

NOTE

Translational Diffusion of Atactic 1,2-Polybutadienes in Tetrahydrofuran

INTRODUCTION

The chain flexibility of 1,2-polybutadienes decreases with the increase of the 1,2-unit content (i.e., the concentration of pendant vinyl groups on the main chain), and the energy of rotational isomerization is enhanced more than 30% when the 1,2-unit content is changed from 30% to 90%.¹ The 1,2-units and 1,4-units of polybutadienes are chemical isomers, which make different contributions to the flexibility and unperturbed dimension $(r_0^2/M)^{1/2}$ of polymer chains. A question raised is how they influence the translational diffusion property of polybutadienes in solutions. The answer will be of help in understanding the dynamics and draining effect, that is, the drainage of the solvent through the polymer domain, and will be influenced by hydrodynamic interaction of polymer coils in dilute solutions.²

Photon correlation spectroscopy (PCS) is used to measure the intensity-intensity time correlation function $G^2(t, q)$ with the form

$$G^2(t, q) = A(1 + b|g^1(t, q)|^2) \quad (1)$$

where A is the base line, b is an adjustable parameter mainly depending on the coherence area, and g^1 is the first-order normalized scattering electric field time correlation function. The translational diffusion coefficients and hydrodynamic radii can be obtained on a best-fit basis from the spectrum. PCS is a powerful and almost routine technique to study the dynamics of polymers in solutions³ and even in the bulk state.⁴

EXPERIMENTAL

1,2-polybutadienes (1,2-PB) were prepared in solution with *n*-butyllithium as the catalyst and tetrahydrofuran as the microstructure regulating agent. The details of the polymerization procedure have been reported in the literature.⁵ Before making the samples for light scattering experiments, the polymers were purified to remove additives. Characterization results are listed in Table I. The regularity was determined by infrared spectroscopy and the mol wts were calculated according to the intrinsic viscosities in toluene at 30°C, using the Mark-Houwink equation.¹ The glass transition temperatures were measured by using a torsional pendulum.

Light scattering experiments were carried out on a Brookhaven 2030 correlator with 128 data channels. The 6328 Å line from a helium-neon laser was used as the light source. Cylindrical glass sample cells were used and mounted at the center of a temperature-controlled sample holder.

The concentration range was between 0.02 ~ 1% g/mL, depending on the mol wts of polymer. All solutions of 1,2-PB in tetrahydrofuran (THF) were filtered using Millipore Teflon filters with pore size of 0.2 μm to obtain dust-free samples. Temperatures were controlled at 20 ± 0.2°C.

To obtain the diffusion coefficients of 1,2-PB in THF, the correlation functions measured by PCS were fitted using the second cumulant and Williams-Watts methods, which have been described in literature.³ The experimental and curve fitting results are shown in Figures 1 and 2.

RESULTS AND DISCUSSION

When $Rq \ll 1$, the following relations hold:

$$\bar{\Gamma} = Dq^2 \quad (2)$$

$$D = D_o(1 + kc) \quad (3)$$

where $\bar{\Gamma}$ is the half width at half height of Rayleigh line, R is the particle size that is the light scattering center, q is the scattering vector, which is mainly defined by the wave length of the incident light and the scattering angle, D and D_o are the diffusion coefficient at a finite and an infinite concentration, respectively, and k is a constant, which is related to diffusion second virial coefficient. By using the method shown in Figure 3, D_o of the 1,2-PB samples were obtained, and the dependence of D_o on the mol wt M is calculated from the linearly regressed line in Figure 4:

$$D_o(20^\circ\text{C}) = 6.934 \times 10^{-4} M^{-0.638} \quad (4)$$

The friction coefficients, f_o and the hydrodynamic radii, R_h , of 1,2-PB molecules in THF are listed in Table II, which are calculated in line with Einstein equation and Stokes's rule:

$$D_o = KT/f_o \quad (5)$$

$$f_o = 6\pi\eta_o R_h \quad (6)$$

Table I Characterizations of the Polybutadiene Samples

Samples	V-2	V-44	V-43	D-4	V-29
T_g °C	-85	-49	-31	-77	-72
$M \times 10^{-5}$	1.49	1.58	2.35	4.36	8.46
1,2-unit %	25	58	73	36	38
cis-1,4 %	43	20	11	32	29
trans-1,4 %	42	22	16	32	33

where K is the Boltzmann constant, η_0 is the viscosity of solvent, and T is temperature in degrees Kelvin.

The rigidity of 1,2-PB chain is enhanced with increasing pendant vinyl groups. The energy of rotational isom-

erization increases to 1.19 Kcal/mol from 0.87 Kcal/mol, and the glass transition temperature rises about 60°C, when the contents of 1,2-unit change to 90% from 30%.¹ The diffusion coefficients of polybutadienes at infinite

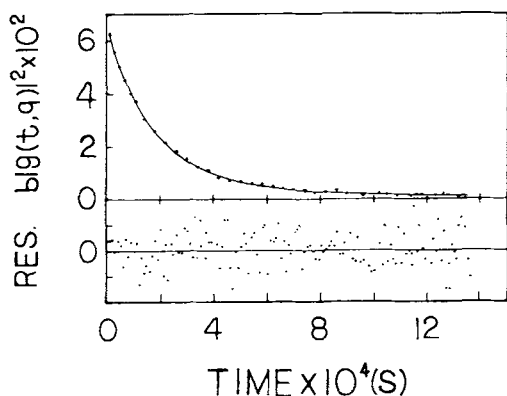


Figure 1 The correlation function of sample V-29 with the concentration of 0.8604 mg/mL at 20°C; the curve is the calculated fit of the experimental result (points) to the second cumulant.

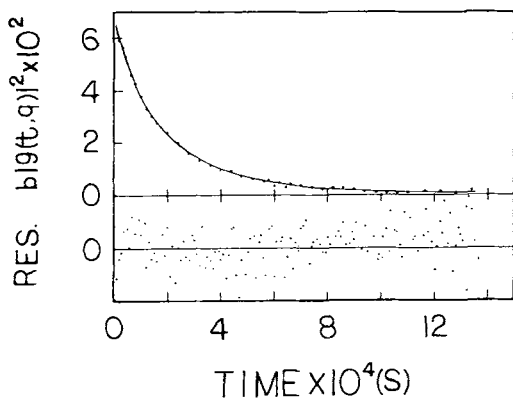


Figure 2 The correlation function fitted to the Williams-Watts equation of sample V-29 at the same condition as given in Figure 1.

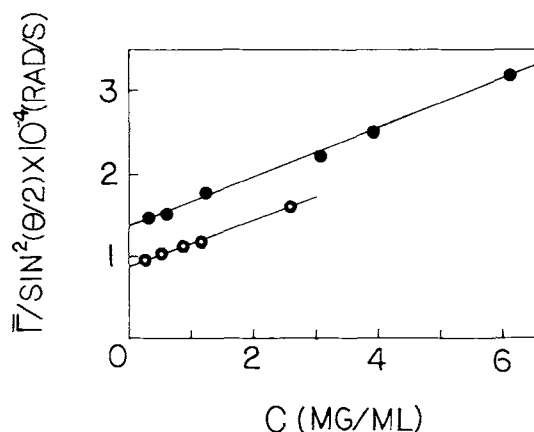


Figure 3 The extrapolation of $1/\sin^2(\theta/2)$ data, obtained at different concentrations to calculate D_0 ; only the data of sample D-4 (●) and V-29 (○) are plotted for clarity.

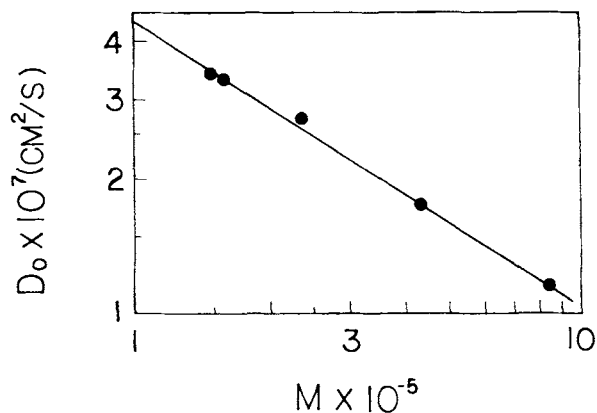


Figure 4 The plot of $\log D_0 \sim \log M$; the straight line is the linear regression fit of the points.

Table II Diffusion Properties of 1,2-Polybutadienes

Samples	V-2	V-44	V-43	D-4	V-49
$D_o \times 10^7 \text{ cm}^2/\text{s}$	3.383	3.282	2.705	1.784	1.115
$f_o \times 10^7 \text{ g/s}$	1.197	1.233	1.497	2.295	3.361
$R_n \text{ \AA}$	115.5	118.9	144.4	223.0	350.2
$R_g \text{ \AA}$	178.5	183.8	223.2	344.7	541.3

concentration are not influenced obviously by the vinyl content, since all the data fall along the same line (Fig. 4).

Translational diffusion is the motion of the mass center of the polymer coils. It should be affected by the coil volume and the draining effect. It was shown that in the previous studies of T. B. He¹ and S. R. Ni⁶ the changes of the characteristic ratio, C_∞ , and the segmental motion can be distinctly observed once the vinyl contents are different. Hadjichristidis⁷ also found that there was a little, but not a significant, increase of the gyration radius of polybutadienes containing 7% 1,2-structures in a dilute solution.

It is suggested in this study that the intramolecular motions and chain flexibility do not make any difference to the translational diffusion properties of polybutadienes, provided that the mol wts are alike. It is supposed that the samples with the same mol wt have the equivalent hydrodynamic volumes in a solution, no matter how many pendant vinyl groups exist on the polybutadiene chains. This could be attributed to the fact that, although the radius of gyration of the 1,2-PB molecules may be somewhat different, when mol wts are identical, but with different contents of 1,2 structures, the draining effects should simultaneously alter too, and these two factors match each other inversely. Of course, there may be some other possibilities, for instance, the coil densities of all the samples could be identical since 1,2-units contribute less flexibility and shorter chain length at the same time, which would have reverse effects on the coil volume of polybutadienes.

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