Dynamics of Polymer–Polymer–Solvent Ternary Systems
I. Characterization of Polystyrene and Poly-(methymethacrylate) in Thiophenol

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It has been shown with several physico-chemical methods that dynamics of a polymer chain in semidilute solutions of another polymer of different species can be studied by the use of polystyrene (PS) and thiophenol (TPh) for preparation of the semidilute solution; *i. e.*, (1) dynamic light scattering (DLS) measurements have shown that PS and TPh are isorefractive; (2) specific density and sedimentation velocity (SV) measurements have indicated that they are isopycnic; (3) intrinsic viscosity measurements have shown that TPh is a good solvent to PS. The diffusion coefficient D and the sedimentation coefficient s of poly(methylmethacrylate) (PMMA) in a semidilute TPh solution of PS have been measured in the low PMMA concentration region. Values of D and s at zero concentration of PMMA have been accurately determined by linear extrapolation. The values have been compared with corresponding values in pure TPh. The retardation effect of PS on the diffusion behavior of PMMA in the semidilute solution of PS has been briefly discussed in relation to the entangled network structure of PS in the solution.

INTRODUCTION

Measurements of the self diffusion (or the translational diffusion) coefficient D_s of single chain in condensed systems such as concentrated polymer solutions, polymeric gels and membranes are of fundamental importance from both scientific and practical point of view. The forced Rayleigh scattering (FRS) and pulsed field gradient NMR (PFG-NMR) methods have proven very powerful for accurate estimate of D_s of polymer molecules in solutions[1-5] and also in the bulk.[6-9] Amis and Han[10] have reported that the conventional dynamic light scattering (DLS) can be also used to detect the slow reptation motion of a polymer chain as well as the fast cooperative motion of chains in entangled polymer solutions. As later studies have shown,[11-14] however, absolute values of D_{slow} obtained from the slow mode have been always smaller than D_s values obtained from either FRS or PFG-NMR by about one order of magnitude. Thus it seems indeterminate that the DLS technique is a useful method for D_s measurements as far as we deal with binary polymer solutions.

In this article and subsequent reports we will show that if a pair of polymer (A) and solvent with the same refractive index is used for preparation of semidilute polymer

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solutions, the diffusion coefficient D of the third component polymer (B) can be determined fairly accurately by DLS. Here the polymer B is mixed as a probe in the solutions by a small amount. Extrapolation of D to zero concentration of the component B then gives the translational diffusion coefficient D_0. This quantity will allow us to study the relation between the slow diffusive motion of the polymer B and the global structure of semidilute solutions of the polymer A. As a suitable isorefractive pair of the polymer A and the solvent, polystyrene (PS) and thiophenol (TPh) have been selected, because well-characterized narrow-distribution samples are commercially available to PS and dynamics of its semidilute solutions in other solvents have been already investigated in great detail.[10,14-16] As far as the authors are aware of, there are no available solution data of PS in TPh. Thus intrinsic viscosity measurements have been first made in order to obtain information concerning the solvent nature of TPh to PS. Poly(mehylmethacrylate) (PMMA) has been chosen as the polymer B whose D is measured by DLS. PMMA is incompatible with PS but phase separation in solutions which are prepared by using a solvent good to both of PS and PMMA occurs at relatively high concentration of PMMA.[17] Since TPh is isopycnic to PS, the sedimentation coefficient s of PMMA in the PS-TPh system has been easily measured. This has given an unique opportunity to study a relation between D and s in the semidilute concentration region.

EXPERIMENTAL

Materials. Six samples of narrow-distribution molecular weight polystyrenes were used for measurements of intrinsic viscosity $[\eta]$ in thiophenol. The highest molecular weight sample (F-850) was used as the PS component for preparation of binary (PS-TPh) and ternary (PMMA-PS-TPh) solutions for dynamic light scattering and sedimentation velocity experiments. Table I gives M_w and M_w/M_n of the samples used. Poly(methylmethacrylate) was purchased from Scientific Polymer Products. The polymer was purified by dissolving it in benzene and by precipitating in methanol. The freeze-dried polymer was used as the sample. M_w of the sample was calculated as 343,000 from $[\eta]=130$ cm^3 g^{-1} in chloroform at 30°C by the use of the $[\eta]$-M relationship given in Ref. 24.[25] GPC measurements have given $M_{GPC}=342,000$ and $M_w/M_n=1.1$. Reagent

Table I Characterization of Polystyrene

Sample	$M_w \times 10^{-5}$	M_w/M_n	$[\eta]/10^2$cm^3 g^{-1c}
F - 40	4.22[a]	1.04[a]	1.34
F - 80	7.75[a]	1.01[a]	2.03
FF- 8	12.3[b]	1.05[b]	2.26
FF- 33	24.2[b]	1.07[b]	4.60
FF- 35	55.3[b]	1.07[b]	8.36
F -850	84.2[a]	1.17[a]	10.6

(a) From data sheets (Toyo Soda).
(b) Ref. 20.
(c) This work. In thiophenol at 25.0±0.05°C.

Table II　Specific densities of the polymers, the density of the solvent
and their refractive indices.

	ρ or $1/\bar{v}$ $\mathrm{gcm^{-3}}$	$n_D{}^{25}$
Polystyrene (PS)	1.0776	1.59–1.60[a]
Poly(methylmethacrylate) (PMMA)	1.169	1.4947[a]
Thiophenol (TPh)	1.0728	1.5871[b]

a. M. K. Lindemann, "Polymer Handbook", 2nd. ed., J. Brandrup and
E. H. Immergut, John Wiley and Sons, N. Y., Chp. V, 1975.
b. $n_D{}^{20} = 1.5897$ ("Organic Solvents", 2nd. ed., A. Weissberger, E. S.
Proskaver, J. A. Riddick, and E. E. Toops, Jr., Interscience Publishers
Inc., N. Y., 1955.)

grade thiophenol (Nakarai Co.) was distilled under nitrogen atmosphere at 48°C and 7 mm Hg. The distilled solvent has been sealed in test tubes under nitrogen atmosphere until it is used for preparation of solutions. Specific densities of the polymers in TPh and the density of the solvent were measured by using a mechanical oscillator (Shibayama, Model SS-D-200), and are listed in Table II. The table also gives values of refractive index $n_D{}^{25}$. $n_D{}^{25}$ of thiophenol was measured with a Pulfrich refractometer.

　　Solutions were prepared by dissolving the polymers into dust-free thiophenol and made optically clean by filtering with a Millipore filter (nominal pore size, 0.5 or 1.0 μm). Polymer concentrations of the solutions were determined by weighing.

Methods. Viscosities of PS solutions in TPh have been measured by using either a Ubbelohde viscometer or a Cannon–Fenske variable shear viscometer. Intensity autocorrelation function of solutions was measured with the DLS instrument described elsewhere.[18] Sedimentation velocity (SV) experiments have been made by using an analytical ultracentrifuge (Beckman Spinco model E). All measurements have been conducted at 25 ± 0.05°C.

RESULTS AND DISCUSSION

Polystyrene in thiophenol.

　　Figure 1 shows the molecular weight dependence of $[\eta]$ of PS in TPh whose values are given in Table I. Here $[\eta]$ of the highest molecular weight sample (F-850) has been derived by extrapolating η values to zero shear rate. The effect of the shear rate on η of the second highest molecular weight sample (FF-35) was negligible. Over the whole range of molecular weight investigated, the data are well expressed by the straight line 2 given by Eq. (1).

$$[\eta] = 1.461 \times 10^{-2} M_w{}^{0.70 \pm 0.01} \qquad (1)$$

The data may be compared with two $[\eta]$–M_w relations, one (the line 1) obtained in benzene at 25°C as the good solvent limit,[19] and the other (the line 3) in cyclohexane at 34.5°C, *i.e.* in the theta state.[20] It is clear from the figure that thiophenol is not a poor solvent but good one to PS. It is not an extremely good solvent, because $[\eta]$ values in TPh are a little bit smaller than those in benzene. In later discussion, never-
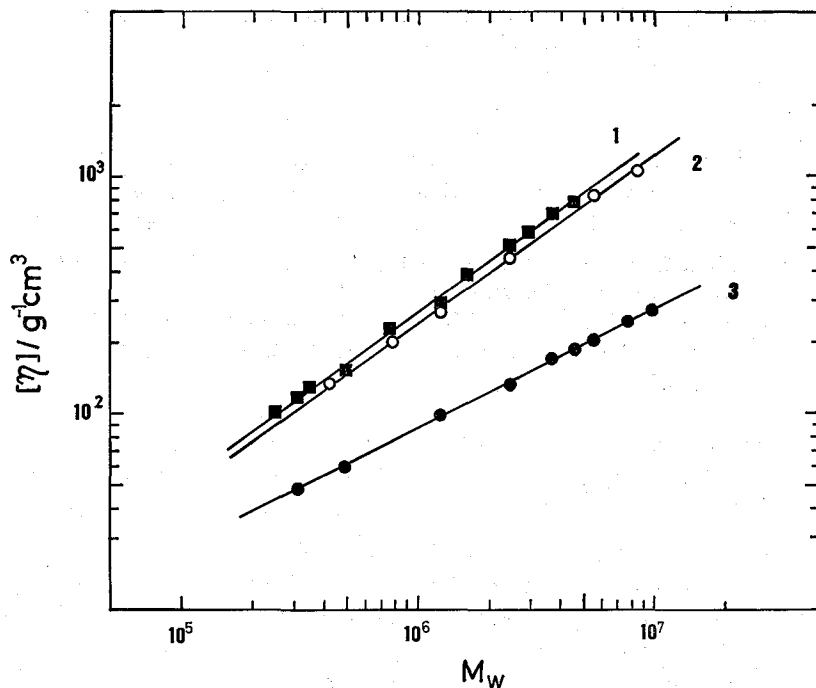
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Figure 1. Intrinsic viscosities $[\eta]$ of polystyrenes in various solvents are plotted against weight average molecular weight M_w. The line 1 : in benzene at 25°C ; 2 : in thiophenol at 25°C ; 3 : in cyclohexane at 34.5°C.

theless, it is assumed that the molecular motion of PS in TPh is approximately same as that in benzene. The stability of PS in TPh has been examined by measuring $[\eta]$ of the sample F-80 again one month later after the first measurement. The both have agreed within an experimental uncertainty of 1 %. This indicates that PS is quite stable in TPh.

There is a small difference in the refractive index between PS and TPh by a few thousandth. In order to see the effect of this difference on DLS, the intensity auto-correlation function $A(\tau)$ of a 1% solution of PS (F-850) in TPh has been measured. Figure 2 shows plots of $A(i)$ vs. channel number i measured at scattering angles θ of 30°, 60°, and 90° where the solid horizontal lines are the baselines at respective angles. The inset in the figure is the magnification of the data at $\theta=30°$ at short delay times, indicating the presence of time correlation with small amplitude factor. The data at 30° and 60° have been fitted with the single exponential type of a decay curve given by Eq. (2),

$$A(\tau) = 1 + \beta \exp(-2\Gamma_q \tau) + \delta \qquad (2)$$

The amplitude β has been estimated as 0.01, for the both data at $\theta=30°$, and 60°. The diffusion coefficient D has been calculated as $(2\pm0.2)\times10^{-7} cm^2 s^{-1}$ by using the relation $\Gamma_q=Dq^2$. This value roughly agrees with a value of the cooperative diffusion coefficient, 2.66×10^{-7}, obtained for a 1 % solution of the same sample in benzene,[14] when correction for the difference in solvent viscosity has been made. Thus it may be
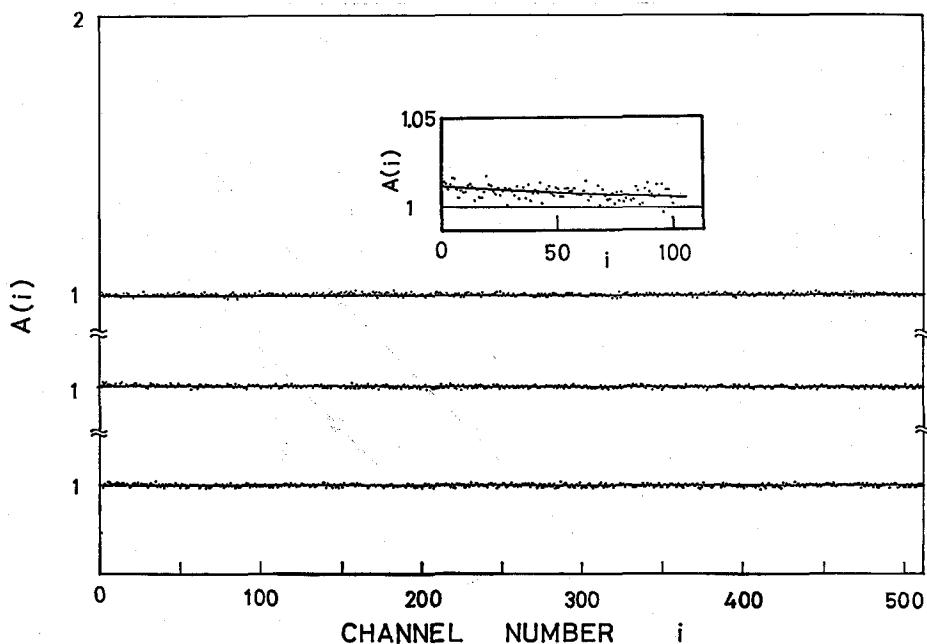
Figure 2. Intensity autocorrelation function A(i) of a 1 % solution of PS (F-850) in TPh measured with the time-interval method at various scattering angles. From the top, $\theta = 30°$, 60° and 90°, and the sampling time=2, 1.5 and 0.5 μs, respectively. The inset is the magnification of the data at $\theta = 30°$ at short delay times.

concluded that the time correlation with low amplitude observed for the PS–TPh system is due to the local cooperative motion of PS chains in TPh. It should be noted that at θ higher than 60° $A(\tau)$ did not show any correlation.

Sedimentation velocity experiments have been made with the highest rotor speed of 59,780 rpm. on the solution same as used for DLS measurements and also on a 1% solution of PS(F-850) in a mixture of monochlorobenzene and benzene whose mixing ratio is adjusted so as to have the density same as that of TPh. For the both solutions sedimentation of the polymer has not been detected with the schlieren method. Thus PS and TPh are isopycnic.

Poly (methylmethacrylate) in thiophenol.

Dynamic light scattering (DLS) and sedimentation velocity (SV) measurements have been made on dilute solutions of poly(methylmethacrylate) in thiophenol. $A(\tau)$ of the solutions has been fitted with Eq. (2). The variance has been found less than 0.08 at six scattering angles from 10° to 150° measured, although a slight increase with increasing θ has been observed. By taking into account that the produt of the scattering vector q and the radius of gyration R_G is less than unity at $\theta = 150°$, no attempt has been made to decompose the distribution of the decay rate into the translational and the internal modes. The proportionality of Γ_q to q^2 has been confirmed, for example, as is shown by the straight line 1 with the slope of unity in Fig. 3 for the solution
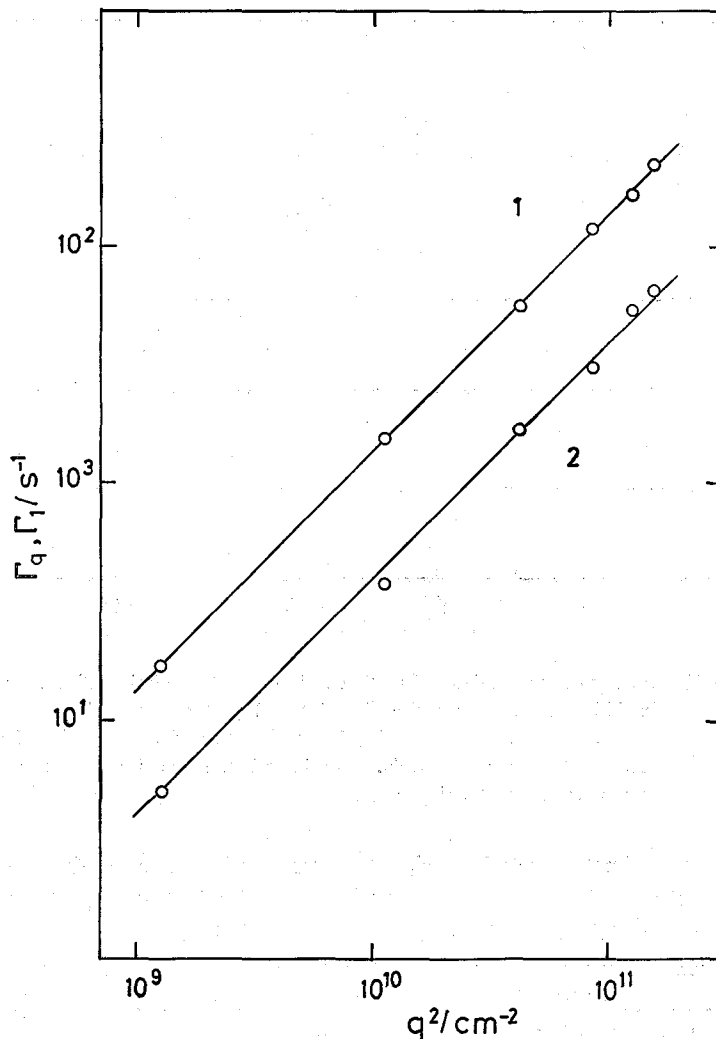
Figure 3. The plot of Γ_q and Γ_1 against the scattering vector q. 1 : PMMA in TPh at $c_{PMMA} = 1.10 \times 10^{-3} g\ cm^{-3}$; 2 : PMMA in 1% PS(F-850)-TPh, at $c_{PMMA} = 3.14 \times 10^{-3} g\ cm^{-3}$.

with $c_{PMMA} = 1.10 \times 10^{-3}$. The concentration dependence of the diffusion coefficient D is shown in Fig. 4. The dependence is well expressed by the straight line 1, from which the translational diffusion coefficient at infinite dilution, D_0, and the concentration coefficient, k_D, in Eq. (3), have been estimated as $1.32 \times 10^{-7} cm^2\ s^{-1}$ and $63.8\ cm^3\ g^{-1}$, respectively.

$$D = D_0(1 + k_D c) \tag{3}$$

The sedimentation coefficient s has been derived from the time variation of the peak position of the sedimentation curve. The pressure effect was negligible. As is shown in Fig. 5, s^{-1} is linearly dependent on c. By fitting Eq. (4) to the data we obtain the sedimentation coefficient at infinite dilution, $s_0 = 1.63 \times 10^{-13} s$ and the concentration coefficient $k_s = 126\ cm^3\ g^{-1}$.
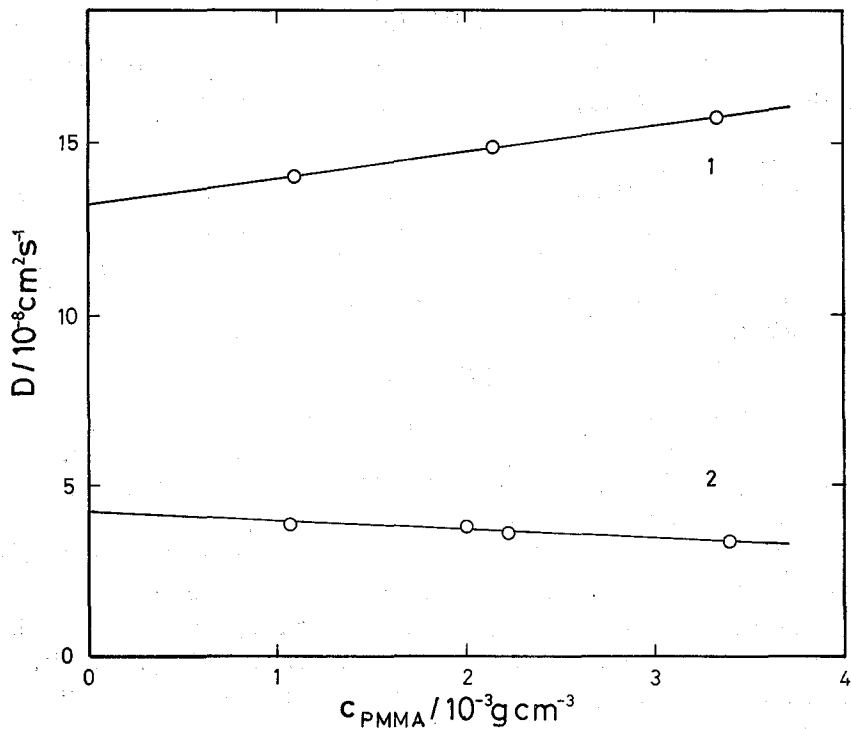
Figure 4. The plot of D against the concentration of PMMA. 1 : PMMA in TPh ;
2 : PMMA in 1 % PS(F-850)-TPh.
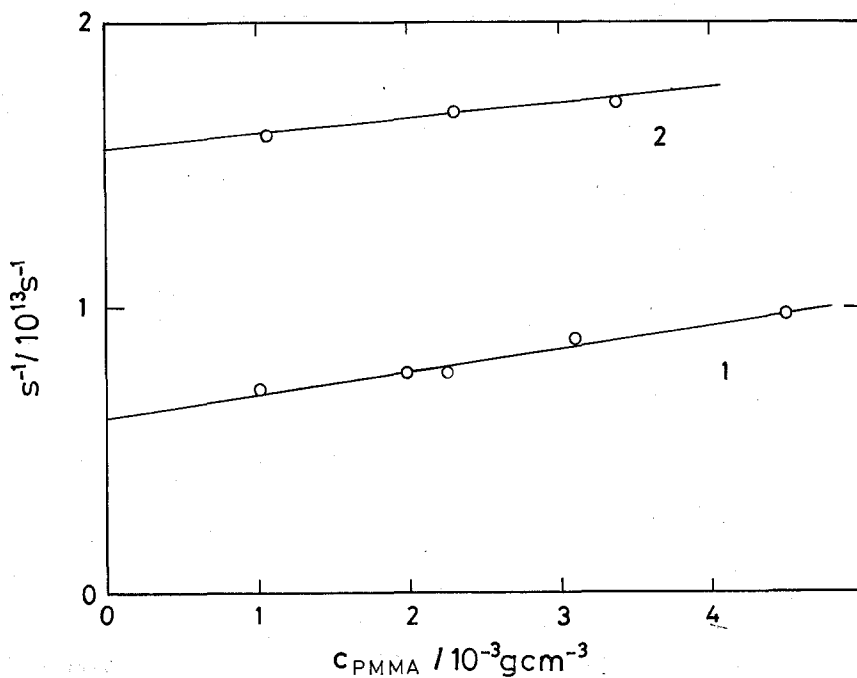

Figure 5. The plot of s^{-1} against the concentaation of PMMA. 1 : PMMA in TPh ;
2 : PMMA in 1 %PS(F-850)-TPh.

$$s^{-1} = (s_0)^{-1}(1+k_s c) \tag{4}$$

The second virial coefficient A_2 has been calculated by using a theoretical expression, Eq. (5)[21] and values of k_D, k_s and $\bar{v}$ measured.

$$k_D = 2A_2 M - k_s - \bar{v} \tag{5}$$

$A_2 = 3.86 \times 10^{-4}$ mol cm^3 g^{-2} has been obtained. The pretty large positive A_2 value strongly suggests that thiophenol is a good solvent to PMMA.

When the molecular weight distribution of the polymer is sufficiently narrow, the well-known relation between D_0 and s_0, Eq. (6), may be used for determination of molecular weight.

$$M = s_0 RT/D_0(1-\bar{v}\rho_s) \tag{6}$$

By substituting values of s_0, D_0, $\bar{v}$ and ρ_s into Eq. (6), we obtain $M = 372,000$, which is close to the M_w value obtained by intrinsic viscosity measurements. Thus we may conclude that D_0 and s_0 have been estimated to an accuracy of 5 % as expected. *Poly(methylmethacrylate) in a 1 % polystyrene-thiophenol system.*

DLS and SV measurements have been made on ternary solutions of PMMA, PS and TPh, of which the PS concentration is fixed at 1×10^{-2} g cm^{-3} and the PMMA concentration is varied from 1×10^{-3} to 3.41×10^{-3} g cm^{-3}. Typical raw data obtained by the both measurements are exemplified in Figs. 6 and 7, respectively. In Fig. 6, the solid curve is a fitted one to the data of the solution with $c_{PMMA} = 3.41 \times 10^{-3}$ at $\theta = 60°$ by the use of Eq. (2) which assumes the single exponential type of decay. The

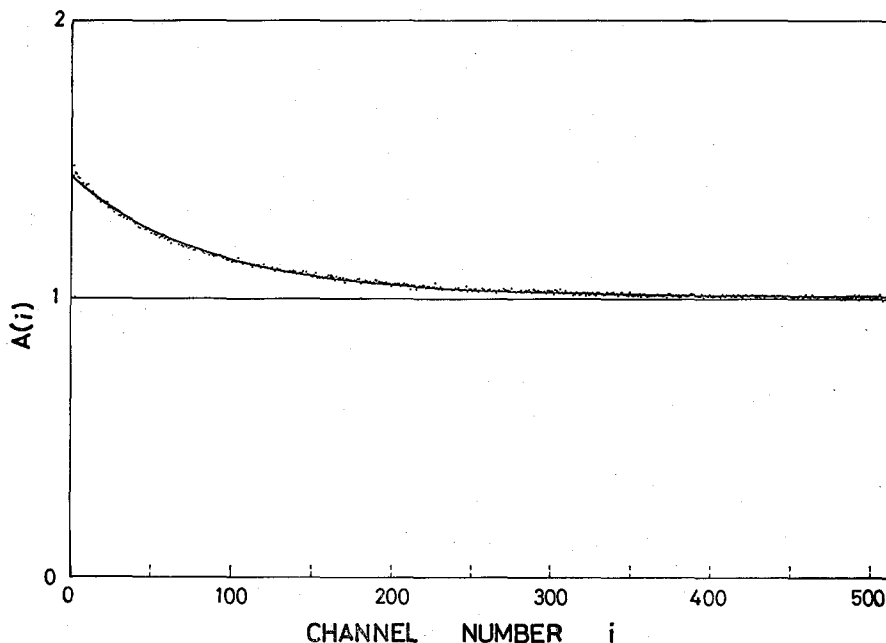Figure 6. An example of A(i) of the PMMA-PS-TPh ternary solution with $c_{PMMA} = 3.41 \times 10^{-3}$ g cm^{-3} and $c_{PS} = 1.0 \times 10^{-2}$ g cm^{-3} measured at $\theta = 60°$. The sampling time is 4 μs. The solid curve is a fitted one by the use of Eq. (2).

deviation from the data is appreciable. By assuming that the Γ distribution is a bimodal type, the data have been analyzed by using a five-parameter equation.

$$A(\tau) = (1+\delta) + \{\alpha_1 \exp(-\Gamma_1\tau) + \alpha_2 \exp(-\Gamma_2\tau)\}^2 \qquad (7)$$

Here $\Gamma_1 < \Gamma_2$ and the deviation δ of the baseline from unity is kept less than 0.003 in the analysis. The histogram method[22] has been applied on a couple of data as an alternative procedure for data analysis. The analysis has confirmed not only the bimodal nature of the Γ distribution but also has given good agreement between Γ_1 values obtained by the two methods. On the other hand, uncertainties of the amplitude factor α_2 of the fast mode and also those of Γ_2 have been found considerably large. As general tendency, (1) α_2 has increased with increasing θ ; $\alpha_2/(\alpha_1+\alpha_2) \sim 0.3$ at $\theta = 150°$; (2) $\Gamma_2 \propto q^2$ seems to be satisfied and $\Gamma_2/\Gamma_1 \sim 10$. Since time correlation due to the cooperative motion of PS chains has been undetectable at high θ as described in a previous section, (1) and (2) impliy that the fast mode may be attributed to the local motion of a PMMA chain excited by the motion of surrounding PS chains. lt may be noted that, theoretically, this ternary system may have the two modes in which the fast mode has a decay rate close to a Γ value corresponding to the gel-like motion of PS chain and the slow mode represents the translational diffusion motion of a PMMA chain where the interaction between PMMA and PS may be regarded as the random force.

Figure 3 shows an example (the line 2) that Γ_1 satisfies the relation $\Gamma_1 = Dq^2$, from which D has been estimated. The linear dependence of D on c_{PMMA} has been found as is shown by the straight line 2 in Fig. 4. By applying Eq. (3) to the data, we obtain $D_0(c_{PS}) = D_0(0.01) = 4.15 \times 10^{-8}$ cm^2 s^{-1} and $k_D = -57.0$ cm^3 g^{-1}.

As the photographs in Fig. 7 show, an only peak due to the sedimentation of PMMA particles has been observed. Therefore s has been accurately estimated by the standard procedure and is plotted against c_{PMMA} in Fig. 5. Both the pressure effect and the concentration effect were negligible. From the fit of Eq. (4) to the data, $s_0(0.01) = 0.642 \times 10^{-13}$ s and $k_s = 33.7$ cm^3 g^{-1} have been obtained.

We now compare values of $D_0(0.01)$, $s_0(0.01)$, k_D and k_s with the corresponding values obtained in pure thiophenol. Both $D_0(0.01)$ and $s_0(0.01)$ have decreased to about one-thirds of D_0 and s_0, respectively. This retardation effect of PS chains on the translational diffusion and the sedimention of a PMMA chain is however, quite
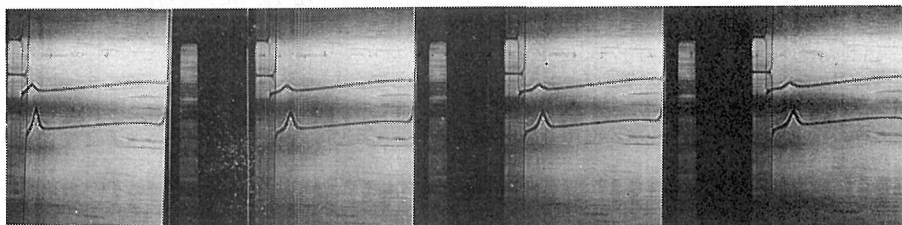

Figure 7. Typical sedimentation patterns of PMMA-PS-TPh ternary solutions with $c_{PMMA} = 1.07 \times 10^{-3}$ (top curves) and 3.41×10^{-3} (bottom curves) g cm^{-3}. The concentration of PS, $C_{PS} = 1.0 \times 10^{-2}$, is same for the both solutions. The photographs have been taken at 32 minutes interval. Rotor speed is 59,780 rpm.

small compared with an increase in macroscopic viscosity by about two orders of magnitude. We have shown in a previous report[14] that a 1% solution of the same PS polymer in benzene can be completely regarded as the semidilute polymer solution (the critical concentration for chain overlapping $c^* \cong 0.1\%$), and its hydrodynamic correlation length, ξ_H, and average distance between entanglement points, ξ_e, are 1.56 $\times 10^{-6}$ and 1.49×10^{-5} cm, respectively. The hydrodynamic radius of a PMMA molecule in the solution, $R_H(0.01)$, may be less than R_H in pure TPh, since PS and PMMA are an incompatible pair of polymers. R_H has been calculated as 1.39×10^{-6} cm by using the Einstein–Stokes relation $R_H = k_B T/6\pi\eta_s D_0$ and $D_0 = 1.32 \times 10^{-7}$. $R_H(0.01)$ is obviously much smaller than ξ_e and even smaller than ξ_H which is interpreted as a blob size of the PS molecule in the semidilute concentration region. Therefore it seems improbable that a PMMA chain diffuses through the PS network by the reptation mechanism. In a subsequent report we will show experimental results that the dependence of $D(c_{PS})$ of PMMA on PS concentration can be described by an exponential type of function, $D(c_{PS}) \propto \exp(-Bc_{PS}^\delta)$ $(0.5 \leq \delta \leq 1)$. $\delta = 0.5$ and 1 have been predicted by Ogston[23] for the diffusion of particles in gels with point barriers and one dimensional barriers, respectively.

It is interesting to note that the ratio $D(0.01)/D_0$ is smaller than the ratio $s(0.01)/s_0$ by 20%. If the both quantities D and s have been described by the same friction coefficient as is verified in the dilute concentration range, they have to coincide each other. More detailed study concerning this problem will be given in a forthcoming article.

Finally, A_2 of this solution has been estimated by assuming that Eq. (5) is also applicable for the ternary system. Substitution of $k_D = -57.0$ and $k_s = 33.7$ into Eq. (5) has given $A_2 = -1.71 \times 10^{-4}$ mol g^{-2} cm^3. The negative value of A_2 is consistent with that PMMA and PS are incompatible. This suggests that, in the use of much higher molecular weight samples, experiments have to be done in the range of low PMMA concentration where the linear dependence of D and s on c_{PMMA} are satisfied.

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