Macromolecules **1996,** *29,* 3157−3160

Laser Light-Scattering Study of Novel Thermoplastics. 2. Phenolphthalein Poly(ether sulfone) (PES-C)

Chi Wu,*,[†] Mohammad Siddiq,[†] Shuqin Bo,[‡] and Tianlu Chen[‡]

Department of Chemistry, The Chinese University of Hong Kong, N. T. Shatin, Hong Kong, and Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academy of Science, Changchun 130022, China

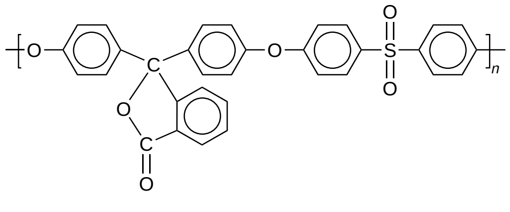
Received September 20, 1995; Revised Manuscript Received January 17, 1996[⊗]

ABSTRACT: Five narrowly distributed fractions of phenolphthalein poly(ether sulfone) (PES-C) were studied in $CHCl_3$ by both static and dynamic laser light scattering (LLS) at 25 °C. The dynamic LLS showed that the PES-C samples contain some large polymer clusters as in previously studied phenolphthalein poly(ether ketone) (PEK-C). These large clusters can be removed by a 0.1-μm filter. Our results showed that $\langle R_g^2\rangle_z^{1/2} = (3.35 \pm 0.13) \times 10^{-2} M_w^{(0.52 \pm 0.03)}$ and $\langle D\rangle = (2.26 \pm 0.02) \times 10^{-4} M_w^{-(0.54 \pm 0.03)}$ with $\langle R_g^2\rangle_z^{1/2}$, M_w, and $\langle D\rangle$ being the *z*-average radius of gyration, the weight-average molecular weight, and the z-average translational diffusion coefficient, respectively. A combination of static and dynamic LLS results enabled us to determine $D = (2.45 \pm 0.04) \times 10^{-4} M^{-(0.55 \pm 0.05)}$, where D and M correspond to monodisperse species. Using this scaling relationship, we have successfully converted the translational diffusion coefficient distribution into the molecular weight distribution for each of the five PES-C fractions. The weight-average molecular weights obtained from dynamic light scattering have a good agreement with that obtained from static laser light-scattering measurements.

Introduction

High-performance thermoplastics with excellent heat resistance are currently receiving considerable interest as advance materials. Among them are poly(aryl ether ketones), well-known in the form of poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK). They have been used as matrix resins for advanced composite materials for aircraft and automobiles because of their high mechanical strength, excellent thermal stability, and good chemical resistance.[1,2] However, poly(aryl ether ketones) have several limitations in preparation,[3] molding, and processing[4] and low thermo-oxidative stability.[5] Also, these polymers are only soluble in strong acids or solvents with a boiling point higher than their melting points, mainly due to their insoluble crystalline structures. So far, few studies on dilute solution properties of PEEK have been done because PEEK can only be dissolved in concentrated H_2SO_4, HSO_3Cl, and CH_3SO_3H.[6,7]

Previously, we have studied a thermoplastic: phenolphthalein poly(ether ketone) (PEK-C) which has viscoelastic properties similar to those of PEEK but is soluble in various common solvents, such as chloroform ($CHCl_3$). In this paper, we will show the characterization of another novel thermoplastic phenolphthalein poly(ether sulfone) (PES-C) which was recently developed in the Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia of Sinica, China. It is a linear aromatic polymer with the following chemical structure:



PES-C not only has outstanding physical and mechanical properties but also is soluble in polar organic solvents, such as $CHCl_3$, *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAc), and *N*-methylpyrrolidinone (NMP). Some solution properties of PES-C, such as the Mark−Houwink equations of $[\eta] = 1.21 \times 10^{-2} M_w^{0.66}$ in $CHCl_3$ and $[\eta] = 6.88 \times 10^{-3} M_w^{0.67}$ in DMF[8] and the Flory characteristic ratio (C_∞) of 1.84−1.93, have been determined previously.[9] In comparison with other engineering plastics, such as PEEK ($C_\infty = 2.4-2.7$) and PET ($C_\infty = 3.89$), the PES-C chain seems more flexible, which might be attributed to the double ether linkages in its backbone. It should be noted that these C_∞ values were calculated on the basis of their repeating units, not on the basis of their average bond lengths.

In our previous study,[10] we showed that PES-C contains 94% linear chains and 6% high molecular weight clusters. In this study, our emphases are the PES-C chain conformation and flexibility in $CHCl_3$ on the basis of the molecular weight dependence of $\langle R_g\rangle$ and $\langle R_g\rangle/\langle R_h\rangle$, where $\langle R_g\rangle$ and $\langle R_h\rangle$ are the average radius of gyration and average hydrodynamic radius, respectively, and also the relationship between the translational diffusion coefficient from dynamic laser light scattering (LLS) and the molecular weight from static LLS. We will show the characterization of the molecular weight distribution (MWD) of PES-C from its translational diffusion coefficient distribution $G(D)$.

Experimental Section

Sample Preparation. The PES-C samples were synthesized by the following nucleophilic substitution polycondensation: First, equal molar phenolphthalein and 4,4′-dichlorodiphenyl sulfone were dissolved in cyclobutyl sulfone ($TMSO_2$); then, an excess amount of dehydrated K_2CO_3 was added as a catalyst; and finally, the solution mixture was heated to 220 °C and the reaction was carried out under N_2 for 8 h. The PES-C sample was then fractionated in five fractions which were labeled as PES1 → PES5 thereafter. The details of sample preparation can be found elsewhere.[11] Analytical grade chloroform (Merck) was used as a solvent without further purification. For each fraction five concentrations ranging from 2.0×10^{-3} to 5×10^{-3} g/mL were prepared by dilution. All the polymer solutions were filtered at room temperature by using 0.1-μm Whatman filters in order to remove dust.

LLS Measurements. A modified commercial light-scattering spectrometer (ALV/SP-125, equipped with an ALV-5000

---

* To whom correspondence should be addressed.

[†] The Chinese University of Hong Kong.

[‡] Changchun Institute of Applied Chemistry.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

0024-9297/96/2229-3157$12.00/0

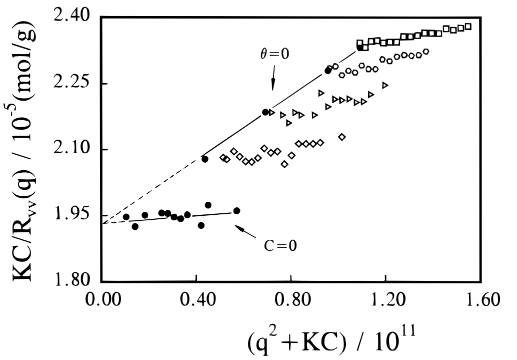


Figure 1. Typical static Zimm plot of PES3 in CHCl$_3$ at $T = 25$ °C, where C ranges from 2.0×10^{-3} to 5×10^{-3} g/mL.

multi-τ digital time correlator) was used with a solid state laser (ADLAS DPY 425II, output power ≈400 mW at $\lambda = 532$ nm) as the light source. The primary beam is vertically polarized with respect to the scattering plane. The detail of the LLS instrumentation and theory can be found elsewhere.[12,13] All the measurements were carried out at 25 ± 0.1 °C.

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_{vv}(q)$, of a dilute polymer solution at concentration C (g/mL) and scattering angle q was measured, and $R_{vv}(q)$ is related to the weight-average molecular weight M_w, the scattering vector q, and C as[14]

$$\frac{KC}{R_{vv}(q)} = \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2\rangle q^2\right) + 2A_2C \qquad (1)$$

where $K = 4\pi^2n^2(dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dC, n, and λ_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in vacuo, respectively. A_2 is the second virial coefficient, and $\langle R_g^2\rangle_z^{1/2}$ is the root-mean square z-average radius of gyration of the polymer. By measuring $R_{vv}(q)$ at a set of C and q, we are able to determine M_w, R_g, and A_2 from a Zimm plot which incorporates q and C extrapolation on a single grid.

In static laser light scattering, it is very important to have a precise value of differential refractive index increment dn/dC, because the measured M_w is proportional to $(dn/dC)^{-2}$. A novel and high precision differential refractometer[15] was used to measure the dn/dC of PES-C. The measured dn/dC of PES-C in CHCl$_3$ at $T = 25$ °C and $\lambda = 532$ nm is 0.204 mL/g.

In dynamic LLS, a precise intensity−intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured, which has the following form [12,13]

$$G^{(2)}(t,q) = \langle I(t,q)I(0,q)\rangle = A[1 + \beta|g^{(1)}(t,q)|^2] \qquad (2)$$

where A is a measured base line, β is a parameter depending on the coherence of the detection, t is the delay time, and $g^{(1)}(t,q)$ is the normalized first-order electric field time correlation function.

Result and Discussion

Figure 1 shows a typical static Zimm plot of PES3 in CHCl$_3$ at 25 °C. On the basis of eq 1 we were able to determine the values of M_w, R_g, and A_2, from the extrapolation of $[KC/R_{vv}(q)]_{q\to0,C\to0}$, $[KC/R_{vv}(q)]_{C\to0}$ vs q^2, and $[KC/R_{vv}(q)]_{q\to0}$ vs C, respectively. The results are summarized in Table 1. The positive values of A_2 show that CHCl$_3$ is a reasonably good solvent for PES-C at room temperature. For samples PES4 and PES5, R_g is too small to be accurately determined. Even for PES2 and PES3, the errors associated with their R_g values are large, so that they can be read only as a reference. Nevertheless, the scaling of R_g with M_w shows that $R_g \propto M_w^{0.52-0.53}$, which indicates that the PES-C chain in CHCl$_3$ at 25 °C might have a random coil conformation.

If modeling PES-C as a wormlike chain, we estimate the persistence length, l, on the basis of $\langle R_g^2\rangle = l^2\{1/3\cdot(L/l) - 1 + (2l/L) - (2l^2/L^2)[1 - \exp(-L/l)]\}$,[21] where L ($= nl_u$) is the contour length, with l_u being the projected length of the segment between two ether linkages and n ($= M_w/M_0$) being the number of the segments. In the case of PES-C, the average values of l_u and M_0 are ~1.1 nm and ~266 g/mol, respectively, from its chemical structure. Strictly speaking, n should be M_z/M_0. The value of l estimated from five PES-C samples is ~1 nm in CHCl$_3$ at 25 °C, which leads to a value of $C_\infty \approx 13$ using the formula $C_\infty = (2l/l_0) - 1$,[22] where l_0 is the average bond length. In comparison with PEK-C, PES-C is more flexible, which may be related to the difference between the sulfone and ketone groups.

Figure 2 shows a typical plot of the measured intensity−intensity time correlation function of PES3 in CHCl$_3$ at $\theta = 20°$ and $T = 25$ °C. For a polydisperse sample, $g^{(1)}(t,\theta)$ is related to the line width distribution $G(\Gamma)$ by

$$g^{(1)}(t,\theta) = \langle E(t,\theta)E^*(0,\theta)\rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}\,d\Gamma \qquad (3)$$

The computer program CONTIN[16] was used in this work to convert $G^{(2)}(t,\theta)$ to $G(\Gamma)$. The line width Γ usually depends on both C and q. This dependency can be expressed as[17,18]

$$\frac{\Gamma}{q^2} = D(1 + k_dC)(1 + f\langle R_g^{\,2}\rangle_z q^2) \qquad (4)$$

where D is the translational diffusion coefficient at $C \to 0$ and $q \to 0$; k_d is the diffusion second virial coefficient. The value of f depends on the chain structure, polydispersity, and solvent quality. The value of f generally increases as the molecular weight decreases. The values of $\langle D\rangle$, f, and k_d can be calculated from $(\Gamma/q^2)_{C\to0,\theta\to0}$, $(\Gamma/q^2)_{C\to0}$ vs q^2 and $(\Gamma/q^2)_{\theta\to0}$ vs C, respectively.

Figure 3 shows the typical translational diffusion coefficient distributions of PES-C in CHCl$_3$ at 25 °C after the solution was clarified with a 0.5-μm filter ("○") and a 0.1-μm filter ("□"), respectively. When a 0.5-μm filter was used, the distribution has two peaks. The large peak with a higher average diffusion coefficient corresponds to single linear PES-C chains, while the small peak with a lower average diffusion coefficient indicates the existence of some large species in the PES-C solution. At first, we thought that these large species are the aggregates of PES-C in CHCl$_3$, but later we found that these large species can be removed by a 0.1-μm filter and the large species did not reappear in the solution even after 15 days. This leads us to speculate that these large species are polymer clusters formed during the polymerization.

Figure 4 shows the translational diffusion coefficient distribution $G(D)$ of five PES-C samples in CHCl$_3$ at $T = 25$ °C, $C \to 0$, and $q \to 0$. From $G(D)$, we were able to calculate the z-average translational diffusion coefficient $\langle D\rangle$ [$=\int_0^\infty G(D)D\,dD$] and, further, the average hydrodynamic radius $\langle R_h\rangle$ by replacing D in the Stokes−Einstein equation with $\langle D\rangle$, i.e., $\langle R_h\rangle$ [$=k_BT/(6\pi\eta\langle D\rangle)$], where k_B, T, and η are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of $\langle D\rangle$, $\langle R_h\rangle$, and $\langle R_g\rangle/\langle R_h\rangle$ of five PES-C samples are also listed in Table 1. The ratio $\langle R_g\rangle/\langle R_h\rangle$ is in the range 1.5−1.8, normally observed for a flexible polymer

Table 1. Summary of Static and Dynamic Laser Light Scattering Results for Five PES-C Samples

samples	$10^{-4}M_w$ (g/mol)	$\langle R_g^2\rangle_z^{1/2}$ (nm)	10^4A_2 (mol·cm^3/g^2)	$10^8\langle D\rangle$ (cm^2/s)	R_h (nm)	R_g/R_h	$10^{-4}(M_w)_{calcd}$ (g/mol)	$(M_w/M_n)_{DLS}$	$(M_w/M_n)_{GPC}$
PES1	8.52	13	3.9	53.9	7.46	1.7	8.48	1.33	
PES2	6.15	~10	4.5	65.0	6.20	~1.6	6.04	1.32	1.68
PES3	5.01	~10	8.6	70.0	5.75	~1.6	5.24	1.21	1.65
PES4	4.15	<9		82.0	4.71		4.11	1.17	1.47
PES5	2.50	<9		103	3.91		2.48	1.17	1.23

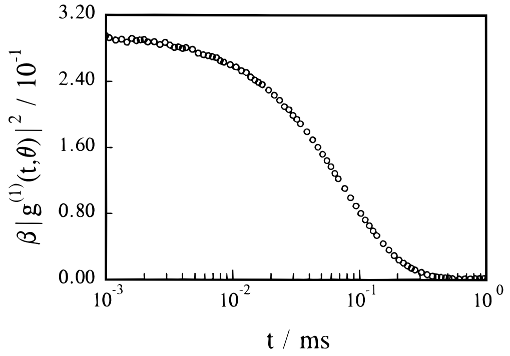


Figure 2. Typical measured intensity–intensity time correlation function of PES3 in CHCl$_3$ at $\theta = 20°$ and $T = 25$ °C.

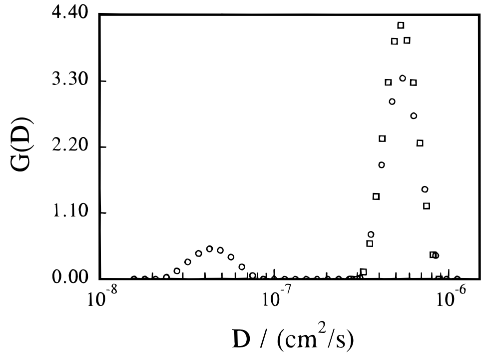


Figure 3. Translational diffusion coefficient distribution $G(D)$ of PES3 in CHCl$_3$ at $T = 25$ °C, where the symbols "○" and "□" respectively represent the clarification of the PES-C solution with a 0.5-μm filter and a 0.1-μm filter.

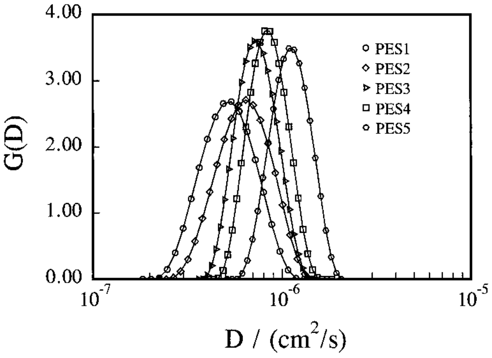


Figure 4. Translational diffusion coefficient distributions of five PES-C samples in CHCl$_3$ at $T = 25$ °C, where the solutions were clarified with a 0.1-μm filter.

chain in a good solvent.[19] They further indicate that the PES-C chain in CHCl$_3$ at $T = 25$ °C has a coil conformation. However, it should be noted that $\langle R_g\rangle$ and $\langle R_h\rangle$ are obtained from different averages. The value of $\langle R_g\rangle/\langle R_h\rangle$ for a real polymer sample with a certain polydispersity is normally larger than that theoretically predicted for an ideal monodisperse polymer sample.

Figure 5 shows a double logarithmic plot of $\langle D\rangle$ versus M_w. The line ("—") shows a least-squares fitting of $\langle D\rangle = \langle k_D\rangle M_w^{-\langle\alpha_D\rangle}$ with $\langle k_D\rangle = (2.26 \pm 0.02) \times 10^{-4}$ and $\langle\alpha_D\rangle = (0.54 \pm 0.03)$, where $\langle\ \rangle$ means that the values of $\langle k_D\rangle$ and $\langle\alpha_D\rangle$ were obtained from $\langle D\rangle$ and M_w rather than D and M for monodisperse species. The value of $\langle\alpha_D\rangle$ also indicates that the PES-C chain has a coil conformation in CHCl$_3$ at $T = 25$ °C. In principle, we can use the scaling relationship between D and M to transfer $G(D)$ into a molecular weight distribution (MWD) by using the following procedure. From dynamic LLS, by the definition of $g^{(1)}(t)$, when $t \to 0$,

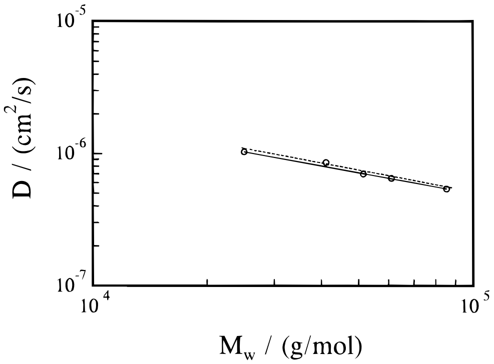


Figure 5. Double logarithmic plot of $\langle D\rangle$ vs M_w, where the solid line represents the least-squares fitting of $\langle D\rangle$ (cm^2/s) = $2.26 \times 10^{-4}M_w^{-0.54}$ and the dotted line, the calibration of D (cm^2/s) = $2.45 \times 10^{-4}M^{-0.55}$, where D and M correspond to monodisperse species.

$$[g^{(1)}(t)]_{t\to0} = \langle E(t)E^*(0)\rangle_{t\to0} = \int_0^\infty G(\Gamma)\,\mathrm{d}\Gamma \propto I \qquad (5)$$

while from static LLS, when $C \to 0$ and $q \to 0$, the net scattering intensity is given by

$$I \propto \int_0^\infty f_w(M)M\,\mathrm{d}M \qquad (6)$$

A comparison of eqs 5 and 6 leads to

$$\int_0^\infty G(\Gamma)\,\mathrm{d}\Gamma \propto \int_0^\infty f_w(M)M\,\mathrm{d}M \propto \int_0^\infty G(D)\,\mathrm{d}D \qquad (7)$$

This equation can be written as

$$\int_0^\infty G(D)D\,\mathrm{d}(\ln D) \propto \int_0^\infty f_w(M)M^2\,\mathrm{d}(\ln M) \qquad (8)$$

where d(ln D) ∝ d(ln M) since $D = k_DM^{-\alpha_D}$, which further leads to,

$$f_w(M) \propto \frac{G(D)D}{M^2} \propto G(D)D^{1+(2/\alpha_D)} \qquad (9)$$

From $f_w(M)$, we can calculate M_w by its definition,

$$(M_w)_{calcd} = \frac{\int_0^\infty f_w(M)M\,\mathrm{d}M}{\int_0^\infty f_w(M)\,\mathrm{d}M} = \frac{k_D^{1/\alpha_D}\int_0^\infty G(D)\,\mathrm{d}D}{\int_0^\infty G(D)D^{1/\alpha_D}\,\mathrm{d}D} \qquad (10)$$

Our previous studies[19,20] have shown that using $\langle k_D\rangle$ and $\langle\alpha_D\rangle$ instead of k_D and α_D can introduce a large error in the final MWD. Therefore, we have to use the measured

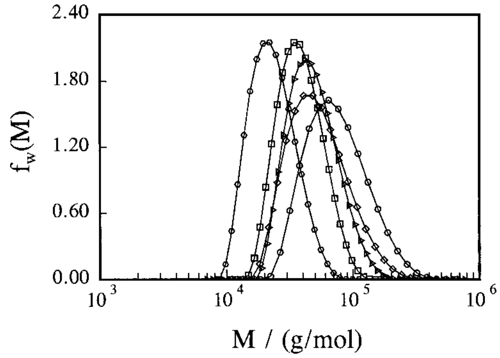


Figure 6. Differential weight distributions of five PES-C samples, where the symbols are the same as in Figure 4.

M_w from static LLS as constraints to find k_D and α_D from $G(D)$ on the basis of eqs 9 and 10. The detail of this method has been reported before.[19] Here, we determined that $\alpha_D = 0.55$ and $k_D = 2.45 \times 10^{-4}$. This pair of k_D and α_D values defines the calibration between D and M for PES-C in CHCl$_3$ at $T = 25$ °C, shown in Figure 5 by the dotted line which slightly deviates from the fitting of $\langle D\rangle = \langle k_D\rangle M_w^{-\langle\alpha_D\rangle}$. With the values of k_D and α_D, we are ready to convert the $G(D)$s in Figure 4 to their corresponding MWDs.

Figure 6 shows five differential weight distributions $f_w(M)$ of the PES-C samples. From each $f_w(M)$ we were able to calculate the weight-average molecular weight $(M_w)_{calcd}$ and polydispersity index $(M_w/M_n)_{DLS}$, which are listed in Table 1. The values of M_w/M_n show that the distribution of the PES-C samples after clarifying with a 0.1-μm filter is fairly narrow. It should be noted that the existence of a small amount of large species in PES-C was not observable in previous gel permeation chromatography (GPC), because GPC is less sensitive to a small amount of large species. For comparison, $(M_w/M_n)_{GPC}$ values obtained in GPC are also listed in Table 1. The values of M_w/M_n from GPC are larger than those from DLS because in light scattering, species with high molecular weights scatter more than those with a lower molecular weight; namely M_n estimated from dynamic light scattering is generally higher than the true M_n, or in other words, a smaller M_w/M_n.

Conclusion

A combination of static and dynamic laser light-scattering studies of five phenolphthalein poly(ether sulfone) (PES-C) samples shows that the PES-C chain in CHCl$_3$ at $T = 25$ °C has a random coil conformation with a persistence length of ~1 nm and $C_\infty \approx 13$, and CHCl$_3$ is a fairly good solvent for PES-C at room temperature. A calibration between the translational diffusion coefficient (D) and molecular weight (M) has been determined, namely, $D = (2.45 \times 10^{-4})M^{-0.55}$. Using this calibration we have determined not only weight-average molecular weights of five PES-C samples but also their molecular weight distributions. The established calibration between D and M together with the values of A_2 will enable us to characterize PES-C with only one concentration in the future.

Acknowledgment. The financial support of this work by RGC (the Research Grants Council of the Hong Kong Government) Earmarked Grants 1994/95 (CUHK A/C No. 220600640) is gratefully acknowledged. M.S. is grateful to the Hong Kong Commonwealth Scholarship Commission (Government of Hong Kong) for its generous financial support which has made his Ph.D. study possible at the Chinese University of Hong Kong. He also acknowledges Gomal University, Pakistan, for granting him the study leave.

References and Notes

(1) Rose, J. B.; Stainland, P. A. U.S. Patent 4,320,224, 1982.
(2) Mijovic. *J. Polym. News* **1989**, *14*, 177.
(3) Critchley, J. P.; Knight, G. J.; Wright, W. W. *Heat Resistant Polymers*; Plenum Press: New York, 1983.
(4) Mullin, M. J.; Woo, E. p. j. *Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27* (2), 313.
(5) Day, M.; Suprunphuk, T.; Cooney, J. D.; Wiles, D. M. *J. Appl. Polym. Sci.* **1988**, *36*, 1097.
(6) Mathew, T. B.; Frank, E. K.; Paul, S. R.; Kenneth, H. L. *Macromolecules* **1985**, *18*, 86.
(7) Roovers, J.; Cooney, T. D.; Topororowski, M. *Macromolecules* **1990**, *23*, 1161.
(8) Bo, S.; Yan, G.; Pan, H. Y.; Hu, H.; Chen, T. *Chem. J. Chin.*, in press.
(9) Bo, S.; Yan. G.; Pan, H. Y.; Chen, T. Unpublished data.
(10) Wu, C.; Siddiq, M.; Woo, K. F. *Macromolecules* **1995**, *28*, 4914.
(11) Bo, S.; Yang, H.; Chen, T. *Funct. Polym.* **1991**, *4*, 147.
(12) Pecora, R.; Berne, J. *Dynamic light Scattering*; Plenum Press: New York, 1976.
(13) Chu, B.*Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.
(14) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(15) Wu, C.; Xia, K. Q. *Rev. Sci. Instrum.* **1994**, *65* (3), 587.
(16) Provencher, S. W. *Biophys. J.* **1976**, *16*, 27; *J. Chem. Phys.* **1976**, *64* (7), 2772.
(17) Stockmayer, W. H.; Schmidt, M. *Pure Appl. Chem.* **1982**, *54*, 407.
(18) Stockmayer, W. H.; Schmidt, M. *Macromolecules* **1984**, *17*, 509.
(19) Wu, C. *Colloid Polym. Sci.* **1993**, *271*, 947.
(20) Wu, C. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 803.

MA951416D