Features of Complexing and the Solution Structure from the Data on Rotational and Translational Mobility of Molecular Probes in Cellulose Acetate Solutions

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ABSTRACT: ^{13}C NMR relaxation and self-diffusion measurements of the molecular probes added to dimethyl sulfoxide–cellulose acetate solutions have been carried out as a function of concentration and degree of substitution of the polymers. The probes differ in their capacity for complexing with the hydroxyl groups of the cellulose acetate. Spin–lattice relaxation rates and self-diffusion coefficients of the hydrogen-bonding probes vary with the hydroxyl group content of the polymer, and the diffusion coefficients of the inert probes are shown to be sensitive to the difference in the supermolecular organization of the solutions. The analysis of molecular probe hydrogen bonding with the polymers allows us to obtain information on the OH groups' binding capacity and their accessibility at high polymer concentrations. The relaxation rates of bound species under the varied conditions are calculated.

Introduction

The characteristics of rotational and translational molecular motion proved to be sensitive to the complexation in solutions caused, for example, by hydrogen bonding.[1-4] Different NMR techniques have been widely employed for studying molecular mobility; e.g., NMR relaxation methods provide information on molecular rotation. Measurements of spin-relaxation times, T_1, of the solvent molecules were shown to be effective for elucidating solvent–solute complex formation and specific solvent–solute interactions in polymer solutions.[5-7] A great amount of work has been done on studying the small molecule mobility in polymer solutions.[8,9] The most frequent use of the small molecule diffusion observations is in the investigation of the shape of macromolecules[10,11] and in that of the supermolecular organization of the solutions,[12,13] though the quantitative information on solvent–polymer bonding may be successfully obtained from data on solvent translational mobility as a function of the concentration of polymer reactive sites.[14,15]

In this paper we propose the use of molecular active and inert probes for studying the chemical properties of polymers and the structural characteristics of polymer solutions. Small molecules added in low concentration to polymer solutions and having varying capacities for complexing with polymer, for example, by hydrogen bonding, are called molecular probes (MP). MP which successfully compete with the solvent in the formation of hydrogen bonds are termed active, while MP with a lower complexation capacity than that of the solvent are termed inert. Structural and chemical information on polymer solutions is obtained from the comparison of the data on longitudinal relaxation rates, $W = 1/T_1$, of ^{13}C nuclei of probe molecules and the self-diffusion coefficient, D, of active and inert MP. The advantage of the combined use of relaxation rates and self-diffusion coefficients of active probes for analyzing their complexation with polymer[4,16] will be discussed later. The data on inert MP dynamics allowed us to model the behavior of free active probes at high polymer concentrations.

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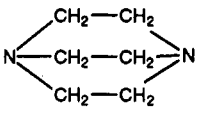
Actually, in case of fast exchange[17] between free probe molecules and those bound to the polymer, the experimentally measured parameter P (P means W or D) is the weighed sum of its values for free and bound probe molecules:

$$P = xP_b + (1 - x)P_f \quad (1)$$

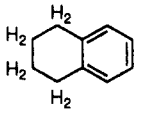
where x is the fraction of bound molecules. P_f is most frequently considered as the parameter of motion in pure solvent, while this is valid only for dilute polymer solutions. In highly concentrated polymer solutions the diffusion of free probes may be reduced because the probe molecules have to move among the obstructions presented by the macromolecules. The theoretical expressions describing the obstruction effect are rather approximate,[11,18] and one should also take into account alternation in intermolecular interactions in polymer solution relative to the pure solvent that may strongly influence the probe molecule's mobility.[19,20] Thus, the experimental data on W and D of free probes would be higly desirable for analyzing hydrogen bonding in the solutions under study.

Experimental Section

Cellulose acetates with different degrees of substitution, γ, of the hydroxyl groups by acetate groups dissolved in totally deuterated dimethyl sulfoxide have been investigated. The value of γ characterizes the number of OH groups substituted in a polymer unit; namely, the polymer with a higher γ has a lower amount of hydroxyl groups. 1,4-Diazabicyclo[2.2.2]octane (DABO) was used as the active probe; in addition to a high capacity for formation of hydrogen bonds with the residual OH groups of cellulose acetates, it also has a simple ^{13}C spectrum. Incorporation of small amounts (3–5%) of DABO improves the solubility of cellulose acetates in dimethyl sulfoxide, which permits working in the region of high concentrations of polymer. 1,2,3,4-Tetrahydronaphthalene (tetraline) was the inert MP. The concentrations of active and inert probes were 18 and 22 g/dm^3, respectively; i.e., the amount of molecules of each species was about 1×10^{20}.



DABO



tetraline

The cellulose acetate samples with γ equal to 0.60, 1.00, 1.66, 2.38, and 2.9 were obtained by saponification and supplied by

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Polymersintez. The average degree of polymerization of the samples was within the limits of 300–400. The prepared solutions were held at 60 °C for 24 h. A further increase in the holding time did not alter the relaxation characteristics of the MP and did not change the optical properties of the solutions. DABO and tetraline used were obtained from MERCK-Schuchardt.

^{13}C NMR relaxation experiments were performed on a JNM-PS-100 spectrometer equipped with a JNM-FT-100 Fourier transform system. The ^{13}C frequency was 25.15 MHz. The spin–lattice relaxation rates were measured by using the normal inversion-recovery experiment [pulse sequence, 180°(^{13}C)–τ–90°-(^{13}C)–AQ] under proton-decoupling. The decoupled ^{13}C spectrum of DABO contains one peak only as all the nuclei in the molecule are equivalent. To determine the relaxation rate of tetraline, we used the peak attributed to the aromatic ^{13}C at the *ortho* and *meta* positions. The interpretation of the relaxation data was performed by assuming that all ^{13}C relaxation occurs by the dipole–dipolar mechanism under motional narrowing conditions. To test this, we carried out the NOE measurements: all NOE were about 2.0; i.e., the assumption was valid for the ^{13}C of DABO and tetraline in the solutions studied.

Self-diffusion measurements were made on a home-built NMR spectrometer at the ^1H resonance frequency of 23 MHz. The pulsed gradient spin-echo method[21] was used. We varied the magnitude of the pulsed gradient at a constant diffusion time, t_d, the time during which diffusion was measured. In order to prevent unwanted signals of solvent and polymer protons from interfering with the probe protons' signal, we used the totally deuterated dimethyl sulfoxide and chose t_d long enough (20 ms) for polymer protons to relax. Their spin–spin relaxation time, T_2, was found to be about 3 ms in the low-concentration solutions and got shorter as the concentration increased. So, we could observe the signal of protons of the only probe molecules. The measurements for active and inert probes were performed separately. The pulse current in the quadrupole coils was 30 A maximum, and the corresponding magnetic field gradient was 25 T/m. Data were acquired on a Torch-CZ computer. The temperature was 23 °C. The experimental curves obtained in the relaxation and diffusion measurements were single exponential, which could be regarded as the crucial test for the validity of the assumption of fast exchange between the free and bound active probe molecules in the solutions under investigation. The error in the measurements did not exceed 7%.

Results and Discussion

In order to check the sensitivity of the MP relaxation parameters and the diffusional constants to the chemical composition of the polymers, we measured W and D for tetraline and DABO in acetate solutions with various γ at a fixed polymer concentration. The values of W for tetraline are almost independent of γ, while for DABO a dependence of W on γ may be considered as linear within the accuracy of the experiment (Figure 1). The wide range of the change in relaxation rates for DABO permits using this dependence for analytical purposes. The sizes of the DABO and tetraline molecules are similar and the drasti difference between the dependences on γ of the rotational mobility (which determines the relaxation rate) of these molecules can only be due to complexation of DABO molecules with the free OH groups of the polymer. The H bonds result in a decrease in the mobility of the bound molecules and hence an increase in the observed values of the relaxation rates of their ^{13}C nuclei.

The γ dependence of D for DABO (Figure 2) is much more pronounced than for tetraline. However, in the case of translational motion, the diffusion coefficients of inert probes are not constant. They decrease somewhat with decreasing γ; i.e., the supermolecular organization of the polymer solution has a greater effect on the translational diffusion of inert MP than on their rotational motion. It is caused by the fact that in the D measurement we observe the displacement of MP over distances much greater than

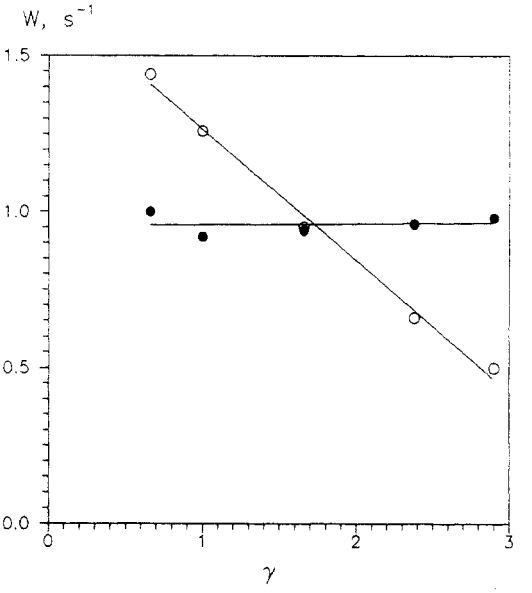

Figure 1. ^{13}C relaxation rates of DABO (○) and tetraline (●) as a function of the substitution degree of cellulose acetates for a 300 g/dm³ concentration of the polymer.

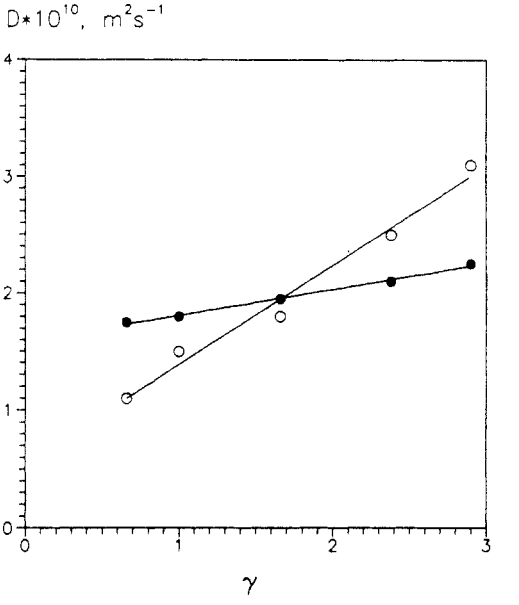

Figure 2. Translational diffusion coefficients of DABO (○) and tetraline (●) molecules as a function of the substitution degree of cellulose acetates for a 250 g/dm³ concentration of the polymer.

the dimensions of one macromolecule. The solutions studied were gel-like at high concentrations, so we assumed existence of the spatial network in the solutions that could be caused not only by entanglements of the chains but also by the hydrogen bonds between the macromolecules. The lower D values of the tetraline molecules in the polymer solutions with lower γ may indicate the difference in the structure of the spatial network formed by the cellulose acetates with different substitution degrees. As γ is decreased, the number of hydroxyl groups increases, and as a consequence, the interaction of the macromolecules with dimethyl sulfoxide and with each other is enhanced. Therefore, one should expect the thickness of the spatial network in the solutions of polymers to increase with decreasing γ due to the greater number of links between the macromolecules. The data on the viscosity of acetate solutions[22] are consistent with this assumption.

The dependences of the W and D of DABO and tetraline on the concentration, c, of cellulose acetates with different values of γ were measured to examine the polymer's

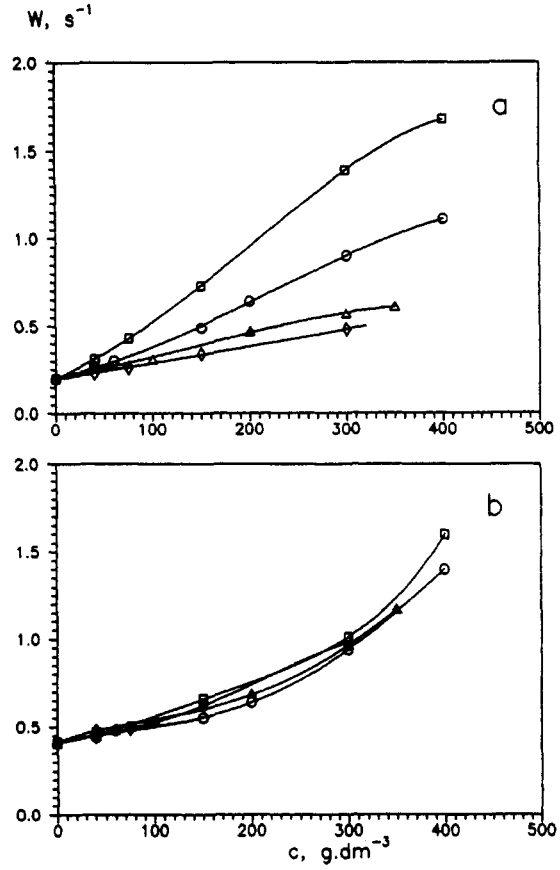

Figure 3. Dependences of the relaxation rates of DABO (a) and tetraline (b) on the concentration of cellulose acetates with different degrees of substitution: 0.60 (□), 1.66 (○), 2.38 (△), and 2.90 (◇).

supermolecular organization and complexing processes in solutions in further detail (Figures 3 and 4). Small molecule mobility in polymer solutions has been most successfully interpreted in terms of free volume theory,[23-25] which is valid for the solutions with not very high solvent volume fractions, v_{sol} ($v_{sol} < 0.8$). In our case, the solvent concentration in the samples under study was rather high and the data on the viscosity of solutions needed for calculation were not available. It can also be noted that the free volume theory does not give the background for understanding the nature of the concentration dependence of the diffusion coefficient in a certain solvent–polymer system. So, we have constrained ourselves with a qualitative description of the dependences and have used the experimental data for characterizing the probe polymer hydrogen bonding. The nature of the dependences of diffusion coefficients of tetraline on c does not contradict the hypothesis of the difference in the solution's spatial network. At low c, the D values are identical within experimental error, while the effect of the structure of the polymer solution on the translational mobility of the MP becomes more pronounced and the variation of the D values of the tetraline molecules in the solutions of acetates with different γ increases with increasing c. Both the enhancement of the relaxation rate and the decrease of the diffusion coefficients of tetraline at higher concentrations of the polymer are most probably caused by the restriction of its rotational and translational mobility because of steric hindrances.

In the case of the active probe, the curves for the concentration dependences of D and W of DABO in cellulose acetate solutions with different γ values (Figures 3 and 4) vary much more significantly since the difference in the nature of the motion of the DABO molecules is a

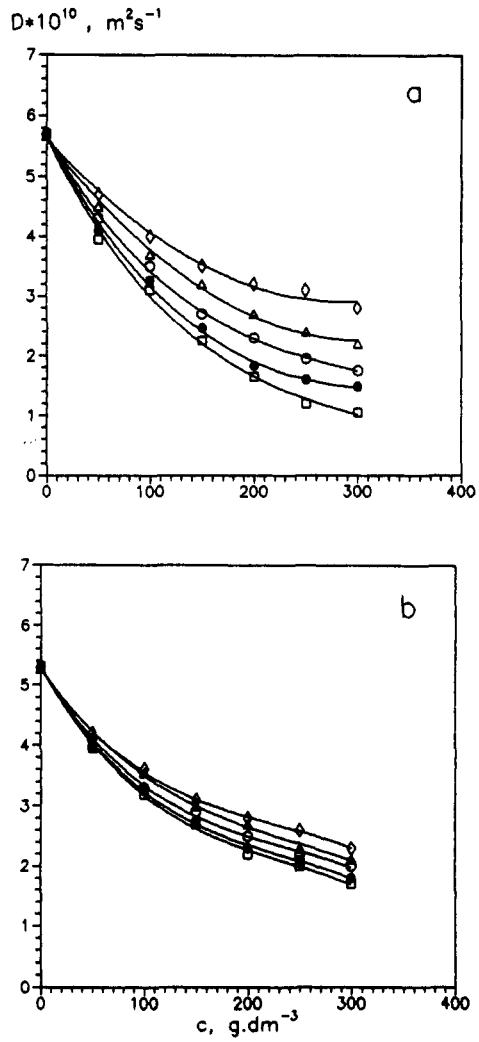

Figure 4. Dependences of the self-diffusion coefficients of DABO (a) and tetraline (b) on the concentration of cellulose acetates with different degrees of substitution: 0.60 (□), 1.00 (●), 1.66 (○), 2.38 (△), and 2.90 (◇).

function not only of the solution structure but also of the various complexations of DABO with the hydroxyl groups of the acetates. For the case of rapid exchange between free and bound DABO molecules, by using eq 1, the experimentally observed values, W and D, can be written as

$$W = xW_b + (1-x)W_f \tag{2}$$

$$D = (1-x)D_f \tag{3}$$

Following Wang,[26] we have neglected the term containing D_b since the polymers used were of sufficiently high molecular weight to be considered as immobile on the time scale of solvent motion even in dilute solutions. This allowed us to evaluate the fraction of bound DABO molecules, x, after determining D_f.

As can be seen in Figures 3 and 4, the characteristics of the molecular probes' mobility are functions of the concentration of the polymer. The W and D concentration dependences of the free active and of the inert probes are caused mainly by the structural change in the organization of polymer solutions. The kind of the concentration dependence of W_f for DABO should be similar to $W(c)$ for tetraline, $W_t(c)$, since the sizes of these molecules are close. Then it seems reasonable to suppose that W_f may be

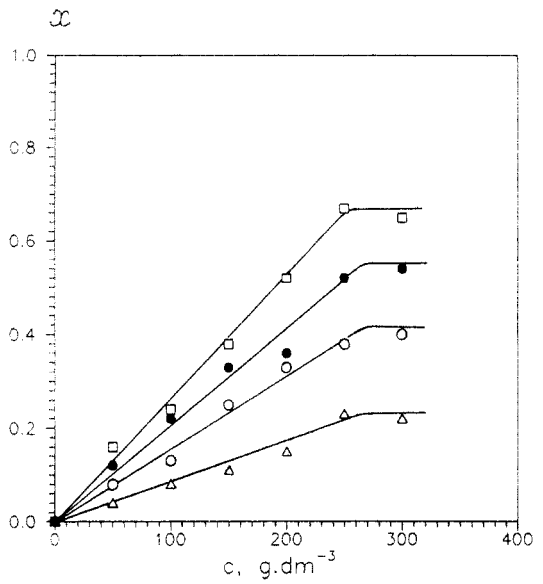

Figure 5. Fraction of bound DABO molecules in the solution relative to the concentration of cellulose acetates with different degrees of substitution: 0.60 (□), 1.00 (●), 1.66 (○), and 2.38 (△).

determined as

$$W_f(c) = W(0)\ W_t(c)/W_t(0) \quad (4)$$

where $W(0)$ and $W_t(0)$ are the relaxation rates of DABO and tetraline, respectively, measured in the pure solvent without polymer. $W_f(c)$ calculated by using this equation for the solutions of cellulose acetates with γ = 0.66, 1.66, and 2.4 were practically equal to the values $W(c)$ of DABO measured in the solution of the polymer with γ = 2.9. This indicates that H bonding of the active MP with the polymer is negligible in the latter case. These $W(c)$ values can thus be used as $W_f(c)$ for DABO molecules in the solutions with γ less than 2.9.

The determination of $D_f(c)$ is complicated by the fact that the diffusion coefficients of the inert probes vary for the cellulose acetate solutions with different γ. So we used as the diffusion coefficients of free DABO molecules in the solution with a certain γ, $D_f\gamma(c)$, the value of $D(c)$ measured in the solution with γ = 2.9 and multiplied it by the appropriate coefficient obtained from the data on the diffusion coefficients of tetraline, D_t:

$$D_f^{\gamma}(c) = D(c)^{\gamma=2.9}(D_t(c)^{\gamma}/D_t(c)^{\gamma=2.9}) \quad (5)$$

The calculated $D_f(c)$ values have been used for evaluating the fraction of bound active probe molecules (eq 3). In Figure 5 values of x are plotted as a function of the total amount of added polymers.

The simplest scheme of the complexation of DABO with the OH groups of the polymer is the following:

$$\text{DABO} + \text{OH} \xrightarrow{k} \text{DABO}\cdots\text{OH}$$

At small concentrations of the polymer we assume all the OH groups to be accessible to the probe molecules. The binding constant, k, is then given as

$$k = c_b/ps = c_b/(p_o - c_b)\ (s_o - c_b)$$

where p and s are the concentrations of free probes and reactive sites, c_b is the concentration of bound probes, and p_o and s_o are the total amounts of probes and reactive sites. In the solution having been investigated the condition $c_b \ll s_o$ substantially correct, so that

$$k \approx c_b/(p_o - c_b)s_o$$

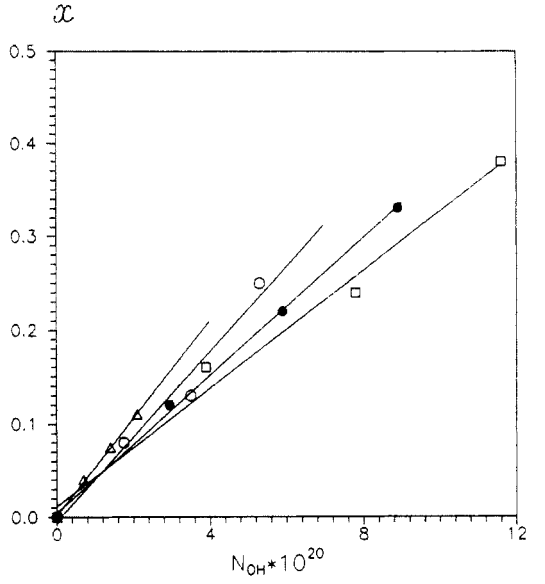

Figure 6. Dependence of the fraction of bound DABO molecules on the total amount of hydroxyl groups in the solutions of cellulose acetates of different substitution degrees: 0.60 (□), 1.00 (●), 1.66 (○), and 2.38 (△).

Table I. Effect of the Cellulose Acetate's Substitution Degree on the Binding Capacity and the Accessibility of Their Hydroxyl Groups

γ	k, mol^{-1}	N^*	γ	k, mol^{-1}	N^*
0.60	11.0	0.05	1.66	14.0	0.08
1.00	12.3	0.06	2.40	18.3	0.10

and

$$c_b \approx kp_os_o/1 + ks_o$$

Using $x \equiv c_b/p_o$, we have

$$x \approx ks_o/1 + ks_o \quad (6)$$

It follows from this expression that the initial slope of the x dependence on the whole number of hydroxyl groups, N_{OH}, is equal to k. These dependences are shown in Figure 6. From the data presented in Figure 6 one may conclude that the complexation capacity of the hydroxyl groups of the cellulose acetates in solutions decreases with decreasing γ. It may be caused by the fact that the active probe bound to a OH group of a polymer with a low substitution degree can shield the neighboring OH groups, and hence the effective number of reactive sites is lower than in solutions with higher γ values. The calculated k values are reported in Table I.

Equation 6 is valid only for dilute solutions of the polymers. For higher amounts of the cellulose acetates, the number of OH groups accessible to the probe is not directly proportional to the polymer concentration. The self-association of macromolecules occurring due to H bond formation between their hydroxyl groups and steric shielding of the groups may cause the situation when the addition of the polymer does not lead to an increase of the amount of free OH groups. This may account for the plateau region of the curves at high concentrations in Figure 5. The x "plateau" values enabled us to evaluate the number of DABO molecules, N^*, bound to a single OH group of the polymer. The total amount of DABO molecules was 1×10^{20} and was constant in all the experiments. The calculated N^* values are presented in Table I and indicate that the hydroxyl groups of the polymers with higher γ are less shielded in the solutions at high concentrations than those of the polymers with lower γ.

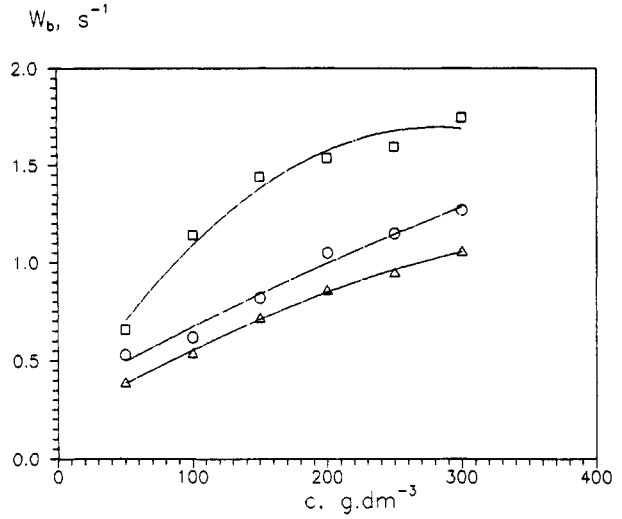

Figure 7. Calculated relaxation rates of DABO molecules bound to a macromolecule as a function of polymer concentration for acetates with different substitution degrees: 0.60 (□), 1.66 (○), and 2.38 (△).

Substituting the determined x values into eq 2, we can obtain the relaxation rates of the bound probes that are very much influenced by the segmental mobility of macromolecules in solutions.[27] As far as we know, the dynamics of dissolved cellulose acetates has not been studied yet. As the polymer concentration is increased, the W_b value rises montonically (Figure 7), indicating that the segmental mobility is slowing. To a certain extent the W_b values are the quantitative characteristics of the thickness of the polymer network in solution. The greater values of W_b in solutions with lower γ support our assumption regarding the higher thickness of the network in these solutions.

Conclusion

The spin–lattice relaxation rates and the self-diffusion coefficients of active molecular probes added to polymer solutions are sensitive to the difference in chemical composition of similar polymers, e.g., to the substitution degree of cellulose acetates. The information on the reactivity and the accessibility of the polymer reactive sites can be obtained by analyzing how the characteristics of rotational and translational motion of the molecular probes depend on the polymer concentration. In cellulose acetate solutions the binding capacity of hydroxyl groups was found to be higher for the polymers with greater γ values while their shielding was less at high polymer concentrations. The polymer network formed by the macromolecules appeared to be thicker in the solutions with lower γ.

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References and Notes

(1) Hertz, H. G.; Zeidler, M. D. In *The* Hydrogen Bond; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; pp 1029–1061.
(2) Kratochwill, A. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 607–610.
(3) Smith, W. B. *Org. Magn. Reson.* **1981**, *17*, 151–152.
(4) Belmajdoub, A.; Boubel, J. C.; Canet, D. *J. Phys. Chem.* **1989**, *93*, 4844–4847.
(5) Sillescu, H.; Brussau, R. G. *Chem. Phys. Lett.* **1970**, *5*, 525–526.
(6) Brussau, R. G.; Sillescu, H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 31–38.
(7) Daragan, V. A.; Ilyina, E. E.; Myasoedova, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1761–1765.
(8) Von Meerwall, E. D. *Adv. Polym. Sci.* **1983**, *54*, 1.
(9) Maklakov, A. I.; Skirda, V. D.; Fatkullin, N. F. *Self-diffusion in Polymer Solutions and Melts*; Kazan University Press: Kazan, 1987.
(10) Callaghan, P. T.; Lelievre, J. *Biopolymers* **1985**, *24*, 441–445.
(11) Clark, M. E.; Burnell, E. E.; Chapman, N. R.; Hinke, J. A. M. *Biophys. J.* **1982**, 289–292.
(12) Karger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* **1988**, *12*, 1–89.
(13) Muhr, A. H.; Blanshard, J. M. V. *Polymer* **1982**, *23*, 1012–1025.
(14) Rhee, K. W.; Gabriel, D. A.; Johnson, C. S. *J. Phys. Chem.* **1985**, *89*, 3193–3196.
(15) Lee, J. A.; Lodge, T. P. *J. Phys. Chem.* **1987**, *91*, 5546–5548.
(16) Daragan, V. A.; Ilyina, E. E.; Myasoedova, V. V.; Prisment, A. E. *The Problems of the Solvation and Complexing in Solutions*, Proceedings of the 4th Soviet Conference; Soviet Chemical Society: Ivanovo, 1989; p 138.
(17) Zimmermann, J. R.; Brittin, W. E. *J. Phys. Chem.* **1957**, *61*, 1328–1333.
(18) Pace, R. J.; Datyner, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 477–488.
(19) Steele, W. A. *J. Chem. Phys.* **1963**, *38*, 2404–2411.
(20) Kirkwood, J. G. *J. Chem. Phys.* **1946**, *14*, 180–201.
(21) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288–293.
(22) Myasoedova, V. V. In *Solutions of Non electrolytes in Liquids*; Krestov, G. A., Ed.; Nauka: Moscow, 1989; p 203.
(23) Fujita, H. *Fortschr. Hochpolym.-Forsch.* **1961**, *3*, 1–32.
(24) Vrentas, J. S.; Duda, J. G. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403–441.
(25) Von Meerwall, E. D. *Rubber Chem. Technol.* **1985**, *58*, 527–560.
(26) Wang, J. H. *J. Am. Chem. Soc.* **1954**, *76*, 4755–4761.
(27) Heatly, F. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. D., Eds.; Pergamon Press: Oxford, 1989; Vol. 1, pp 377–397.