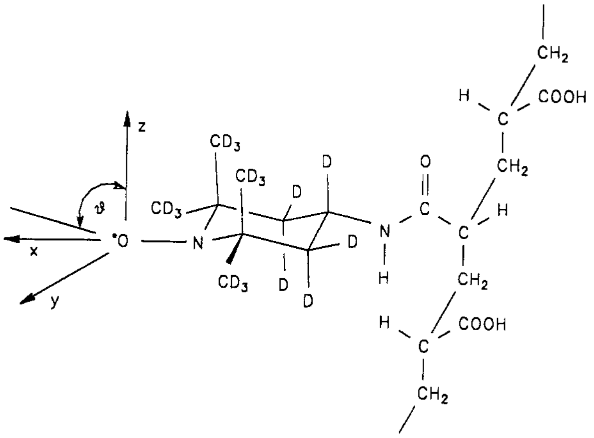
Introduction

Polyelectrolytes offer an excellent opportunity for a study of the effect of polymer chain conformation on the character of local segmental motions. In aqueous solutions polyelectrolyte molecules may be greatly expanded by electrostatic repulsion between polar groups, leading to a significant increase of the 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 poly(acrylic acid) (PAA), which is a typical polyelectrolyte and shows a normal polyelectrolyte behavior in aqueous solution, increases with α increasing to α = 0.4 and then slowly decreases due to the saturation effect.[1]

Data on segmental rotational motions can be obtained by an EPR study of dilute solutions of spin-labeled polymers. We assume that the rotational diffusion of a nitroxide spin label, which is attached to chain segments of the polymer at randomly distributed sites, consists of an approximately isotropic rotational diffusion of the polymer chain segment to which the spin label is attached with a rotational diffusion rate R_S and an internal rotation of the spin label about the chemical bond through which it is attached to the polymer chain segment with a rotational diffusion rate 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 to the rotational diffusion symmetry axis, is tilted in the *xz* plane from the *z* axis of the nitroxide axis system (Chart 1). It is possible to determine all three parameters mentioned above by comparing the line shapes of slow motional experimental EPR spectra with the simulated ones. The 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.[2]

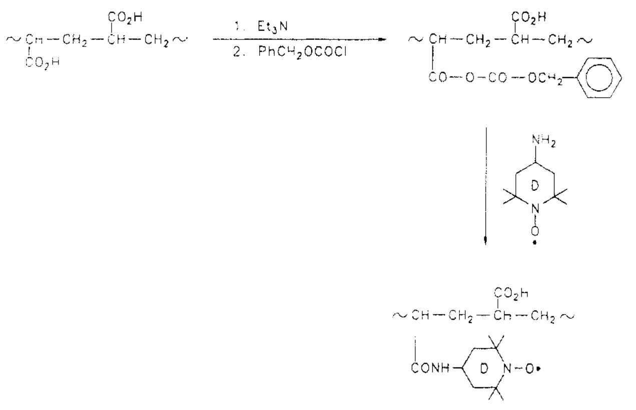
Our previous paper[3] reported an EPR study of dilute aqueous solutions of spin-labeled poly(methacrylic acid) (SL-PMA) at different degrees of neutralization α. The properties of PMA in water deviate from the normal polyelectrolyte behavior described above, because its coil is subjected to a conformational transition at α = 0.15. PMA is known[3] to exist in a very compact conformation stabilized by short-range interactions at low α values, whereas at α > 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 a further increase of α. The segmental rotational mobilities and their activation energies characterizing the very compact PMA conformation were found[3] to be much lower than the values for the extended PMA conformation. Coexistence of both conformations in the α range from 0.0 to 0.2 at higher temperatures is in agreement with spectrophotometric data.[4] The observed increase of the segmental rotational mobility of PMA in aqueous solutions when α increases from 0.0 to ≃0.5, which is due to the expansion of the polyelectrolyte coil, was qualitatively explained by the increasing number of segments in the moving sequence of the PMA chain.[3] This number is closely related to the polyelectrolyte persistence length which is believed to increase with the increasing degree of PMA neutralization.

Chart 1



[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

Scheme 1



This paper reports an EPR study of dilute aqueous solutions of SL-PAA performed in order to detect differences in segmental rotational mobility between SL-PAA and SL-PMA, with an emphasis on the effect of the occurrence of conformational transition of the polyelectrolyte coil. Soutar et al.[5] report values of 1.3 and 4.2 ns, respectively, for the rotational correlation times characterizing the segmental motions of PAA and PMA in methanolic solutions at 298 K, deduced from a synchrotron-generated time-resolved fluorescence anisotropy study of these polyelectrolytes. Other papers[6–8] stimulated our attempt to study the effect of hydrogen bonded complex formation between PAA and PEO and of complexes of PAA with other polymers, such as PVP, on the segmental rotational dynamics of SL-PAA.

Experimental Section

Synthesis of SL-PAA. SL-PAA was prepared using the mixed carboxylic acid anhydride method[9] (Scheme 1). Triethylamine (Fluka, 0.004 mol) was added to the solution of PAA (3 g, Polyscience, M_w = 450 000) in dried dimethylformamide (DMF, 200 mL), and the mixture was cooled to 273 K; benzyl chloroformate (Fluka, 0.004 mol) under dried nitrogen was added, and after 1 h (273 K, stirring) the reaction mixture was combined with 4-aminoperdeuterio-2,2,6,6-tetramethylpiperidine-*N*-oxyl[10] (0.006 mol) dissolved in DMF (5 mL). After 24 h the rest of the free nitroxide was removed by dialysis (Serva tube, 20-mm diameter) against quartz-bidistilled water with NaOH added to speed up the dialysis and improve the solubility of the dried product. The dialysis was continued until the EPR spectrum of free nitroxide disappeared completely; the polymer was then dried under standard conditions (2 days at room temperature). Molar concentrations of acrylic acid, sodium acrylate, spin-labeled units, and water in the dried polymer (18.60, 20.48, 1.75, and 59.16 mol %, respectively) were determined by elemental analysis using C, H, N, and Na data (found 35.13, 6.16, 1.04, 10.00; calc 35.13, 6.16, 1.04, 9.97). The cations present were removed by mixing a solution containing the dried polymer in quartz-bidistilled water with sulfonated polystyrene–divinylbenzene copolymer (Ostion, Lachema Brno) till no ash content was found after SL-PAA mineralization. Because some polymer was lost during this treatment, the concentration of SL-PAA in the resulting solution was determined gravimetrically by evaporation of a small sample at room temperature to constant weight. The concentration of the COOH groups in the solution (0.06 mol/L), which was determined by titration with 0.1 N NaOH (phenolphthalein), agreed well with the value calculated from the elemental analysis for $\alpha = 0.0$, taking into account the mentioned loss of the polymer. The pH of this solution (2.2), determined by potentiometric titration, was in agreement with the published data[11] extrapolated toward higher PAA concentrations. A lower accuracy of measurements of the spin label concentration in the samples and possible transformation of some of the nitroxides into diamagnetic products in an acid environment (during mixing of SL-PAA with sulfonated polystyrene–divinylbenzene copolymer) are probably responsible for the 20% difference between the calculated and observed (0.0016 mol/L) concentrations of the spin label in the solution. Each of the spin-labeled chain units thus corresponds approximately to 40 acrylic acid chain units.

Sample Preparation. A dilute solution of SL-PAA neutralized to the required degree with NaOH was prepared by mixing a polyacid stock solution ($\alpha = 0.0$) in quartz-bidistilled water with an appropriate amount of a stock solution of SL-PAA completely neutralized with NaOH ($\alpha = 1.0$). The degree of neutralization α achieved was checked by titration. The solution was transferred to a JES-LC-01 quartz aqueous solution sample tube (active volume 0.02 mL), and the EPR spectra were recorded in the temperature range 273–353 K. Rigid limit EPR spectra were obtained by recording EPR spectra of frozen solutions in quartz sample tubes (5-mm o.d.) at 113 K. Stock solutions of PEO 10 (Fluka, M_w = 10 000), PEO 100 (Aldrich, M_w = 100 000), and PVP (Fluka, M_w = 360 000) in quartz-bidistilled water (concentration of repeating units 0.3 mol/L) were used in the studies of SL-PAA complexation. 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 interfaced to a PC 386. The measurements were performed with 100-kHz magnetic modulation at a microwave output of 2 mW in the case of liquid samples and at lower outputs (0.4–1.0 mW) in the case of frozen 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 Poznań. All *g* factors were measured relative to the fourth line of the Mn^{2+} cation in the MgO EPR marker by 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. Rigid limit EPR spectra were calculated using the Rigid Limit EPR Spectral Calculation Program[12] EPRR PC Version 1.0 assuming an orientationally-dependent line width. Motionally narrowed EPR spectra were calculated by using Slow-motional EPR Lineshape Calculation Programs[12] EPRLL PC Version 1.2 based on the Schneider–Freed set of programs.[13] An axially symmetric 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 assumed. All programs were run on a PC 386 computer.

Results and Discussion

Magnetic Tensor Components of the Spin Label. The 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-PAA measured at 113 K (Figure 1). It was found that the line shapes of these spectra are practically independent of the degree of neutralization α. The simulated rigid limit spectrum calculated using the *A* tensor components A_x = 0.68 mT, A_y = 0.55 mT, and A_z = 3.82 mT, the *g* tensor components g_x = 2.0096, g_y = 2.0066, and g_z = 2.0027, and Lorentzian line shape with line width parameters $T_{2x} = T_{2y}$ = 0.36 mT and T_{2z} = 0.38 mT fits the experimental rigid limit EPR spectra best (Figure 1). The values of the *A* tensor components are very close to the values determined previously[3] from the rigid limit EPR spectra of SL-PMA; values determined for all three components of the *g* tensor are higher by approximately 0.0007.

EPR Spectra of SL-PAA in Liquid Aqueous Solutions. Typical motionally narrowed EPR spectra were observed for most of the samples in the temperature range studied (273–353 K). Only EPR spectra of samples at low α taken at 273 K exhibit some features of slow motional

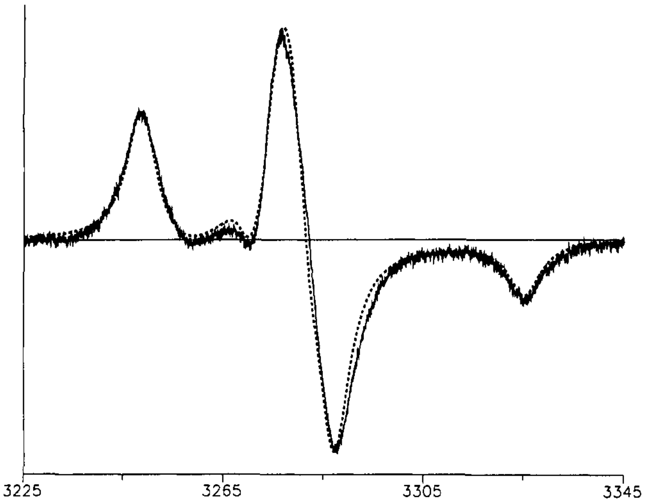


Figure 1. Rigid limit EPR spectrum of SL-PAA in dilute aqueous solution at $\alpha = 0.0$ measured at 113 K (—) and the simulated spectrum calculated using the parameters given in the text (- - -).

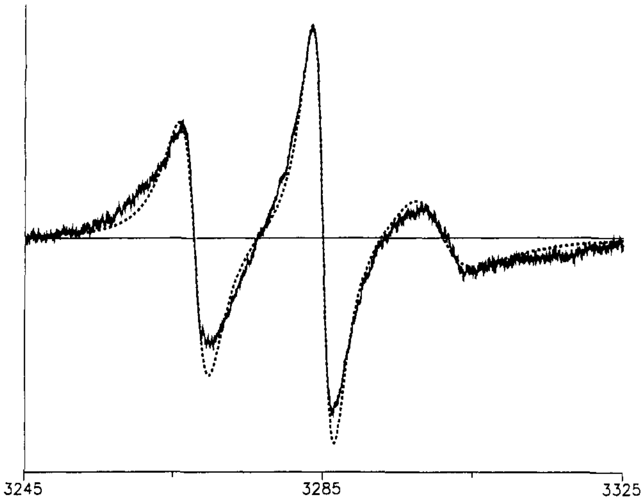


Figure 2. EPR spectrum of SL-PAA in dilute aqueous solution at $\alpha = 0.0$ measured at 273 K (—) and the simulated spectrum calculated using the parameters $R_\perp = 0.064 \times 10^8$ s^{-1}, $R_\parallel = 0.64 \times 10^8$ s^{-1}, $\vartheta = 40°$, and $\Delta H_{\rm pp} = 0.03$ mT (- - -).

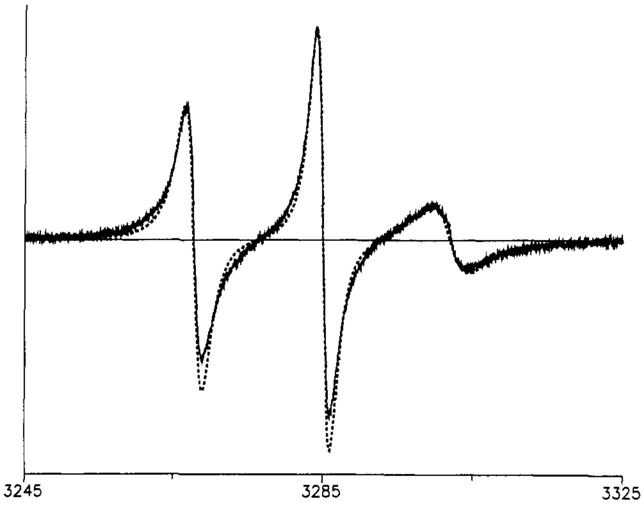


Figure 3. EPR spectrum of SL-PAA in dilute aqueous solution at $\alpha = 0.3$ measured at 273 K (—) and the simulated spectrum calculated using the parameters $R_\perp = 0.095 \times 10^8$ s^{-1}, $R_\parallel = 1.1 \times 10^8$ s^{-1}, $\vartheta = 40°$, and $\Delta H_{\rm pp} = 0.01$ mT (- - -).

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 the experimental spectra recorded. This spectrum was subtracted from the experimental spectra before their analysis whenever necessary and possible. The value of the isotropic splitting constant determined from the motionally narrowed spectra was found to increase somewhat with the degree of neutralization α within the limits $a^{\rm N} = 1.705 \pm 0.02$ mT; one-third of the trace of the A tensor determined from the rigid limit EPR spectra ($a^{\rm N} = 1.683$ mT) agrees satisfactorily with the lower limit of the mentioned range. A higher concentration of cations in the more neutralized solutions is probably responsible for this effect. Accordingly, the values of the A tensor components used in the calculation of the particular simulated spectra for higher α were proportionally increased to match the isotropic nitrogen splitting constant in the experimental spectra. The spectra discussed in this paper were calculated using the basis set[13] defined by $L^{e}_{\max} = 10$, $L^{o}_{\max} = 7$, $K_{\max} = 6$, $M_{\max} = 2$, and $p^{I}_{\max} = 2$; full convergence was usually reached after less than 100 Lanczos steps and required about 100 s of computer time.

Motionally narrowed EPR spectra offer no opportunity to determine all three parameters characterizing the axially symmetric rotational diffusion of the spin label (the two components of the rotational tensor $R_\perp = R_{\rm S}$ and $R_\parallel = R_{\rm S} + R_{\rm I}$ and angle ϑ) due to the limited amount of resolved features.[14] For this reason we have adopted the orientation of the rotational tensor symmetry axis characterized by an angle $\vartheta = 40°$ when simulating experimental SL-PAA spectra. This orientation generated simulated spectra fitting well the slow motional EPR spectra of PMA carrying the same spin-labeled chain unit.[3] Even then we were not able to determine $R_\perp$ and $R_\parallel$ with an accuracy better than about ±50%. The reason lies in the fact that a particular experimental motionally narrowed EPR spectrum (amplitudes and line widths of its three components) may be fitted by simulated spectra calculated for a particular correlation time τ ($\tau = [6(R_\perp R_\parallel)^{1/2}]^{-1}$ in the case of Brownian rotational diffusion) within a range of degrees of anisotropy $N = R_\parallel / R_\perp$. Examples of the experimental EPR spectra together with best fits are given in Figures 2–5. Arrhenius plots of $R_{\rm S}$ and $R_{\rm I} = R_\parallel - R_\perp$ (in units s^{-1}) are presented in Figure 6. The error in the determination of both $R_{\rm S}$ and $R_{\rm I}$, together with their minor dependence on the degree of neutralization α, prevents us from discussing the temperature dependences of the rotational rates separately for different α. Solid lines in Figure 6 thus represent linear best fit lines, calculated using the data for all the degrees of neutralization studied. The average apparent activation energies $E_{\rm S}^{\rm appear}$ and $E_{\rm I}^{\rm appear}$ ($\simeq$27 and 18 kJ/mol, respectively) were determined from the slopes of these lines, using the expression $R_{\rm S}(T) = R_{\rm S}^0 \exp(-E_{\rm S}^{\rm appar}/RT)$ and a similar expression for $R_{\rm I}$. The values of the preexponential factors $R_{\rm S}^0$ and $R_{\rm I}^0$ of the order of 10^{12} s^{-1} were found.

Dependences of $R_{\rm S}$ and $R_{\rm I}$ on T and α; Comparison between SL-PAA and SL-PMA. Two remarkable differences in segmental rotational dynamics between SL-PAA and SL-PMA follow from a comparison of Arrhenius plots presented in Figure 6 with the plots given in Figure 7 of ref 3. First, the very slow segmental rotational mobilities of PMA in the very compact conformation at low α were not observed for PAA. Second, segmental rotational mobilities in PAA at all degrees of neutralization α and at all temperatures studied were found to be higher than segmental rotational mobilities in the extended

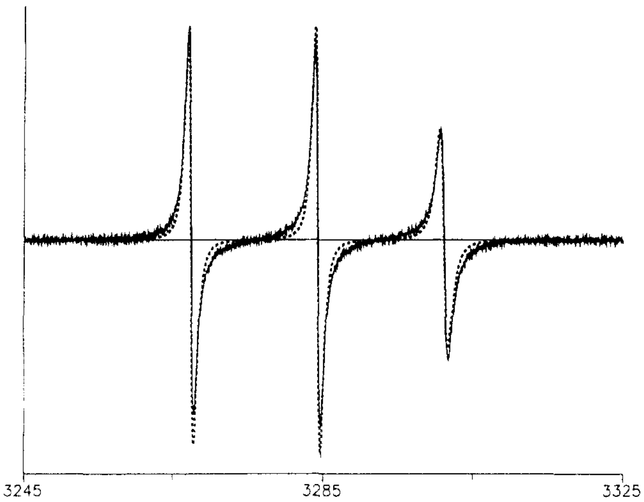


Figure 4. EPR spectrum of SL-PAA in dilute aqueous solution at $\alpha = 0.0$ measured at 353 K (—) and the simulated spectrum calculated using the parameters $R_\perp = 1.3$ and $10^8\ s^{-1}$, $R_\parallel = 4.8 \times 10^8\ s^{-1}$, $\vartheta = 40°$ and $\Delta H_{pp} = 0.06$ mT (- - -).

Figure 5. EPR spectrum of SL-PAA in dilute aqueous solution at $\alpha = 0.3$ measured at 353 K (—) and the simulated spectrum calculated using the parameters $R_\perp = 1.6 \times 10^8\ s^{-1}$, $R_\parallel = 8.0 \times 10^8\ s^{-1}$, $\vartheta = 40°$, and $\Delta H_{pp} = 0.04$ mT (- - -).

conformation of PMA at $\alpha > 0.2$ at corresponding temperatures. On the other hand, the value of the average apparent activation energy characterizing the temperature dependence of PAA segmental rotational mobility E_S^{appar} was found to be close to the values obtained for extended PMA conformations at $\alpha = 0.4$, 0.5, and 1.0 (27 and 33, 34 and 31 kJ/mol, respectively). A similar conclusion is valid for the average apparent activation energy for the temperature dependence of internal rotation of the spin label attached to PAA, E_I^{appar}.

These conclusions are in agreement with the generally accepted normal polyelectrolyte behavior of PAA and suggest the absence of the conformational transition characteristic of PMA at $\alpha = 0.15$. The absence of the methyl group and consequently the lower potential barrier for segmental rotational reorientation resulting in a more extended coil conformation may explain the higher segmental rotational mobility in PAA when compared with PMA. The lower potential barrier for segmental rotational reorientation in PAA seems to be confirmed also by the value of E_S^{appar} determined for PAA, which is slightly lower when compared with the values found for extended PMA conformations previously.[3] We would like to note that even though the high error in the determination of rotational diffusion rates prevented us from discussing their α dependence, the data in Figure 6 seem to indicate that the PAA segmental rotational mobility is lowest for $\alpha = 1.0$, as in the case of extended PMA conformation (Figure 7 of ref 3), and that the internal rotational mobility of the spin label (and consequently also the degree of anisotropy N) increases with increasing α. Such behavior is in full agreement with the expected stiffening and uncoiling of the polyelectrolyte chain due to electrostatic repulsion between charged COO^- groups, the concentration of which increases with increasing α.

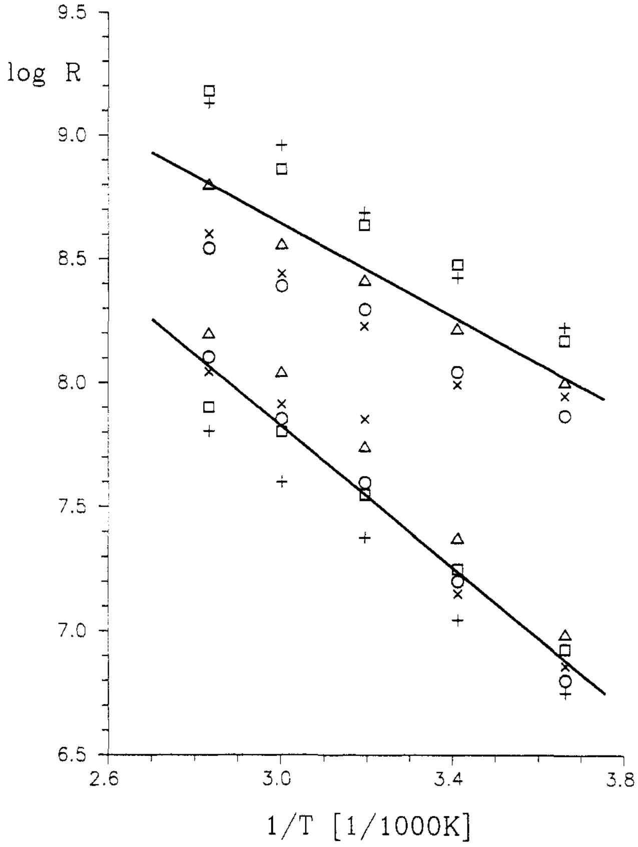


Figure 6. Arrhenius plot of parameters R_S and R_I (lower and higher values, respectively), characterizing the segmental rotational mobility of SL-PAA and internal rotational mobility of the spin label attached to PAA, respectively, in dilute aqueous solutions: $\alpha = 0.0$ (○), $\alpha = 0.2$ (×), $\alpha = 0.3$ (△), $\alpha = 0.5$ (□), and $\alpha = 1.0$ (+). Both linear best fits (—) were calculated using the data for all degrees of neutralization α studied.

Complexation of SL-PAA with PEO and PVP. We tried to prepare soluble complexes of SL-PAA by mixing aqueous solutions of PEO or PVP with solutions of SL-PAA neutralized to different degrees. The volumes of component solutions were adjusted to reach the same concentration of repeating units of both polymers in the mixed solutions. In contrast to published data, we observed immediate precipitation of the complex when mixing the SL-PAA solution at $\alpha = 0.0$ and 0.1 with both PEO and PVP solutions. EPR measurements proved that the remaining aqueous solvent contained only a trace concentration of the free spin label in this case. The same effect was observed for both PEO samples and also in mixed 20% aqueous dioxane solvent. When a smaller volume of PEO or PVP solution was added to the same SL-PAA solution, the intensity of the EPR spectrum of SL-PAA was roughly proportional to the difference between the concentration of PAA and PEO or PVP repeating units. The mixing of more neutralized SL-PAA solutions at $\alpha = 0.2$–1.0 with PEO or PVP has practically no effect on the EPR spectra, except for the slight decrease in intensities due to dilution.

These experiments proved the formation of a strong complex between SL-PAA containing long unperturbed sequences of acrylic acid repeating units (at $\alpha = 0.0$ and 0.1) and PEO or PVP. Precipitation of the complex from an aqueous solution made impossible intended studies of the effect of complexation on PAA segmental rotational dynamics. The precipitation, which was not observed in previous fluorescence studies,[6–8] may have occurred due to the high molecular weight and high concentration of SL-PAA in the solution. The concentration used in our experiments represents a compromise, with respect to the sensitivity of the EPR technique, between the molar concentration of the spin-labeled chain units in PAA and the concentration of SL-PAA in aqueous solution. The presence of spin labels attached to PAA chains, which are not able to contribute significantly to the creation of hydrogen bonds, should rather prevent PAA from complexation due to the shortening of unperturbed sequences of acrylic acid chain units. Complex formation and precipitation from the solutions strongly depend on the degree of PAA neutralization. Another possible reason for the disagreement observed may consist of inaccuracy of the adjustment of the degree of neutralization of PAA samples used in the fluorescence studies. This inaccuracy may result from accidental slight neutralization of the PAA stock solution considered to be completely nonneutralized ($\alpha = 0.0$); we mention this possibility because no data excluding such an event (comparison of the concentrations of the PAA chain units determined by weight with the concentrations determined by titration) are given in the quoted papers.

Conclusions

EPR spectra in the temperature range 273–253 K of SL-PAA in aqueous solutions at degrees of neutralization α ranging from 0.0 to 1.0 were simulated using an axially symmetric Brownian rotational diffusion as a model for the rotational diffusion of the spin label. The temperature dependence of the parameters characterizing both the segmental rotational mobility and the internal rotation of the spin label relative to the PAA chain was determined by this process. The segmental rotational dynamics of SL-PAA, which is expected to show normal polyelectrolyte behavior in aqueous solutions, was found to be nearly independent of its degree of neutralization. The resulting minor effect of the PAA coil extension on its segmental rotational dynamics contrasts with the significant effect of the PMA conformational transition reported previously.[3] The absence of the methyl group is probably responsible for a higher segmental rotational mobility in SL-PAA at all degrees of neutralization and in the entire temperature range studied, in comparison with SL-PMA under the same conditions. The formation of strong complexes between SL-PAA in aqueous solutions at $\alpha = 0.0$ and 0.1 and PEO or PVP, which immediately precipitate from the solution, was observed. Complexation of SL-PAA neutralized to higher degrees ($\alpha = 0.2$–1.0) with PEO or PVP was not observed in aqueous solutions, probably due to the absence of sufficiently long unperturbed sequences of acrylic acid chain units in such solutions.

Acknowledgment. This research was supported by the Grant Agency of the Academy of Sciences of the Czech Republic, Grant No. 45023, by the Grant Agency of the Czech Republic, Grant No. 203/93/1058, and by the U.S.-Czech Science and Technology Program, Grant No. 92064. We are very grateful to Dr. M. Bohdanecký, Dr. H. Pospíšil, and Mrs. D. Kotíková from this Institute for stimulating discussions, for valuable assistance in the implementation of computer programs, and for a number of analytical determinations.

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