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Dynamic light scattering studies of poly(methyl methacrylate)–polystyrene copolymers in their theta solvents

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Abstract

The coil-globule transitions of random (statistical) and alternating copolymers of styrene and methyl methacrylate in their theta solvents, cyclohexanol and 2-ethoxy ethanol were studied by using dynamic light scattering technique. The dimensions of the copolymeric chains show smooth and continous contractions below θ temperatures. The hydrodynamic size, R_h, of a random copolymer P(St-*co*-MMA) ($M_w = 4.59 \times 10^6$ g/mol) in cyclohexanol ($\theta = 68.6$°C) decreases to 48% of that in the unperturbed state at 56.5°C. This copolymer shows a similar contraction behavior in a second theta solvent 2-ethoxy ethanol ($\theta = 58.4$°C). The R_h of this copolymer decreases again to 48% of that in the unperturbed state at 45.3°C. An alternating copolymer of the same monomers P(St-*alt*-MMA) ($M_w = 2.62 \times 10^6$ g/mol) displayed a comparable chain contraction. The hydrodynamic size of this sample in cyclohexanol was reduced to 59% of that in the unperturbed state by decreasing temperature from 60.8 to 53.3°C. For the random and alternating copolymers studied in this work, the temperature interval from the θ-state to the collapsed state is narrower compared to that of the PMMA homopolymer. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic light scattering; Poly(St-*co*-MMA); Coil-globule transition

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1. Introduction

The transition of macromolecular chains from a random-coil behavior in the theta state to a globular compact form (coil-globular transition) in the collapsed state, has been the subject of extensive studies [1–6]. Most of the coil-globule transition experiments were carried out for polystyrene solutions at extremely low concentrations. Various experimental methods such as static and quasielastic light scattering, small angle neutron scattering, ultracentrifuge and viscometric measurements have been used for the determination of linear polymer dimensions. Two sets of contradictory experimental data for contraction of polystyrene in cyclohexane were reported in earlier works [1,4], one giving a very sharp transition and the other indicating a gradual contraction. The chain contraction reported for a polystyrene–cyclohexane system was only about 75% of the unperturbed theta state [4]. This small decrease in size does not satisfy the criteria of a densely packed collapsed globule.

The collapse from a coil to a compact globular state is now also established experimentally for poly(methyl methacrylate) (PMMA) in various solvents. Detailed static [7,8] and dynamic [9,10] light scattering as well as viscosimetric [11] measurements have been carried out. Since phase separation occured very slowly in this system, the molecular dimensions could be determined reliably even far below the phase separation temperature [7]. In each of these solvent systems, a gradual contraction of PMMA chains was observed and the chain size was reduced to about 40% of its θ-state dimensions. The segment volume fraction was estimated as $\varnothing = 0.56$, which indicates that the density in the polymer domain of the globule is relatively high [10].

Since the prediction of the collapse of a polymer chain from a coil to a rather dense form by Stockmayer in 1960 [12], the coil-globule transition has been subject to extensive theoretical research. The expansion of a random coil and the temperature dependence of the expansion factor α can be obtain from the classical Flory equation for the

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excluded volume [13]. For the contracted coil, Birshtein and Pryamitsin derived the following equation for the expansion factor α as

$$\alpha^3 - \alpha - C(\alpha^{-3} - 1) = BN^{1/2}\tau, \quad (1)$$

where N represents the number of Kuhn segments in the chain, B and C are parameters that do not depend on molecular weight M or temperature T, but rather on chain stiffness, and $\tau = (T - \theta)/\theta$ is the reduced temperature; C is related to the third virial coefficient [14].

The theory of the coil-globule transition of homopolymers has been developed now with quantitative accuracy [15–17]. Theoretical studies have utilized a variety of approaches in focusing on different aspects of the polymer collapse problem. Langevin models, phenomenological models and computer simulations have been used to consider kinetics of collapse in the absence of topological constrains [18]. The extensive theoretical studies have also been motivated by the perceived relation to the protein folding problem, and indeed initiation of protein folding indicates certain similarities to contraction of flexible synthetic polymers.

Recently, we have studied the time dependence of the coil-globule chain collapse of PMMA in isoamyl acetate and *n*-butyl chloride by dynamic light scattering [19]. The coil-globule transition time of a high molecular weight PMMA chain rapidly cooled from the θ-state (61°C) to the lowest possible temperature (18.5°C) attainable without complete aggregation was found to be of the order of the thermal equilibration time of the solution [10,19].

In the last few years, a large amount of work has focused attention on the conformational properties of heteropolymers. One of the questions is whether chain disorder could affect polymer behavior at the theta state. Recent theoretical work on model randomly charged polymers in 2D and 3D has shown that disorder does not eliminate the universality of theta transition [20]. However, there are indications that a sufficient degree of chain disorder can modify the theta behavior of heteropolymers, compared to homopolymers [21].

A theoretical approach to the description of the coil-globule transition of random copolymers with a fixed sequence of units is based on self-consistent minimization of intramolecular free energy has been published recently [22]. In all cases a first-order coil-globule transition, unlike the analogous homopolymer was predicted.

While the number of theoretical contributions on homopolymer and copolymer collapse is increasing [23–27], there is relatively little experimental work describing the collapse process in copolymer chains. Some experimental studies have been reported on the dilute, semidilute and concentrated solutions of random and block copolymers [28,29].

In this contribution, we have studied the coil-globule transitions of random (statistical) and alternating copolymers of styrene (St) and methyl methacrylate (MMA) in cyclohexanol and 2-ethoxy ethanol. Thermodynamical and solution properties of these two copolymers in the respective solvents were established some time ago [30–33].

2. Experimental

2.1. Sample preparation

Random copolymers of styrene and methyl methacrylate, P(St-*co*-MMA), were prepared by thermal bulk polymerization of the pure monomers of styrene and methyl methacrylate. The monomers (Fluka) were freed from inhibitors by washing with 5% aqueous NaOH solution and distilled water, dried with Na_2SO_4 and freshly distilled under reduced pressure before use (b.p. 24°C at 6 mmHg for St, and 20°C at 7 mmHg for MMA). Equimolar mixtures of monomers were degassed three times under high vacuum and polymerized for 12 days. The conversion to copolymer was 1.87%. Fractionation of the copolymer P(St-*co*-MMA) was carried out by fractional precipitation at 25°C using toluene as solvent and methanol as nonsolvent. In this process, 1.00 g of copolymer was dissolved in 0.1 w/w% toluene and 0.20 g P(St-*co*-MMA) as the first (highest molecular weight) fraction was obtained. This fraction was further fractionated and the resulting product was 0.097 g random copolymer. This sample was redissolved in toluene, precipitated into methanol and dried in vacuo at 40°C.

Alternating copolymer P(St-*alt*-MMA) and block copolymer P(St-*b*-MMA) were obtained from Polymer Source Inc. (Dorval). The characteristics of these materials are given in Table 1.

2.2. Characterization

2.2.1. Gel permeation chromatography

Gel permeation chromatography (GPC) was used to determine the molecular weight of copolymer samples. The copolymers were dissolved in tetrahydrofuran (THF) and then filtered through a 0.45 μm teflon filter. The measurements were in THF at a flow rate of 1.3 ml/min using a Jordi Gel 10^5 Å DVB Mixed Bed column, 50 cm × 10 mm (ID), at a column oven temperature of 35°C. The injection volume was 100 μl of a 0.25% (w/v) solution. The samples were monitored at a sensitivity of 8 × and a scale factor of 20 on a Waters Model 410 DRI.

2.2.2. ^{1}H Nuclear magnetic resonance

^{1}H NMR spectra of the three copolymer samples were obtained on a Bruker MX-500 spectrometer at 500 MHz. The spectra were taken in deuterated chloroform at 20°C and are shown in Fig. 1.

2.2.3. Dynamic light scattering measurements

Dust free solutions for dynamic light scattering (DLS) measurements was prepared as follows. Copolymer

Table 1
Characterization of copolymer samples

Samples	Styrene[a] (mol%)	M_w ($\times 10^{-5}$g/mol)	M_n ($\times 10^{-5}$g/mol)	η (dl/g)[b]	M_w/M_n
Random copolymer					
P(St-*co*-MMA)[c]	50	36.0	11.8	4.08	3.05
P(St-*co*-MMA)[d]		45.9	34.2	5.81	1.35
Alternating copolymer					
P(St-*alt*-MMA)	50	26.2	17.0	–	1.54
Block copolymer					
P(St-*b*-MMA)	11.5	PS:(1.34)	PS:(1.27) PMMA:(11.03)	–	1.30

[a] ^{1}H NMR, $CDCl_3$, 500 MHz; and elemental analysis.
[b] In methyl ethyl ketone, 25°C.
[c] Unfractionated.
[d] Fractionated.

solutions with a concentration of $\sim 9 \times 10^{-5}$ g/ml were prepared in the θ-solvents, cyclohexanol and 2-ethoxy ethanol. The solutions were held in an oven at 90 and 80°C, respectively, for complete dissolution. The solutions were then filtered carefully into a dust-free light scattering cell using 0.2 μm Millipore filters. The filtration of hot solutions into the cells is carried out in the same oven at elevated temperatures. The cells were then transferred to the vat of DLS spectrometer.

DLS measurements were conducted using a commercial DLS spectrometer (ALV/LSE 5000) operating at $\lambda =$ 514.5 nm with an Ar laser. Thin walled cylindrical cells (0.30 mm wall thickness, 10 mm outer diameter and 75 mm length) (Wilmad Glass, New Jersey) were used. Temperature was controlled to ±0.01°C.

The solutions were quenched to the selected temperature from the θ-temperature and the consequent size change, was determined by DLS measurements in terms of hydrodynamic radius (R_h).

The raw output of DLS experiment, namely the autocorrelation function of the scattered light intensity, $G_2(\tau)$, was plotted with a logarithmic time scale. The correlation functions were measured at a scattering angle of 33°. $G_2(\tau)$ is related to the normalized first-order electric field

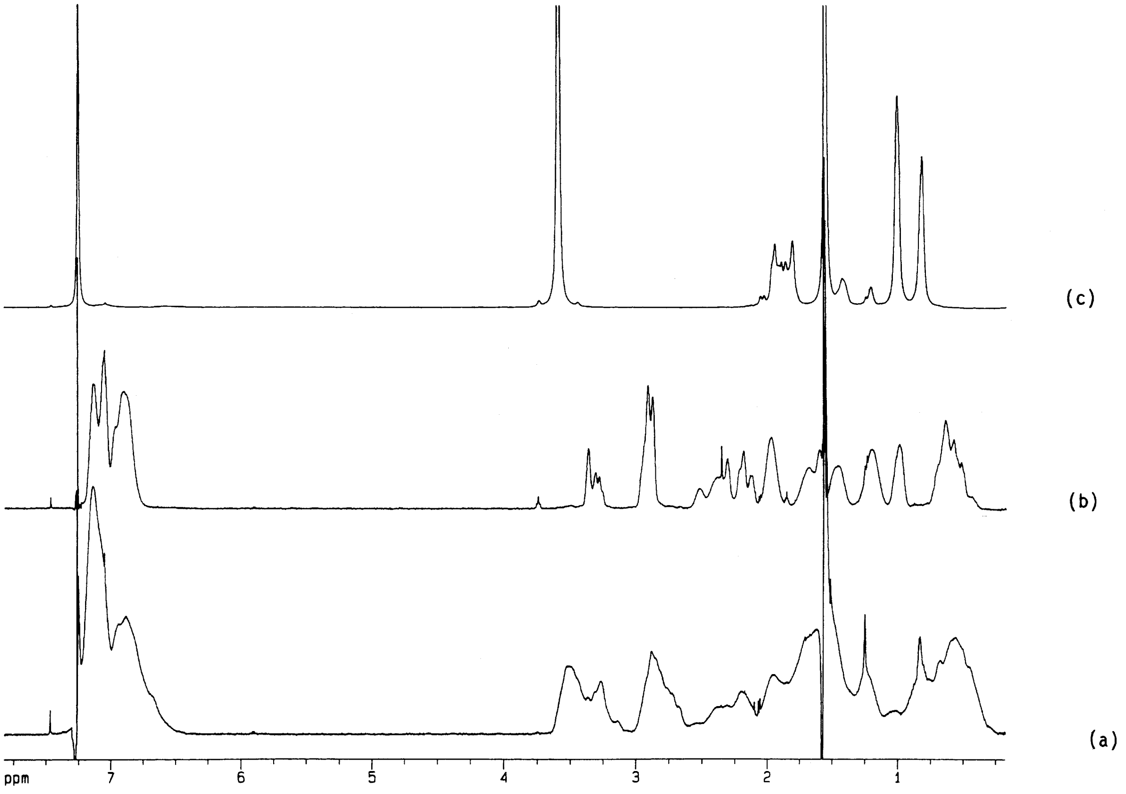

Fig. 1. ^{1}H NMR spectrum of copolymers. (a) P(St-*co*-MMA), (b) P(St-*alt*-MMA), (c) P(St-*b*-MMA).

Table 2
Hydrodynamic radii and expansion factors of copolymers in theta solvents (CH: cyclohexanol; EE: 2-ethoxy ethanol; T: the lowest temperature at which polymer coil is stable)

Sample name	θ-temperatures [28-31]	R_h (nm) at θ	$\alpha = R_h(T)/R_h(\theta)$	∅
P(St-*co*-MMA)	68.6 (CH)	36.0	0.48	0.04
	58.4 (2-EE)	38.0	0.48	0.03
P(St-*alt*-MMA)	60.8 (CH)	16.0	0.59	0.23
P(St-*b*-MMA)	84 (CH)	–	–	–
PS	83 (CH) insoluble in 2-EE	–	–	–
PMMA	78.8 (CH) soluble (2-EE)	–	–	–

correlation function $g_1(\tau)$ by [34,35]

$$G_2(\tau) = A[1 + \beta|g_1(\tau)|^2], \tag{2}$$

where A is a baseline constant, β the coherence parameter depending on the instrumental optics and $\tau(\equiv \Gamma^{-1})$ is delay time.

For polydisperse and concentrated systems, $g_1(\tau)$ is expressed by the distribution function $G(\Gamma)$ of the decay rate Γ as

$$g_1(\tau) = \int G(\Gamma)\exp(-\Gamma\tau)\,d\Gamma, \tag{3}$$

where $\int G(\Gamma)\,d\Gamma = 1$. That is, $g_1(\tau)$ is the Laplace transform of $G(\Gamma)$.

For a diffuse relaxation, in the limit of $qR_g < 1$ and at very dilute solution concentrations, Γ can be further related to the average translational diffusion coefficient D by $D = (\Gamma/q^2)_{q\to 0}$, where $q = 4\pi n/\lambda(\sin\theta/2)$, $\lambda = 514.5$ nm, $n =$ refractive index of the solvent and θ is the scattering angle. By using the Stokes–Einstein equation, the hydrodynamic radius, R_h may be evaluated from the diffusion coefficient at infinite dilution D_0

$$R_h = k_B T/6\pi\eta D_0, \tag{4}$$

where k_B is the Boltzmann constant, η the solvent viscosity and T is the absolute temperature. We have measured the solvent viscosities of cyclohexanol and 2-ethoxy ethanol at different temperatures by a precision capillary viscometer. Cannon–Ubbelohde 1C-330 and 1C-660 were used for these two solvents, respectively. The solvent viscosities, η, in centipoise (cp) were obtained by multiplying the efflux time in seconds by the viscometer constant and the density of the solvent in g/cm^3. The respective viscosities of the solvents cyclohexanol and 2-ethoxy ethanol were calculated by using the following equations:

$$\log\eta(T) = -5.66 + 2191/T, \tag{5}$$

$$\log\eta(T) = -2.35 + 786/T, \tag{6}$$

where η is the solvent viscosity in cp and T is the temperature in K. Data analysis of the electric field time correlation curve was performed by using the method of cumulants and the CONTIN method [36,37].

3. Results and discussion

Dilute solution properties of styrene–methyl methacrylate copolymers with different architectures were studied in detail. Theta temperatures are reported in cyclohexanol and 2-ethoxy ethanol for random (statistical), alternating and

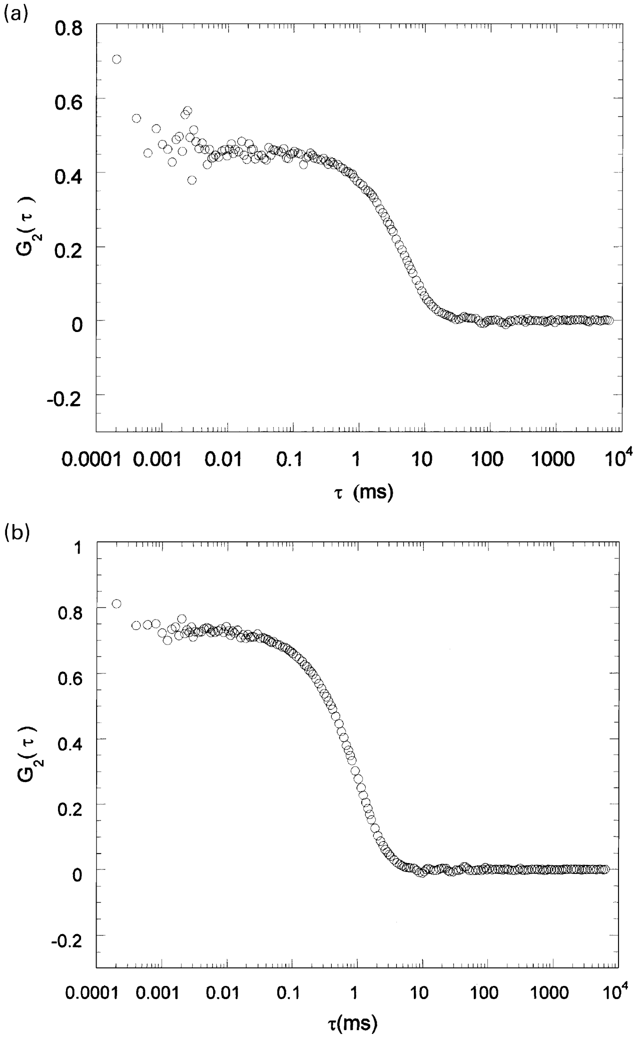

Fig. 2. The intensity autocorrelation function $G_2(\tau)$ of P(St-*co*-MMA) in cyclohexanol solution: (a) ($C = 9\times10^{-5}$ g/ml) at 68.6°C (θ-temperature) and P(St-*co*-MMA) in 2-ethoxy ethanol solution, (b) ($C = 9\times10^{-5}$ g/ml) at 58.4°C (θ-temperature).

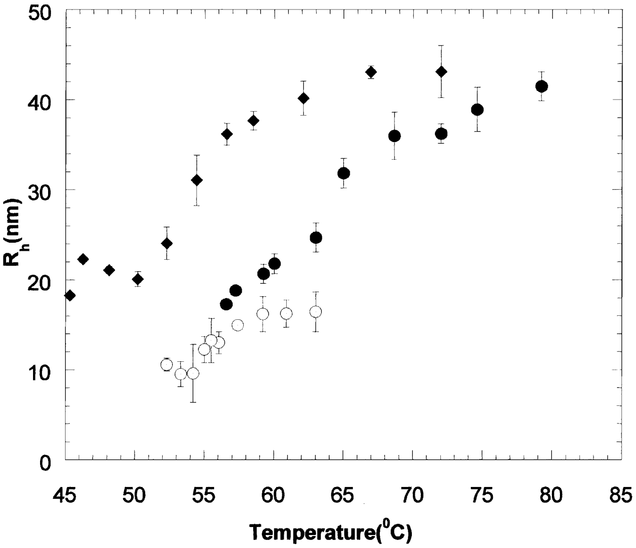

Fig. 3. Plot of the hydrodynamic radius (R_h) versus temperature for P(St-*co*-MMA) in cyclohexanol solution (●); P(St-*co*-MMA) in 2-ethoxy ethanol solution (◆) and P(St-*alt*-MMA) in cyclohexanol solution (○).

block copolymers of these monomers [30–33]. The theta temperatures for these copolymers and for the respective homopolymers are given in Table 2.

Fig. 2 shows the intensity autocorrelation functions $G_2(\tau)$ of the dilute ($C = 9 \times 10^{-5}$ g/ml) solutions of the random copolymer P(St-*co*-MMA). Fig. 2(a) shows $G_2(\tau)$ at 68.6°C (θ-temperature) in cyclohexanol, and yields an average decay rate, $\Gamma = 0.114$ m/s, a variance, $\mu_2/\Gamma^2 = 0.03098$, at a scattering angle of 33° (where for this sample, the value of $R_{g,\theta}(\approx 0.36) < 1$). M_z/M_w was estimated as 1.12 for this solution using the relation [38] $M_z/M_w \cong 1 + 4(\mu_2/\Gamma^2)$. Fig. 2(b) shows a $G_2(\tau)$ at 58.4°C (θ-temperature) in 2-ethoxy ethanol ($\Gamma = 0.534$ m/s, $\mu_2/\Gamma^2 = 0.0253$, $M_z/M_w = 1.10$) also at a scattering angle 33° (where the value of $R_{g,\theta}(\approx 0.367) < 1$). The average hydrodynamic radii of this copolymer at the θ-temperatures were calculated from Eq. (4) as 36 and 38 nm in cyclohexanol and 2-ethoxy ethanol, respectively. In Fig. 3, the contraction of the hydrodynamic radius determined from the correlation function measurements is shown as a function of temperature for the dilute solutions of random copolymer P(St-*co*-MMA) in cyclohexanol and 2-ethoxy ethanol. The R_h values for alternating copolymer P(St-*alt*-MMA) in dilute ($C = 9 \times 10^{-5}$ g/ml) cyclohexanol solution is also included in Fig. 3 for comparison. The average hydrodynamic radius for this alternating copolymer at the θ-temperature (60.8°C) is 16 nm. The overall trend for the behaviors of these copolymers is similar.

DLS measurements at each temperature were conducted after equilibrium was reached. By measuring the temperature profile of a typical DLS cell quenched from 68.6 to 56.5°C and 58.5 to 45.3°C for cyclohexanol and 2-ethoxy ethanol, respectively (Fig. 4), it can be seen that the time to reach thermal equilibrium (t_e) is about 15 and 10 s for these solvents, respectively. For these measurements, a thermocouple read by a digital thermometer (Omega Engineering, Inc., model 115 KC) was inserted into the center of the cell filled with cyclohexanol and 2-ethoxy ethanol for simulation of the temperature changes in the quenching process.

The hydrodynamic size distribution of P(St-*co*-MMA) in cyclohexanol at the θ-temperature ($\theta = 68.6$°C) and poor solvent condition ($T = 56.5$°C) are given in Fig. 5. Although the R_h distribution follows a single modal pattern, an apparent decrease in the normalized variance (μ_2/Γ^2) was observed and the polydispersity of the R_h distribution (M_z/M_w) changed from 1.12 to 1.07. This experimental

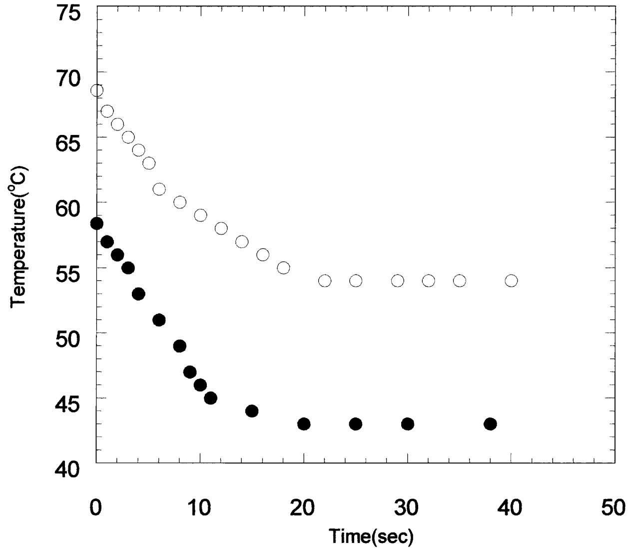

Fig. 4. Temperature-time curve of cyclohexanol (○) and 2-ethoxy ethanol (●) filled DLS cell on quenching from 68.6 to 56.5°C and 58.5 to 45.3°C, respectively.

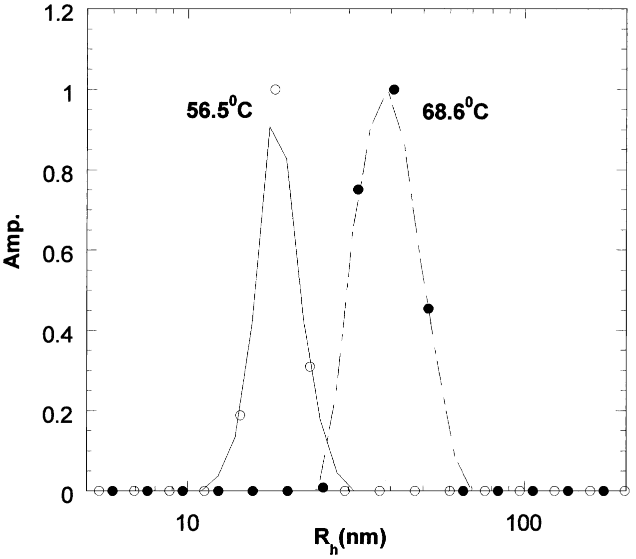

Fig. 5. Typical hydrodynamic radius distribution of P(St-*co*-MMA)/cyclohexanol at theta conditions (●: $T = 68.6$°C, $R_h = 36.0$ nm) and poor solvent conditions (○: $T = 56.6$°C, $R_h = 17.4$ nm).

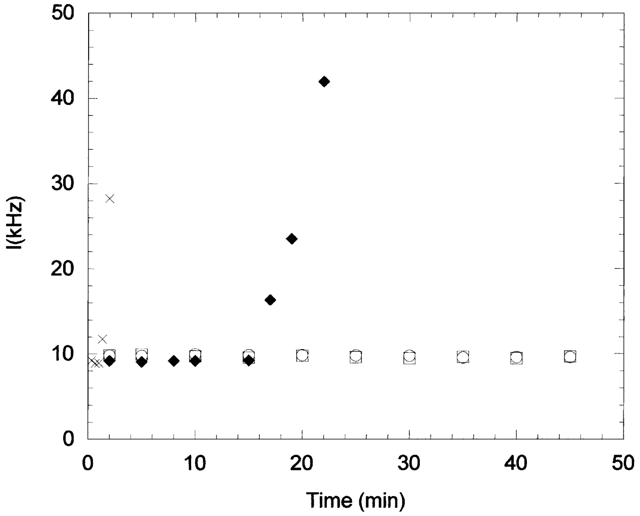

Fig. 6. Time dependence of the intensity of light for P(St-*co*-MMA) in cyclohexanol at 74.5°C (□); 68.5°C (○); 60°C (◆) and 56.5°C (×).

observation could imply that the shrinkage of polymer coils occured yielding a lower value in terms of M_z/M_w. Fig. 6 shows the time dependence of light intensity at several temperatures. There was no noticable increase in intensity with time at θ-temperature (68.5°C) and above. However, at 60°C the intensity was stable for only about 16 min. After that time the intensity increased sharply indicating an aggregation of the chains. Complete precipitation was observed after 23 min. At 56.5°C the polymer chain in the contacted form for only about 60 s.

Fig. 7 shows the hydrodynamic size distribution of this random copolymer in 2-ethoxy ethanol at θ-temperature (58.5°C) and poor solvent condition ($T = 45.3$°C). Again the R_h distribution is obeyed a single modal distribution, the polydispersity of R_h distribution (M_z/M_w) remains constant at 1.10.

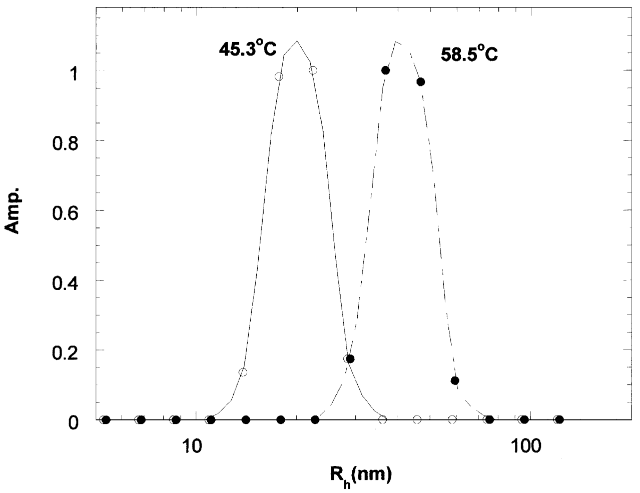

Fig. 7. Typical hydrodynamic radius distribution of P(St-*co*-MMA)/2-ethoxy ethanol at theta conditions (●: $T = 58.5$°C, $R_h = 38.0$ nm) and poor solvent conditions (○: $T = 45.3$°C,$R_h = 18.2$ nm).

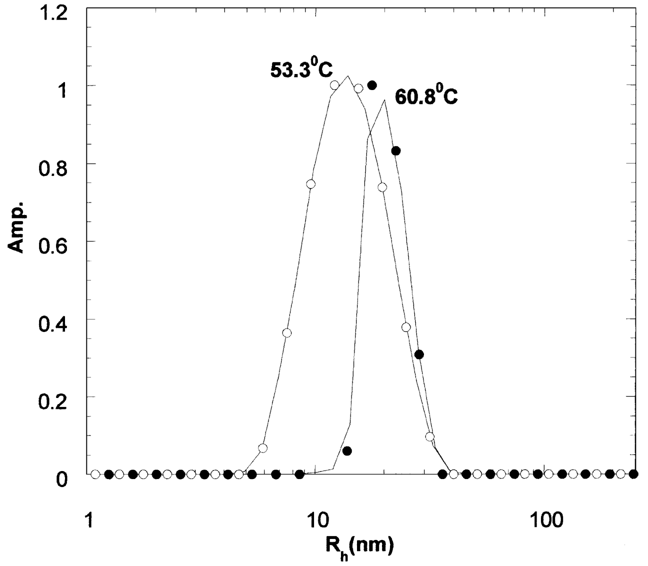

Fig. 8. Typical hydrodynamic radius distribution of P(St-*alt*-MMA)/cyclohexanol at theta conditions (●: $T = 60.8$°C, $R_h = 15.9$ nm) and poor solvent conditions (○: $T = 53.3$°C, $R_h = 10.1$ nm).

Fig. 8 shows the hydrodynamic size distribution of the alternating copolymer P(St-*alt*-MMA) in cyclohexanol at θ-temperature ($\theta = 60.8$°C) and under poor solvent conditions ($T = 53.3$°C). The shape of the R_h distribution still obeyed a single modal distribution, but the polydispersity of R_h distribution (M_z/M_w) changed from 1.19 to 1.39. The polymer coil was stable in the contracted state for a time period of 13 min, and a second growing peak was not seen in the CONTIN analysis. At 52.3°C which is some 8.6°C below the theta temperature, the system was not stable and it was not possible to measure R_h value. The scattered intensity increases gradually confirming that the aggregation of polymer chains is in progress. Fig. 9 also shows the time dependence of the intensity of light in highly dilute solution at

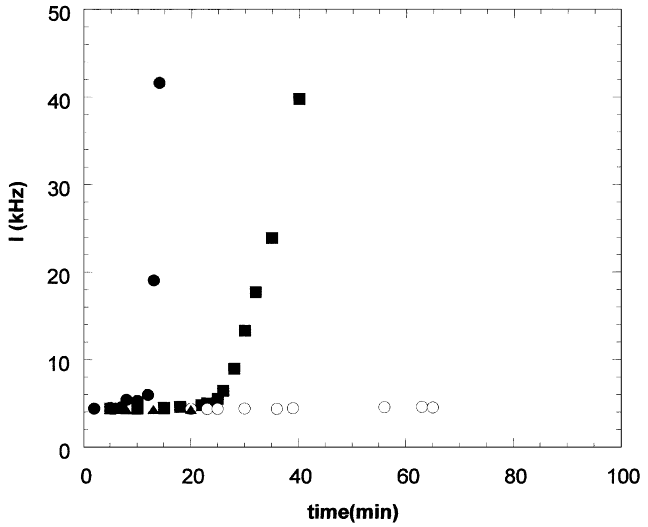

Fig. 9. Time dependence of the intensity of light for P(St-*alt*-MMA) in cyclohexanol at 63°C (▲); 60.8°C (○); 54.2°C (■) and 53.3°C (●).

several temperatures. At 63.0 and 60.8°C the intensity of light is stable through a long period of time. At 54.2°C there is no noticable increase in intensity during the first 25 min, under these conditions which have been described in this manuscript. As we mentioned previously, at 53.3°C the polymer coil is stable in the contracted state for about 13 min.

Fig. 10 shows the temperature dependence of the squared linear expansion factor α_h^2 [$\alpha_h = R_h(T)/R_h(\theta)$] of the random and alternating styrene–methyl methacrylate copolymers. Dynamic light scattering results exhibit a continous rather than a discrete transition. A theoretical two stage model of a single-chain collapse for polystyrene in cyclohexane had been proposed earlier [40–42]. This theory predicted a rather fast crumpling of the unknotted polymer chain (crumpled globule with 'blobs') and a subsequent slow rearrangement of the blobs of the collapsed polymer chain into a compact globule. Chu, Grosberg and their co-workers reported experimentally two-stage kinetics in a single chain collapse of polystyrene in cyclohexane [36]. However, Allegra and co-workers considered the possibility of chain clustering or aggregation during the second stage of collapse and found that clusters of two to five polystyrene chains have a smaller radius than a single globular chain [43,44]. Two stage collapse was not observed for poly(methyl methacrylate) in various solvents [7–11]. Our results show that there is no indication of a two stage collapse for the copolymers studied in this work. On the other hand, the temperature interval from the θ-state to the collapsed state is narrower than for PMMA homopolymer. In PMMA-isoamyl acetate system, a contraction ($\alpha = 0.41$) was observed after about 40°C decrease from the θ-temperature ($\theta = 61$°C). For P(St-*co*-MMA) a contraction ($\alpha = 0.48$) is observed after a temperature drop of only 12°C in cyclohexanol and 13°C in 2-ethoxy ethanol. For P(St-*alt*-MMA)–cyclohexanol system, the temperature interval is 7.6°C when $\alpha = 0.59$.

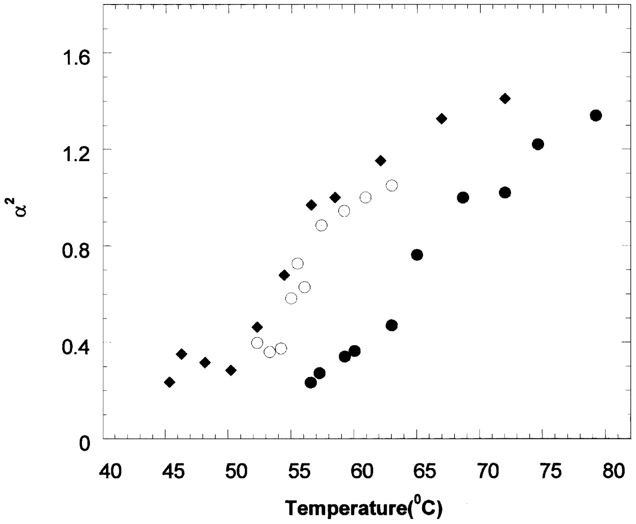

Fig. 10. The plot of expansion factor α_h^2 versus temperature for P(St-*co*-MMA) in cyclohexanol (●); in 2-ethoxy ethanol (◆); and P(St-*alt*-MMA) in cyclohexanol (○).

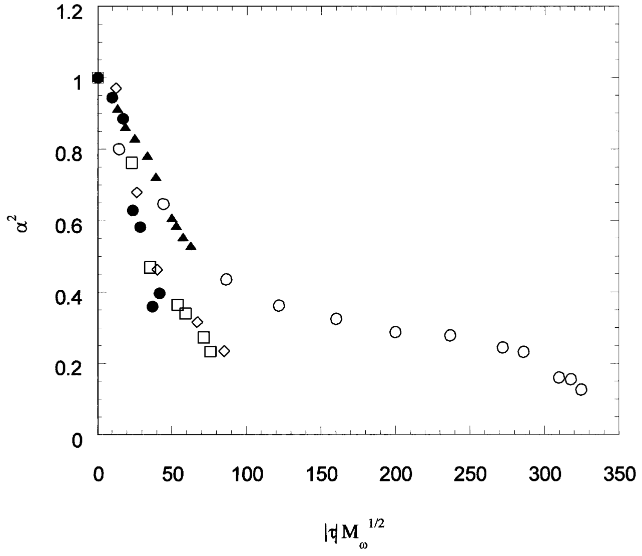

Fig. 11. Plot of expansion factor of α^2 versus $|\tau|M_w^{1/2}$ with $\tau = 1 - (T/\theta)$ and molecular weight M_w (g/mol). (●) P(St-*alt*-MMA)/cyclohexanol; (□) P(St-*co*-MMA)/cyclo hexanol; (◇) P(St-*co*-MMA)/2-ethoxy ethanol; (○) PMMA isoamylacetate; (▲) PSt cyclohexane.

In Fig. 11, the observed expansion factors α^2 were plotted against $|\tau|M_w^{1/2}$ for PS [4], PMMA [19] and for the copolymers used in this work. It will be seen again that α^2 values of copolymers decrease more rapidly than the homopolymers with increasing $|\tau|M_w^{1/2}$. At the lowest attainable temperature the expansion factor of random copolymer, P(St-*co*-MMA), in both solvents is very close to PMMA homopolymer.

Fig. 12 shows scaled expansion factor of the hydrodynamic size $\alpha_h^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ for P(St-*co*-MMA) in cyclohexanol and 2-ethoxy ethanol and P(St-*alt*-MMA) in

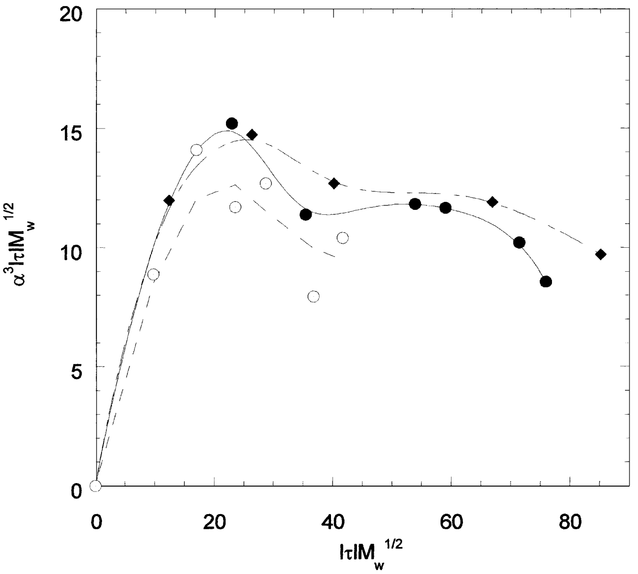

Fig. 12. Scaled expansion factor $\alpha_h^3\tau M_w^{1/2}$ of the hydrodynamic radius versus $\tau M_w^{1/2}$ for P(St-*co*-MMA)/cyclohexanol (●); P(St-*co*-MMA)/2-ethoxy ethanol (◆) and P(St-*alt*-MMA)/cyclohexanol (○).

cyclohexanol solutions. Well defined plateau regions similar to those observed in the homopolymer–solvent system were not seen [2–11,39]. However, the shapes of the curves indicate the validity of Eq. (1) for these copolymer–solvent systems.

The segment volume fraction $\varnothing$ of the globule is given by $\varnothing = (M_w/\rho)/(4\pi/3R_h^3N_A)$ where $\rho = 1.1$ g/ml is the density of copolymers in the amorphous state, M_w is the weight average molecular weight of copolymers and N_A is the Avogadro number. The segment volume fractions are estimated as $\varnothing = 0.04$ and 0.03 in cyclohexanol and 2-ethoxy ethanol, respectively, for random copolymer; while for the alternating copolymer we have obtained a much more dense globule ($\varnothing = 0.23$) in cyclohexanol.

It would be interesting to study contraction behavior of a block copolymer, P(St-*b*-MMA). Unfortunately θ-temperature of our sample in cyclohexanol was too high (84°C). At this temperature we were not able to report any reliable DLS data.

4. Conclusion

In this contribution, we have studied the temperature dependence of the dimensions of random (statistical) and alternating P(St-MMA) chains in two solvents: cyclohexanol and 2-ethoxy ethanol. Kinetic studies have shown that the coil-globule transition time of a high molecular weight PMMA chain rapidly cooled from θ-state to the lowest temperature attainable without complete aggregation is of order or lower than the thermal equilibration time (about 15 s) of the solution [19]. We compared the collapse of copolymers with the contraction of corresponding homopolymers.

For the random and alternating copolymers in the same solvent the θ-temperatures are about 70 and 60°C, respectively. For copolymers the temperature interval from θ-state to reach to that in the collapsed state is rather short compared to homopolymers. These observations suggest that, the early stage of collapse of copolymer chains is more facile compared to that in homopolymers. Further DLS studies on copolymers, terpolymers and especially block copolymers comprised of different units will provide quantitative information on coil-globule collapse problems.

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