Motion of Polymer Chains in Solutions. 2. Reorientational Motion of Phenyl Groups of Polystyrene Chains in Solutions of Carbon Disulfide and Chloroform by Raman Line Shape Analysis

Shinobu Koda,[†] Hiroyasu Nomura,*[‡] and Yutaka Miyahara[‡]

Departments of Chemical Engineering and Synthetic Chemistry, Faculty of Engineering, Nagoay University, Chikusa-ku, Nagoya-shi, 464 Japan. *Received October 7, 1977*

ABSTRACT: The reorientational relaxation time in carbon disulfide and chloroform of the phenyl groups of polystyrene chains was measured by Raman line shape analysis. In the low molecular weight region, the molecular weight dependence was almost linear. However, in the higher molecular weight region, $\tau_{\rm or}$ approaches a constant value. Clear molecular weight dependence of $\tau_{\rm or}$ can be found at higher concentration but dependence becomes less clear as the concentration decreases. The limiting reorientational relaxation times ($\tau_{\rm or}{}^0$) of phenyl groups of polystyrene were obtained from the concentration dependence. These values increase with an increase in the molecular weight. However, over the molecular weight 1000, the $\tau_{\rm or}{}^0$ reached a constant value.

I. Introduction

To study the molecular motions of polymer chains in solutions, there are a group of techniques such as ultrasonic absorption,[1] dielectric dispersion,[2] life-time measurements of fluorescence,[3] depolarized Rayleigh scattering,[4] electron spin resonance,[5] and pulsed nuclear magnetic resonance.[6] Various relaxation times in molecular motions of polymer chains can be obtained by means of these techniques.

The relaxation times obtained by these methods are related to the local segmental motions of the backbone and to the motions of side chains of polymer molecules. Such local motions are determined by local forces surrounding the segments, that is, by some short range forces. Therefore, it is usually believed that these relaxation times should be independent of molecular weight.

Nevertheless, there are a number of experimental results in which the physical quantities to be determined by local forces show clear molecular weight dependence until the molecular weight reaches a fairly high value. For example, partial molar volume,[7] partial specific compressibility,[8] optical anisotropy,[9] specific refractive index,[9] and hydration number[10] show such effects.

In a previous paper,[11] we also reported the molecular weight dependence of the reorientational relaxation time of phenyl groups in polystyrene chains in carbon tetrachloride, determined by laser Raman spectroscopy. The same quantities can also be extracted in principle from NMR relaxation experiments, infrared band shape analysis, and depolarized Rayleigh scattering. Compared with these methods, the Raman studies can give the information of interest more directly.

In the present paper, we will report the molecular weight and the concentration dependence of the reorientational relaxation times of phenyl groups in polystyrene chains in carbon disulfide and chloroform solutions.

II. Experimental Section

For obtaining the reorientational relaxation times ($\tau_{\rm or}$) of phenyl groups in polystyrene chains in solution, the Raman line shape of the $\nu_2(A_{1g})$ fundamental mode of ring stretching was used. Its Raman frequency is 1002 cm^{-1}.

An argon ion laser was used for the light source excited at 488 nm in all measurements. The scattered light was analyzed with a double monochrometer, JRS-U1 Laser Raman spectrometer, manufactured by Japan Electronic Co. The details of experimental procedures have been reported previously.[12]

The polystyrene samples used were the monodisperse standard polystyrene obtained from Pressure Chemical Co. All measurements were carried out at room temperature.

III. Data Analysis

All experiments were done using 90° scattering and linearly polarized incident light. With the parallel and polarized Raman intensities representing the strong and weak component of the scattered light, one can write

$$I_{\parallel}(\omega) = I_{\rm isot}(\omega) + {}^4\!/_3 I_{\rm anis}(\omega) \tag{1}$$

$$I_{\perp}(\omega) = I_{\rm anis}(\omega) \tag{2}$$

$$\rho = I_{\perp}(\omega)/I_{\parallel}(\omega) \tag{3}$$

where ρ is the depolarization ratio. The isotropic scattered light represents the intrinsic vibrational line shape whereas the anisotropic scattered light is a convolution of the vibrational line shape and the reorientational spectrum. The problem is to separate the two accurately.

However, as the depolarization ratio of the ν_2 band is very small, 0.01%, the intrinsic vibrational line shape is the same as the measured line shape of the parallel scattering without introduction of significant errors.

Generally, however, the measured spectrum is a convolution of the true spectrum and a slit function. Using the slit function $S(\omega)$, one can write

$$I'_{\rm isot}(\omega) = \int_{-\infty}^{\infty} I_{\rm isot}(\omega - \omega')S(\omega')\,{\rm d}\omega' \tag{4}$$

$$I'_{\rm anis}(\omega) = \int_{-\infty}^{\infty} I_{\rm anis}(\omega - \omega')S(\omega')\,{\rm d}\omega' \tag{5}$$

where the primed and unprimed functions denote the measured and the true line shape, respectively. To avoid the large error associated with the procedure, the true line widths were determined directly as a function of slit width and extrapolate to zero slit width. As an example, a plot of measured linewidths against the slit widths is shown in Figure 1. From these curves in Figure 1, we can obtain the true line widths of isotropic and anisotropic Raman lines at zero slit width.

Isotropic scattering is related only to the vibrational motions. The vibrational correlation function $C_{\rm v}(t)$ can be expressed in terms of a time-dependent correlation function such that

$$C_{\rm v}(t) = \int I_{\rm isot}(\omega)\exp(-i\omega t)\,{\rm d}\omega \tag{6}$$

where ω is the frequency measured from the band center. A relaxation time can be determined directly from the slope of $\log C_{\rm v}(t)$ against t plot. When $I_{\rm isot}(\omega)$ has a Lorentzian shape, the lifetime of the upper state in the Raman transition of in-

---

[†] Department of Synthetic Chemistry.

[‡] Department of Chemical Engineering.

0024-9297/78/2211-0604$01.00/0

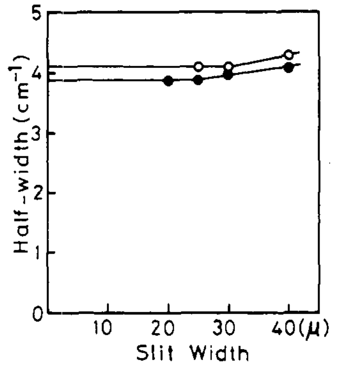

Figure 1. Line width of ν_2 of the phenyl group in polystyrene (M = 600) in chloroform as a function of slit width at the concentration 20 wt %: (○) ω_r, (●) ω_v.

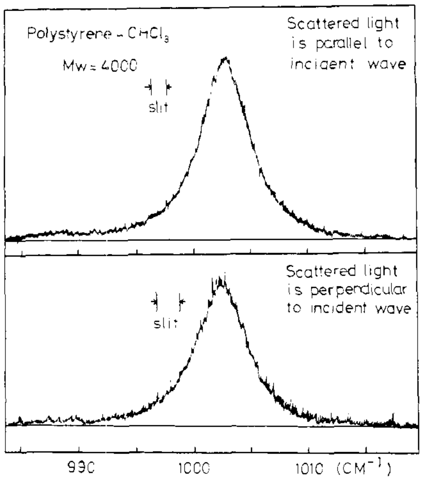

Figure 2. Polarized Raman spectrum, $I_{\parallel}(\omega)$ (upper), and depolarized Raman spectrum, $I_{\perp}(\omega)$ (bottom), of ν_2 of the phenyl groups in polystyrene (M = 4000) in chloroform.

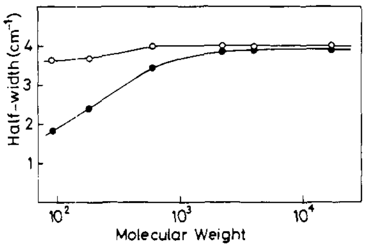

Figure 3. Dependence of ω_r (○) and ω_v (○) and ω_v (●) with the molecular weight of polystyrene in carbon disulfide.

terest is given by the relation

$$\tau_v = (2\pi C\omega_v)^{-1} \quad (7)$$

where ω_v is the half-width of the Lorentzian band.

Because the anisotropic scattering band contour contains information concerning both vibrational and reorientational motions, and these are assumed to be uncoupled, the complete correlation function is a product of individual vibrational and reorientational correlation functions

$$C_{or}(t)C_v(t) = \int I_{anis}(\omega)\exp(-i\omega t)\,d\omega \quad (8)$$

where $C_{or}(t)$ represents the reorientational correlation function.

When $I_{anis}(\omega)$ is Lorentzian and $I_{isot}(\omega)$ is also Lorentzian, the measured half-width of $I_{anis}(\omega)$ is expressed as a sum

$$\omega_r = \omega_v + \omega_{or} \quad (9)$$

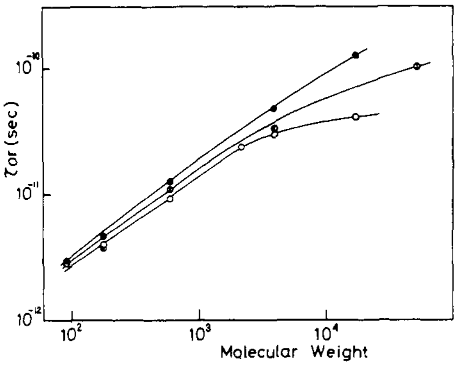

Figure 4. Dependences of τ_{or} with the molecular weights of polystyrene in various solvents at the concentration 10 wt %: (●) chloroform, (○) carbon tetrachloride, (○) carbon disulfide.

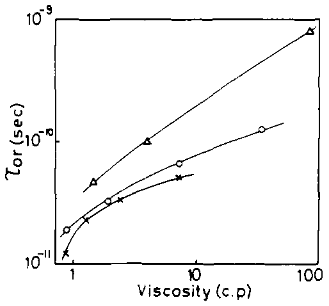

Figure 5. Relationships between reorientational relaxation times and viscosities of polystyrene–chloroform solutions: (△) M = 4000, (○) M = 2200, (X) M = 600.

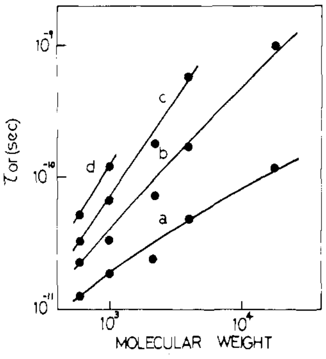

Figure 6. Relationships between τ_{or} and molecular weights at various concentration of polystyrene–chloroform solutions: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %.

The values of ω_{or} can be determined from this equation and the reorientational relaxation time can be written as

$$\tau_{or} = (2\pi C\omega_{or})^{-1} \quad (10)$$

Examples of the measured $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ are shown in Figure 2. As is seen in Figure 2, both $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ have Lorentzian line shapes. All other Raman line shapes in these experiments also have Lorentzian ones. These experimental results clearly indicate that the previous assumptions and data reduction are valid.

IV. Results and Discussions

For a 10 wt % solution of polystyrene in carbon disulfide, both half-widths of isotropic and anisotropic scattered light are plotted against molecular weight in Figure 3. Toluene and diphenylmethane are assumed to correspond to monomer and dimer of polystyrene, respectively.

The molecular weight dependences of reorientationl re-

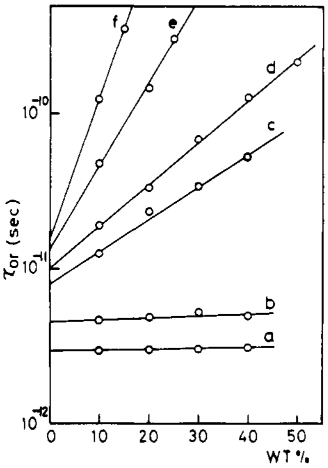

Figure 7. Relationships between τ_{or} and the concentration of polystyrene–chloroform solutions: (a) toluene, (b) diphenylmethane, (c) $M = 600$, (d) $M = 2200$, (e) $M = 4000$, (f) $M = 17500$.

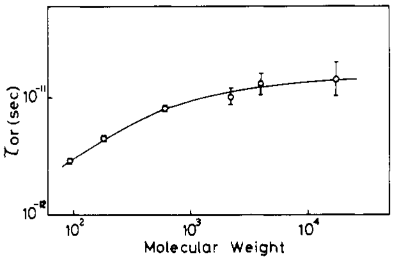

Figure 8. Dependence of τ_{or}^0 with the molecular weight of polystyrene in chloroform.

laxation times (τ_{or}) of phenyl groups in polystyrene chains in various solvents are summerized in Figure 4. As is seen in Figure 4, the τ_{or} increases with increasing molecular weight of polymers in solution. In the low molecular weight region, the molecular weight dependences are almost linear. However, in the higher molecular weight region, τ_{or} approaches a constant value.

At molecular weights higher than about 10 000, the τ_{or} are of the order of 10^{-10} s and these values are in very good agreement with those reported by Inoue et al.[6] from NMR data at molecular weight 230 000 and the concentration 15%.

τ_{or} vs. molecular weight relationships at various concentrations are shown in Figure 5. Clear molecular weight dependence becomes less clear as the concentration decreases.

In the measurement of rotational relaxation times by means of ESR it is also found that τ_{or} of the phenyl groups of polystyrene chains in solution depend on the concentration of polymer.[3]

Usually, in ordinary liquids or liquid mixtures, the relationship between the τ_{or} and the viscosity η of a liquid or solution is represented by the Einstein–Stokes relation

$$\tau_{or} = \frac{\overline{V}_m}{rT} \cdot \eta \qquad (11)$$

where V_m is the volume of the rotating molecule. If this Einstein–Stokes relation is applicable to this system, the relationship between τ_{or} and viscosity of polymer solution should be linear. In Figure 6, this relationship is shown. As is seen in Figure 6, the relationship between the τ_{or} and viscosity of solutions does not show such a straight line. This means that the τ_{or} of the phenyl groups of polystyrene chains in solution is affected only by the local fields surrounding the phenyl groups, whereas the viscosity of polymer solutions at moderate concentrations is affected by polymer–polymer interactions in addition to the local fields. The reason for the dependence of τ_{or} on the polymer concentration is not clear at present.

To remove the effects of the concentration of polymer on the τ_{or}, the reorientational relaxation times are replotted against concentration in Figure 7. It is observed that τ_{or} is linear in weight concentration, though there is at present no theoretical basis for this linear relationship. By assuming this linear extrapolation to infinite dilution, we can obtain the limiting reorientational relaxation time (τ_{or}^0) which should yield information on the intramolecular interaction between phenyl groups in a polystyrene chain.

The molecular weight dependence of the τ_{or}^0 is shown in Figure 8. The τ_{or}^0 still increases with increasing molecular weight.

Although it is not absolutely certain that the concentration dependence of τ_{or} can be eliminated in the linear extrapolation in Figure 7 and also that toluene and diphenyl methane correspond to the monomer and dimer, it appears to us that τ_{or}^0 reaches a constant value at molecular weights higher than 1000.

The reason for this dependence of the reorientational relaxation time on the molecular weight may be as follows: The reorientational relaxation time of phenyl groups is related to its rotational motion, that is, its rotational friction constant. The rotational motion is determined by the strong interaction among phenyl groups in a polystyrene chain. The larger the molecular weight, the longer becomes the reorientational relaxation time. However, in the region of sufficiently high molecular weight, the interaction among phenyl groups in a polystyrene chain must be constant.

Acknowledgments. The authors are deeply indebted to Professor M. Nagasawa for his most helpful encouragement and discussion. We have also benefited from the use of facilities provided by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References and Notes

(1) H. Nomura, S. Kato, and Y. Miyahara, *Mem. Fac. Eng., Nagoya Univ.*, **27**, 72 (1975).
(2) S. Mashimo, *Macromolecules*, **9**, 91 (1976).
(3) Y. Nishijima and K. Tanaka, *Rep. Prog. Polym. Phys. Jpn*, **15**, 437 (1972); M. Uchida, M. Yamamoto, and Y. Nishijima, Annual Meeting in Polymer Science in Japan, Tokyo, 1976.
(4) D. R. Bauer, J. I. Brauman, and R. Pecora, *Macromolecules*, **8**, 443 (1975); O. Kramer and J. E. Frederik, *Macromolecules*, **5**, 69 (1972).
(5) Z. Veksli and W. G. Miller, *Macromolecules*, **8**, 248 (1975).
(6) Y. Inoue and T. Konno, *Polym. J.*, **8**, 457 (1976).
(7) J. Lawrence and B. E. Conway, *J. Phys. Chem.*, **75**, 2353 (1971).
(8) H. Nomura and Y. Miyahara, *Nippon Kagaku Zasshi*, **89**, 142 (1968).
(9) T. Kamata, H. Nakamura, and S. Hattori, *Bull. Chem. Soc. Jpn.*, **50**, 2558 (1977).
(10) K. Gekko and H. Noguchi, *Biopolymers*, **10**, 1513 (1971).
(11) H. Nomura and Y. Miyahara, *Polym. J.*, **8**, 30 (1975).
(12) H. Nomura and Y. Miyara, *Bull. Chem. Soc. Jpn.* **48**, 2779 (1975).