affected by entanglements. Another approach to these questions will be proposed in the next paper of this series, using probes with short chains of variable length.

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References and Notes

(1) B. Valeur, J. P. Jarry, F. Geny, and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 667, 675 (1975).
(2) A. A. Jones and W. H. Stockmayer, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 847 (1975).
(3) J. T. Bendler and R. Yaris, *Macromolecules*, **11**, 650 (1978).
(4) C. K. Hall and E. Helfand, *J. Chem. Phys.*, **77**, 3275 (1982).
(5) J. L. Viovy, L. Monnerie, and J. C. Brochon, *Macromolecules*, **16**, 1845 (1983).
(6) See, for instance, J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, 1970.
(7) See, for instance, "Dielectric Properties of Polymers", F. E. Karasz, Ed., Plenum Press, London, 1972.
(8) H. W. Spiess, *J. Chem. Phys.*, **72**, 6755 (1980).
(9) P. Lindner, E. Rossler, and H. Sillescu, *Makromol. Chem.*, **182**, 8653 (1981).
(10) O. W. Howarth, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1219 (1980).
(11) See, for instance, P. Törmala, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C17**, 197–357 (1979).
(12) J. P. Jarry and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 443 (1978); **18**, 1879 (1980).
(13) G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1971).
(14) B. Valeur and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 11, 29 (1976).
(15) J. C. Brochon in "Protein Dynamics and Energy Transduction", Shin'ishi Ishiwata, Ed., Taniguchi Foundation, Japan, 1980.
(16) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.
(17) D. M. Rayner, A. E. McKinnon, A. G. Szabo, and P. A. Hacket, *Can. J. Chem.*, **54**, 3246 (1976).
(18) J. Durbin and G. S. Watson, *Biometrika*, **37**, 409 (1950); **38**, 159 (1951).
(19) K. Kinosita, S. Kawato, and A. Ikegamai, *Biophys. J.*, **20**, 289 (1977).
(20) G. Williams, *Adv. Polym. Sci.*, **33**, 59 (1979).
(21) G. D. Patterson, C. P. Lindsey, and J. R. Stevens, *J. Chem. Phys.* **70**, 643 (1979).
(22) G. D. Patterson and C. P. Lindsey, *Macromolecules*, **14**, 83 (1981).
(23) G. D. Patterson, *Adv. Polym. Sci.*, **48**, 125 (1983).
(24) T. A. Weber and E. Helfand, *J. Phys. Chem.*, **87**, 2881 (1983).
(25) J. L. Viovy, Thêse, Université Pierre et Marie Curie, Paris, 1983.
(26) An exponential decay of the orientation autocorrelation function at long time would lead to a monomer translation diffusion coefficient which tends toward infinity when the length of the chain increases. Thus, the exponential behavior should cross over somewhere to a $t^{-1/2}$ behavior in order to be consistent with the Rouse regime (P. G. De Gennes, *Physics*, (*Long Island City, N.Y.*) **3**, 37 (1967)).

Effect of Main-Chain Double Bond on Dynamics of Polystyrene: An ESR Study of Macromolecules Spin Labeled by Copolymerization

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ABSTRACT: ESR relaxation measurements were carried out for a dilute toluene solution of in-chain-labeled polystyrene containing double bond in the main chain next to the spin label. The temperature was varied from −20 to +93 °C. It was found that the correlation time is larger by an order of magnitude than that of the unlabeled polystyrene, which can be explained by the influence of double bond on the segmental motion. The number of monomer units involved in the ESR relaxation process was estimated as 2–4. The preparation of spin-labeled polystyrene copolymer was also described.

Introduction

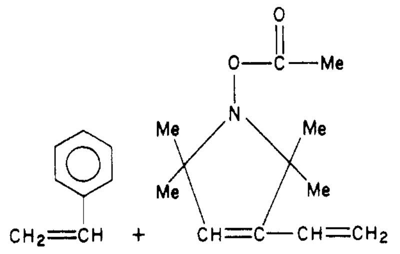
ESR spectroscopy is a useful technique for investigating the dynamics of spin-labeled macromolecules, in the present work, polystyrene. The labels can be covalently bound to different parts of the polystyrene: at the end of the chain, in the side chain, or within the chain. Friedrich et al. have reviewed the intramolecular motion of polystyrene in dilute solution.[1] The measurements have clearly demonstrated the segmental character of motion involved in the relaxation process since the correlation time was found to be independent of the molecular weight above 10 000.

Correlation times of polystyrene samples spin labeled within the chain ($\tau_c(317\text{ K}) = 1.6 \times 10^{-10}$ s)[1] and in the side chain ($\tau_c(317\text{ K}) = 3.5 \times 10^{-10}$ s)[2] respectively coincide with that of the segmental motion of unlabeled polystyrene ($\tau_c(317\text{ K}) = 2 \times 10^{-10}$ to 6×10^{-10} s, studied by ^{13}C NMR).[3-5] This indicates that the correlation time of the spin label is mainly affected by the segmental motion of the polystyrene chain and is not altered significantly by the conformational changes of the label itself. Consequently, the correlation time measured in polystyrene samples reflects the local motion of segments in the vicinity of labels in the polymer chain.

The aim of this paper is to investigate the effect of main-chain double bond on the local segmental motion of polystyrene in dilute solution via monitoring the correlation time of rotational diffusion motion of a special spin label. A double bond in the polymer backbone can hinder the motion of segments in its vicinity and alter the correlation time with respect to the unlabeled polystyrene. In order to carry out experiments we have synthesized a special in-chain-labeled polystyrene copolymer in which the spin label has a double bond in the main chain next to the in-chain five-member ring containing the nitroxide group (II). The synthesis was carried out by copolymerization of the unsaturated spin label precursor and styrene. Our paper reports the synthesis of this polystyrene and determination of the correlation time for the labeled polymer and give a comparison of this correlation time with literature data in order to estimate the influence of double bond on the local segmental motion of polystyrene.

Experimental Section

Synthesis. The in-chain-labeled polystyrene copolymer (M_w = 67 400) was synthesized as follows. A mixture of 5 mL of purified and freshly distilled styrene, 82 mg of azobis(isobutyronitrile), and 10 mg of 1-acetoxy-2,2,5,5-tetramethyl-3-vinylpyrroline[6] (I) (suitable for labeling and not inhibiting the radical copolymerization) was deoxygenated, sealed in an ampule, and then polymerized at 90 °C for 90 min. The product was dissolved in 80 mL of benzene, precipitated in 800 mL of methanol at 0 °C, filtered, and dried. It weighed 4.061 g. In order to prepare the stable spin label 2,2,5,5-tetramethylpyrroline 1-oxyl in the polystyrene backbone, the acetyl groups were eliminated. The copolymer (2.01 g) in 100 mL of 1 N NaOH solution was intensively stirred for 25 min. The mixture was then filtered, the product was washed until free of alkali and dried. The substance (1.06 g) was dissolved in 20 mL of benzene, stirred intensively with 1.5 g of PbO_2 for 30 min, and filtered. The copolymer was precipitated from the filtrate by methanol, filtered, dried, and stored in a nitrogen atmosphere until used. The ratio of spin labels to monomer units in the polystyrene copolymer was 1:~10^5.



I

Procedure. Samples of dilute toluene solution (10% by weight) were prepared and subjected five times to freeze-pump-thaw cycles. ESR spectra were recorded on a JEOL JES-FE 3X spectrometer at 100-kHz modulation frequency. Temperature was varied from -20 to +93 °C with an accuracy of ±1 °C. At lower temperatures the asymmetric line shape prevented the application of second-order relaxation theory for isotropic rotation, while at higher temperature the nitroxide spin label was unstable. Magnetic field was measured by a Systron digital gauss meter with a precision of 2 μT.

Analysis of Spectra

The rate of rotational motion of the spin labels was analyzed according to the second-order relaxation theory for isotropic rotation.[7,8] Rotational correlation time was determined from the Kivelson equation[9]

$$W_{-1} + W_{+1} - 2W_0 = 2C$$

where

$$W_i = 1/T_2(m_i)$$

$$C = (b^2/8)\tau_c$$

$$b = \frac{2}{3}\left(A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})\right)$$

Here W_i is the half-width of the ith line, T_2 is the spin relaxation time, m_i is the magnetic quantum number, τ_c is the correlation time, and A_{ii} are the tensor elements of hyperfine interaction. Diagonal elements of the hyperfine tensor were calculated from the spectra of the frozen solution detected at -120 °C: A_{zz} = 93.77 MHz (3.35 mT) and $A_{xx} = A_{yy}$ = 7.28 MHz (0.26 mT). For the correlation time we have the expression

$$\tau_c = 1.59 \times 10^{-15}\left[\left(\frac{h_0}{h_{-1}}\right)^{1/2} + \left(\frac{h_0}{h_{+1}}\right)^{1/2} - 2\right]W_0$$

where h_i is the amplitude of ith line and W_0 is the half-width of central line expressed in hertz.

The ESR line width of nitroxide spin label with four methyl groups vicinal to the NO group is inhomogeneously broadened by unresolved hyperfine structure of hydrogens in the ring. The effect of inhomogeneous broadening was taken into account by the method outlined in detail by Bales.[10] The intrinsic line width was obtained by using eq 9 in ref 10.

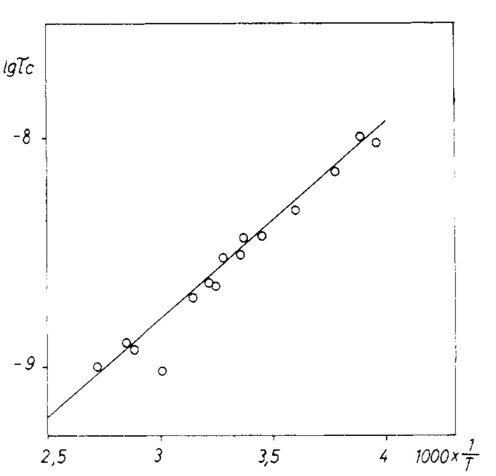


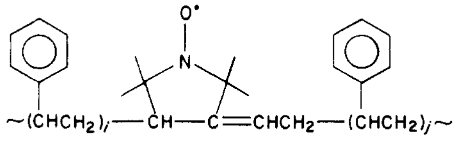
Figure 1. Least-squares Arrhenius plot of log τ_c against $1/T$ for in-chain-labeled polystyrene with double bond.

Discussion

ESR measurements were carried out at different temperatures in order to determine the correlation time of spin-labeled copolymer synthesized previously. The correlation time, calculated from the corrected width of inhomogeneously broadened lines, was fitted to the Arrhenius equation in Figure 1

$$\tau_c = \tau_0 \exp(E/RT)$$

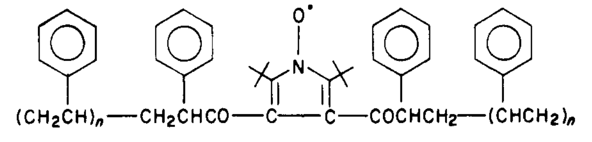
where $\tau_0 = 4.2 \times 10^{-12}$ s and E = 16.38 kJ/mol. This correlation time (τ_c(317 K) = 2.1×10^{-9} s) is much longer than that of the segmental motion of polystyrene (τ_c(317 K) = 1.6×10^{-10} to 6×10^{-10} s).[1-5,11] The long correlation time indicates the presence of rigid in-chain labels in the copolymer backbone whose structure was formed by copolymerization of styrene with spin label I via a diene-type reaction[12]



II

The label can be considered to be the =$CHCH_2$ group next to an in-chain five-member ring containing the nitroxide group. We compared the relaxation time of copolymer II to that of the in-chain-labeled polystyrene studied by Friedrich et al.[1]

Macromolecules **1985,** *18,* 1139–1144



The long correlation time measured in samples of copolymer II corresponds to the presence of main-chain double bond which slows down the local segmental motion of the polystyrene chain.

The effect of the double bond on the segmental motion can be treated on the analogy of crankshaft transitions of the polystyrene chain. The number of monomer units involved in the relaxation process can be obtained according to the treatment described in detail by Mashimo[13] and Friedrich et al.[1] On the basis of Kramers'[14] and Helfand's[15] theory (in the limit of high viscous damping and for the crankshaft motion) the correlation time is related to the solvent viscosity η and the temperature T

$$\tau_c \sim \frac{2\pi}{\gamma}\sum_i r_i^2 \xi_i \exp(E^*/RT)$$

where E^* is the height of the internal potential barrier for the rotational motion of monomer units. The potential barrier has a form $U = {}^1/_2E^*(1 - \cos 3\theta)$ with the curvature $\gamma = \mathrm{d}^2U/\mathrm{d}\theta^2$ in its minimum and maximum, r_i is the distance of the ith monomer unit from the shaft, and ξ_i is the frictional coefficient. If the monomer unit is treated as a sphere of radius a, then $\xi_i = 6\pi a\eta$ according to the Stokes law. Using a value of 3 Å for a[13] and $E^* = E - E_\eta = 7.69$ kJ/mol, where $E_\eta = 8.69$ kJ/mol is the activation energy for the viscosity of toluene,[1] we obtain

$$24 \text{ Å}^2 < \sum_i r_i^2 < 73 \text{ Å}^2$$

The mean of r_i cannot be affected significantly by the double bond; therefore it is taken to be 4 Å according to the literature.[11,13,16] Consequently, the motion of the label in structure II is analogous to the crankshaft motion of the chain in which 2–4 monomer units are involved, in contrast to the case of unlabeled polystyrene as well as spin-labeled polystyrene without a double bond, where only one monomer unit is involved in the ^{13}C NMR and ESR relaxation processes.[1]

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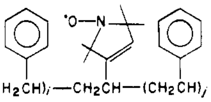
References and Notes

(1) Friedrich, C.; Lauprete, F.; Noel, C.; Monnerie, L. *Macromolecules* **1981**, *14*, 1119.
(2) Bullock, A. T.; Cameron, G. G.; Reddy, K. *J. Phys. Chem.* **1973**, *77*, 1635.
(3) Gronski, W.; Schäfer, T.; Peter, R. *Polym. Bull.* **1979**, *1*, 319.
(4) Inoue, Y.; Konno, T. *Polym. J.* **1976**, *8*, 457.
(5) Allerhand, A.; Hailstone, R. K. *J. Chem. Phys.* **1972**, *56*, 3718.
(6) The synthesis of the spin label will be published in *Can. J. Chem.*
(7) Freed, J. H.; Bruno, G. V.; Polnaszek, C. F. *J. Phys. Chem.* **1971**, *75*, 3385.
(8) Goldman, S. A.; Bruno, G. V.; Polnaszek, C. F.; Freed, J. H. *J. Chem. Phys.* **1972**, *56*, 716.
(9) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1095.
(10) Bales, B. L. *J. Magn. Reson.* **1982**, *48*, 418.
(11) Miller, W. G. In "Spin Labeling"; Berliner, L. J., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 4, p 173.
(12) Theoretically the copolymerization can proceed also via the vinyl group of spin label I:



In this case a short correlation time is expected which should be close to the value for spin-labeled polystyrene measured by Bullock et al.[2]
(13) Mashimo, S. *Macromolecules* **1976**, *9*, 91.
(14) Kramers, H.-A. *Physica* **1940**, *7*, 284.
(15) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(16) Natta, G. *Macromol. Chem.* **1960**, *35*, 94.

Sequence Distribution of Carboxyl Groups in Hydrolyzed Polyacrylamide

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ABSTRACT: A carbon-13 NMR study of hydrolyzed polyacrylamides has demonstrated that mild alkaline hydrolysis provides a well-spaced distribution of carboxyl groups along the polymer chain. This distribution is somewhat a function of ionic strength during hydrolysis, supporting an electrostatic component in resolution of rate constants. Acid hydrolysis, on the other hand, tends to develop blocks of carboxyl groups. A combination of the two modes suggests the possibility of developing controlled blocks of carboxyl groups along the chain.

Introduction

Fundamental correlations of polymer structural effects on interaction of flocculants with clays require knowledge of the microstructure of polymers. Unfortunately, many publications make tacit assumptions in this area and then look for effects. Although it is generally believed that alkaline hydrolysis of polyacrylamide provides a relatively uniform distribution of carboxyl groups along the polymer chain, evidence has been indirect.[1-5] The present investigation provides a relatively direct, quantitative measure of the sequence distribution generated under mild, homogeneous hydrolysis conditions, using carbon-13 NMR spectroscopy. These polymers, and others differing only in molecular weight, are being used in studies on flocculation of clays. Carboxyl heterogeneity which can develop between chains is discussed elsewhere.[6]

Experimental Section

All the hydrolyzed polymer samples used in this study were obtained from the same sample of homopolymer, designated 8103-88. It had been prepared by free-radical solution polym-

0024-9297/85/2218-1139$01.50/0