Dynamic light scattering studies of poly(4-chlorostyrene) and poly(2-chlorostyrene) in theta solvents

E. Elif Hamurcu[a], L. Akcelrud[d], Bahattin M. Baysal[a,b],* and Frank E. Karasz[c]
[a]*TUBITAK Marmara Research Center, Department of Chemistry, 41470 Gebze-Kocaeli, Turkey*
[b]*Boğaziçi University, Department of Chemical Engineering, 80815 Bebek-İstanbul, Turkey*
[c]*Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA*
[d]*Instituto de Quimica, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*

Most studies of coil-to-globule transitions of macromolecules have dealt exclusively with the standard polystyrene–cyclohexane system. In this work we aim to extend such investigations to halogenated polystyrenes, namely poly(4-chlorostyrene)(PPCS), poly(2-chlorostyrene)(POCS) and poly(chlorostyrene)(PCS), a mixture of 2- and 4- isomers. Changes in R_h of these polymers with temperature in their respective theta solvents were investigated by dynamic light scattering. The hydrodynamic size of PPCS in *n*-propyl benzene(M_w: 2.25×10^6 g mol^{-1}, M_w/M_n: 1.16) decreases to 75% of that in the unperturbed state at 22.2°C. POCS (M_w: 10.32×10^6 and M_w: 4.30×10^6, M_w/M_n: 1.10) in 2-butanone exhibited LCST behaviour and a limited chain collapse was observed with increasing temperature above theta point. The parameters $\alpha_h = R_h/R_h(\theta)$ for POCS with two different molecular weights, (10.32 M and 4.30 M) were found to be 0.67 and 0.77, respectively at 37.0°C. A smooth and continuous contraction was also observed for the mixture of 2- and 4- isomers, PCS (M_w: 2.32×10^6 g mol^{-1}, M_w/M_n: 1.06). © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The transition of a polymer chain in dilute solution from an expanded coil to a collapsed, compact globular structure has been the subject of extensive research in the last decade[1–11]. Williams *et al.*[12] summarized the contributions made by the end of 1970s, and Fujita[13] presented a review on this subject in 1990. The great interest in this coil-to-globule transition is not only due to its importance as a general and fundamental concept in polymer physics and solution dynamics but also its intimate relation to biological processes, including DNA folding and protein denaturation[8,9]. However, the vast majority of published works on chain collapse have been limited to studies of polystyrene in various hydrocarbon solvents[1–11]. Therefore, in this aspect, an extension of current theories and experiments to include the practical problems of hydrogen bonding, dipole–dipole and ionic interactions, block copolymers and macromolecular anisotropy is warranted. In this work, we aimed to extend coil-to-globule studies to highly dilute solutions of macromolecules containing polar groups, such as halogenated polystyrenes, poly-(4-chlorostyrene) (PPCS), and poly(2-chlorostyrene)(POCS). So far, only a limited number of experimental studies on solution properties and coil-to-globule transitions of these polymers have been reported[14–20]. The present contribution considers the coil-to-globule transition behaviour of poly(4-chlorostyrene) and poly(2-chlorostyrene) in their theta solvents; *n*-propyl benzene and 2-butanone, respectively. We report dynamic light scattering data analyzed in terms of the temperature dependence of the hydrodynamic radius (R_h).

EXPERIMENTAL

Sample preparation

Poly(4-chlorostyrene), PPCS-225. Poly(4-chlorostyrene), PPCS-225 was prepared by thermal radical polymerization without initiator. The monomer 4-chlorostyrene (Aldrich) was freed from inhibitor by washing with 5% aqueous NaOH solution and distilled water. It was dried with Na$_2$SO$_4$ and freshly distilled under reduced pressure before use (b.p. 66.3°C at 10 mmHg). Thermal polymerization of the monomer 4-chlorostyrene was carried out at 50°C, in bulk, for 20 days using the high vacuum technique. The conversion of the polymerization was 84% and 6.5 g PPCS was obtained. Fractionation of PPCS was carried out by the fractional precipitation technique at 25°C using 2-butanone (MEK) as solvent and methanol as non-solvent[14]. In our process 6.124 g of PPCS was dissolved in 0.3 w/w % MEK and 1.0429 g PPCS as the first (highest molecular weight) fraction was obtained. This highest fraction was further fractionated and the resulting product was 0.052 g PPCS. This fraction was re-dissolved in MEK, precipitated into methanol and dried *in vacuo* at 30°C. This polymer was designated as PPCS-225.

Poly(2-chlorostyrene), POCS-1032. Poly(2-chlorostyrene) was obtained from Lark Enterprises (No. 5295). For

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Table 1 Characterization of unfractionated samples

Samples	$[\eta]^e$dl/g	$M^f(\times 10^{-6}$ g/mol$)$	$M_w^g(\times 10^{-6}$ g/mol$)$	$M_n^g(\times 10^{-6}$ g/mol$)$	M_w/M_n^g
PPCS[a]	1.034	2.00	1.28	0.976	1.31
POCS[b]	3.22	4.95	4.82	2.98	1.61
POCS[c]	1.077	0.922	1.38	0.889	1.55
PCS[d]	0.840	1.38	—	—	—

[a] Poly(4-chlorostyrene), by thermal polymerization
[b] Poly(2-chlorostyrene), Lark Enterprises(No. 5295)
[c] Poly(2-chlorostyrene), by thermal polymerization
[d] Poly(chlorostyrene), a mixture of 2- and 4- isomers, Polysciences(No. 7041)
[e] Intrinsic viscosities in benzene for PPCS and in toluene for POCS at 30°C
[f] Molecular weights calculated using equation (1) and equation (2) for PPCS and POCS, respectively, *via* viscometry
[g] *Via* LS/SEC

fractionation of POCS, the solvent/nonsolvent system was toluene/methanol. The highest fraction of POCS (1.4554 g) was further fractionated and the resulting product was 0.203 g POCS. This sample was designated as POCS-1032.

Poly(2-chlorostyrene), POCS-430. The monomer, 2-chlorostyrene (Aldrich) was purified as described above and freshly distilled under reduced pressure (58°C/7 mmHg). 3.5 g POCS (88% conversion) was obtained by thermal polymerization at 50°C for 20 days using high vacuum. The product was also fractionated by the technique described above. The highest fraction of POCS obtained from 0.1 w/w % toluene solution was 0.1086 g and was designated as POCS-430.

Poly(chlorostyrene), mixture of 2- and 4-isomers(PCS). PCS was a product of Polysciences Inc. (No. 7041). Detailed characterization of PCS by IR, n.m.r. showed that this commercial product was a mixture of 2- and 4- isomers. Chemical analysis: calc. for $(C_8 H_7 Cl)_x$, Cl = 25.58, C = 69.33, H = 5.09; found Cl = 25.63, C = 69.0, H = 5.37%. The fractionation of PCS was carried out with the same fractionation technique (MEK/methanol) described for PPCS. 0.1003 g PCS as the highest fraction was obtained and designated as PCS-232.

Characterization

Spectroscopic analyses. Infrared spectra (Perkin Elmer 177) of the PPCS-225, PCS-232 and POCS-1032, POCS-430 are consistent with the standards[21]. Typical absorption peaks of the samples were seen in the 1013.4–1092.0 cm^{-1} and 1400–1600 cm^{-1} regions. The position of the peaks within the regions depends on the substitution of chlorine atoms.

^{1}H n.m.r. (Bruker 300 MHz) spectra of the PPCS-225, POCS-1032 and POCS-430 have the same characteristic peaks with the standard poly(4-chlorostyrene) and poly(2-chlorostyrene) supplied from Polymer Standard Service, Germany.

^{1}H n.m.r. and ^{13}C n.m.r. spectra of PCS-232 that seem to be different than those of pure PPCS are consistent with IR results (^{1}H n.m.r. of PCS-232; δ = 6.4482 and 6.9882 ppm phenyl protons; 1.5172 and 2.6521 ppm as CH_2 groups). Also, the ^{13}C n.m.r. spectrum is the same with standard ortho/para mixture of poly(chlorostyrene)[22].

Viscometry. The molecular weights of unfractionated samples were determined by viscosity measurements using the following relationships[17,16]

$$[\eta] = 30.6 \times 10^{-5} M_v^{0.56} \quad \text{(PPCS, benzene, 30°C)} \quad (1)$$

$$[\eta] = 14.3 \times 10^{-5} M_w^{0.65} \quad \text{(POCS, toluene, 30°C)} \quad (2)$$

Table 2 Molecular characteristics of fractionated PPCS, POCS and PCS[a]

Samples	$M_w(\times 10^{-6}$ g/mol$)$	$M_n(\times 10^{-6}$ g/mol$)$	M_w/M_n
PPCS-225	2.25	1.95	1.16
POCS-1032	10.32	9.48	1.10
POCS-430	4.30	3.86	1.11
PCS-232	2.32	2.19	1.06

[a] *Via* LS/SEC

LS/SEC. Light scattering/size exclusion chromatography measurements were carried out to characterize the fractions of poly(4-chlorostyrene), poly(2-chlorostyrene) and poly(chlorostyrene). The samples were dissolved in tetrahydrofuran (THF). The samples were filtered through 0.5 μm teflon disposable filters. They were then run in THF at a flow rate of 1.0 ml min^{-1} using two Jordi Gel DVB mixed bed columns, each 25 cm $\times$ 10 mm (ID), at a column oven temperature of 35°C. The sample injection size was 50 μl of an approximate 0.1% (w/v) solution. The samples were monitored at a sensitivity of 16 $\times$ and a scale factor of 20 on a Waters Model 410 DRI fitted with a Precision Detectors Model PD2000. The detector wavelength was 685 nm. Characterization of unfractionated and fractionated samples are presented in *Tables 1* and 2, respectively.

DLS measurements

The preparation of dust-free solutions for the dynamic light scattering (DLS) measurements was as follows. A mother solution with a concentration $\sim 5 \times 10^{-4}$ g g^{-1} was prepared for each polymer, in their theta solvents *n*-propyl benzene (*n*-PB) and 2-butanone (MEK). For complete dissolution, PPCS solution in *n*-propyl benzene was kept in an oven at 50°C, while the POCS mother solution was held at 4°C for complete dissolution since a butanone solution of poly(2-chlorostyrene) exhibits a lower critical solution temperature (LCST), that is, the solubility of polymer in solvent increases at lower temperatures[20,15]. The mother solution was diluted to the concentration 11.6 $\times$ 10^{-6} g ml^{-1} for the POCS solution. The working concentration for PPCS/*n*-PB and PCS/*n*-PB systems was higher (1.73 $\times$ 10^{-4} g/ml) due to low laser scattering intensities at extremely dilute concentrations for this molecular weight. Each solution was filtered carefully with 0.2 μm Millipore filters.

DLS measurements were carried out by using a commercial DLS spectrometer (ALV/LSE-5000) operating at λ = 514.5 nm with an Ar laser. Thin-walled cylindrical cells (0.3048 mm wall thickness, 10 mm outer diameter and 75 mm length) were used. The borosilicate flat bottom cells

were purchased from Wilmad Glass, New Jersey, U.S.A. Temperatures were controlled to $\pm 0.01°C$.

The polymer solutions were brought to the selected temperature from their θ temperatures to induce the size change, which was determined by means of DLS in terms of the hydrodynamic radius (R_h). The raw output of a dynamic light scattering experiment is $G_{(2)}(\tau)$ the intensity autocorrelation function, typically plotted with a logarithmic time. Measurements of the intensity auto-correlation function $G_2(\tau)$ were made at a scattering angle of 33°. The unnormalized intensity autocorrelation function $G_{(2)}(\tau)$ may be derived through the following Siegert relation with the electric field correlation function, $g_{(1)}(\tau)$:[23,24]

$$G_2(\tau) = B(1 + \beta|g_1(\tau)|^2) \quad (3)$$

where β takes into account deviations from ideal correlation and B is a measure of the baseline. When $qR_g \ll 1$, $g_1(\tau)$ is a single-exponential

$$g_1(\tau) = \exp(-\Gamma\tau) = \exp(-Dq^2\tau) \quad (4)$$

where Γ is the measured relaxation rate and D the mutual diffusion coefficient defined in the limit of the small scattering vector q as $D = (\Gamma/q^2)_{q \to 0}$ where $q = 4\pi n/\lambda(\sin\theta/2)$, $\lambda = 514.5$ nm; n = refractive index of solvent; θ = scattering angle. If there are multiple decay times τ_i, i.e. decay rates Γ_i, present in the system under investigation, then the field correlation function $g_1(\tau)$ is the weighted sum of the individual contributions:

$$g_1(\tau) = \int G(\Gamma)\exp(-\Gamma\tau)d\Gamma \quad (5)$$

where $G(\Gamma)$ is the continuous distribution function of decay rates Γ. $g_1(\tau)$ and $G(\Gamma)$ can be seen to be related by a Laplace transformation.

Data analysis of the electric field time correlation curve was performed by using the method of cumulants[8] and CONTIN method[25] available in the ALV software package. The size distribution based on the hydrodynamic radius was evaluated by CONTIN yielding an average line width $\bar{\Gamma}$ and the variance $\mu_2/\bar{\Gamma}^2$ with

$$\bar{\Gamma} = \int \Gamma G(\Gamma)d\Gamma \quad (6)$$

and

$$\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)d\Gamma. \quad (7)$$

To estimate the polydispersity effect[26] the following relation was used:

$$M_z/M_w = 1 + 4(\mu_2/\bar{\Gamma}^2). \quad (8)$$

The hydrodynamic radius, R_h, may be evaluated from the diffusion coefficient $(\Gamma = Dq^2)$ at infinite dilution D, using the Stokes–Einstein relation

$$R_h = k_B T/6\pi\eta D \quad (9)$$

where k_B is the Boltzmann constant and η is the solvent viscosity. The viscosities of solvents n-propylbenzene and 2-butanone were calculated by using equations (10) and (11), respectively[27,28].

$$\log\eta(T) = -1.9385 + 549.7/T \quad (10)$$

$$\log\eta(T) = -1.69344 + 385.7/T \quad (11)$$

where η is the solvent viscosity in cP and T is the temperature in Kelvin.

RESULTS AND DISCUSSION

To the best of our knowledge, this is the first report of the chain dimensions in terms of R_h as a function of temperature for PPCS and POCS systems. The DLS results obtained here were compared with recent experimental findings for various polystyrene systems. In this work, we used very dilute solutions in order to prevent aggregation and precipitation. In addition, the polydispersities of our fractionated polymeric samples were rather satisfactory.

PPCS-225/n-propylbenzene system

For the PPCS/n-PB system, θ temperature is reported to be 43°C[18,19,29].

Figure 1 shows the intensity autocorrelation function $G_2(\tau)$ of the dilute $(1.73 \times 10^{-4}$ g/ml) PPCS solution with $\bar{\Gamma} = 1.39$ ms^{-1} and $\mu_2/\bar{\Gamma}^2 = 0.098$ at a θ temperature of 43°C and a scattering angle of 33°. M_z/M_w was estimated by using equation (8) and found to be 1.392 for this sample. The average hydrodynamic radius R_h of the polymer is 27.9 nm at 43.0°C. *Figure 2* exhibits the change of R_h as a function of temperature for the dilute PPCS solution where all values of R_h were determined at the
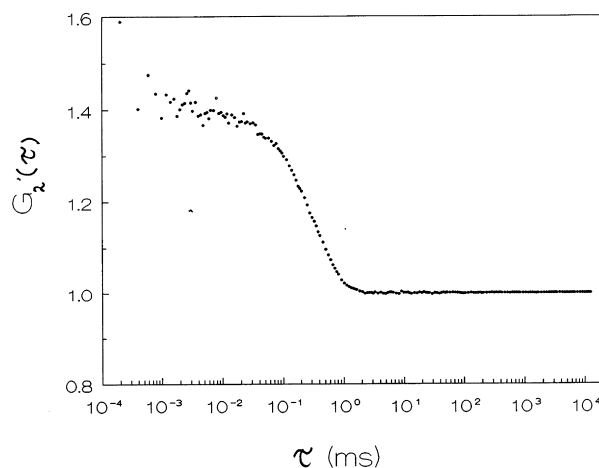
Figure 1 The intensity autocorrelation function $G_2(\tau)$ of PPCS-225 in n-propyl benzene solution $(C = 1.73 \times 10^{-4}$ g/ml) at 43.0°C (θ temperature)
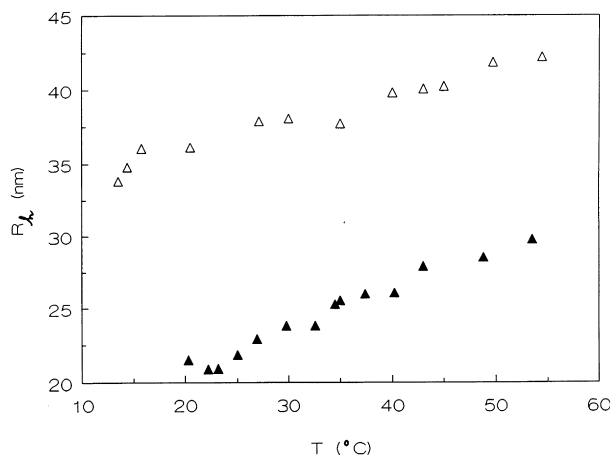
Figure 2 Plot of the hydrodynamic radius (R_H) *versus* temperature for PPCS-225 and PCS-232 in n-propyl benzene solution

scattering angle of 33°. The PPCS-225 solution was quenched from above the θ temperature (43°C) to the designated temperatures and allowed to come to equilibrium; the contraction is seen in *Figure 2*. The PPCS-225/*n*-propylbenzene system was thermodynamically stable and reported hydrodynamic radius values were independent of time down to 23.2°C. Two hydrodynamic radius distributions of PPCS-225 solution under theta conditions (43°C) and poor solvent conditions ($T = 23.2°C$) are shown in *Figure 3*. At 22.2°C, very small aggregates started to appear and were seen as a second growing peak in the CONTIN analysis. The weight fraction of the small size globules was 86.3% at 22.2°C. It was possible to measure R_h value at 20.3°C which is some 22.7°C below the θ temperature before complete aggregation started. On the average, the hydrodynamic size of the PPCS-225 chain at 22.2°C has shrunk to ~75% of the unperturbed θ state. The contraction reported in this work is much more pronounced compared to viscosity data which indicates only ~10% contraction[19].

PCS/n-propylbenzene system

Poly(chlorostyrene), PCS-232 was found to be a mixture of 2- and 4- isomers. n.m.r. and IR spectra of poly(chlorostyrene), obtained from Polyscience (No. 7041) has the same characteristic peaks with the standard para/ortho mixture of poly(chlorostyrene)[21,22]. In the [1]H n.m.r. spectrum of this polymer, from the ratio of the areas under the peaks of phenyl protons ($\delta = 6.4482$ and 6.9882 ppm), the fraction of 4-isomer might be estimated quantitatively as 73.4% for the PCS-232 sample.

We have considered 43°C as the θ temperature for PCS-232 in order to investigate the collapse transition of PCS in *n*-propylbenzene and to compare the results with pure poly(4-chlorostyrene), PPCS-225. Despite the fact that molecular weights are identical the dependence of coil shrinkage of PCS-232 on temperature was different from the behaviour of PPCS-225, as shown in *Figure 2*. There was no aggregation observed down to 14.4°C. At this temperature, a bimodal distribution appeared in CONTIN analysis as can be seen in *Figure 4*. The peak corresponds to smaller size molecules and represents individual collapsed chains and their fraction was found to be 86% at 14.4°C. In contrast to poly(4-chlorostyrene), for example, PCS in *n*-propyl-benzene aggregates at 13.5°C which is some 29.5°C below its θ temperature. Values of $\alpha_h = R_h(T)/R_h(\theta)$ exhibit a shrinkage of about 15% while poly(4-chlorostyrene) shows substantially greater sub-θ shrinkage (25%) in this work.

Figure 5 shows the scaled expansion factor of hydro-dynamic size $\alpha_h^3 \tau M_w^{1/2}$ *versus* $\tau M_w^{1/2}$ where $\alpha_h = R_h(T)/R_h(\theta)$ and $\tau = \theta - T/\theta$ for PPCS-225/*n*-PB and PCS-232/*n*-PB systems. For the PPCS-225/*n*-PB system $\alpha_h^3 \tau M_w^{1/2}$ increased continuously with increasing scaled reduced temperature ($\tau M_w^{1/2}$), the value of $\alpha_h^3 \tau M_w^{1/2}$ at the asymptotic plateau region was found to be 40 g$^{1/2}$ mol$^{-1/2}$. In this experiment, we were able to extend $\tau M_w^{1/2}$ values over 100, which is larger than previously reported using viscosity measurements[19]. However, contraction of the molecules was not still high enough to consider a globular collapse.

It is difficult to assert that the PCS-232/*n*-PB system reaches a plateau region. Fully collapsed regimes based on the hydrodynamic size could not be reached in the PCS-232/*n*-propylbenzene system due to the limited contraction of the hydrodynamic size ($\alpha_h = 0.85$) over a broad temperature range (43°C–13.5°C). The focus of the present work was a comparison between PPCS and PCS sub-θ behaviour,
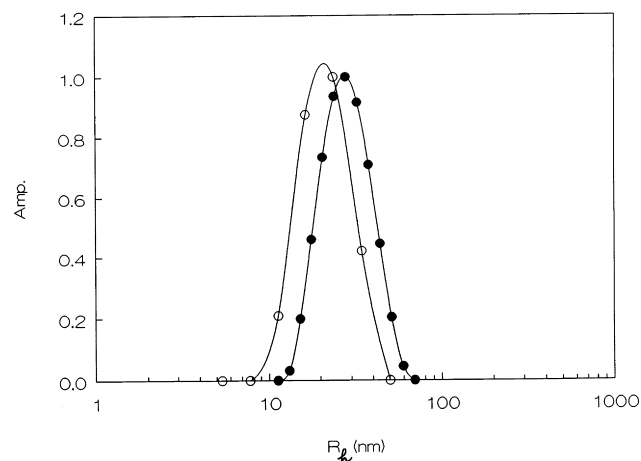

Figure 3 Typical hydrodynamic radius distribution of PPCS-225/*n*-propyl benzene solution at theta conditions ($T = 43°C$, $R_h = 27.9$ nm), ●, and poor solvent conditions ($T = 23.2°C$, $R_h = 20.9$ nm), ○
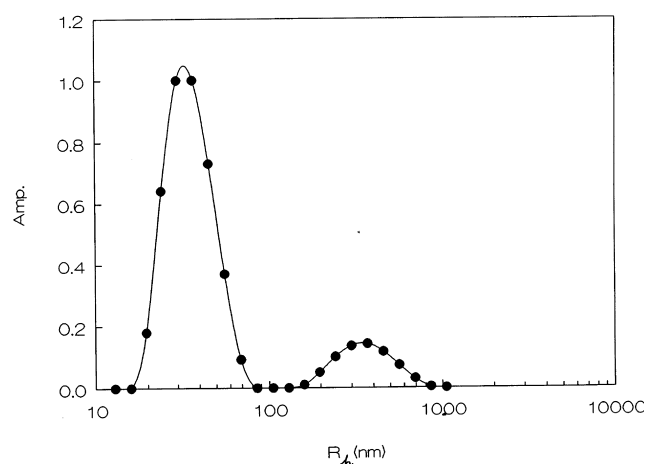

Figure 4 Typical hydrodynamic radius distribution of PCS-232/*n*-propyl benzene solution after the solution was brought from 43°C (θ temperature) to 14.4°C
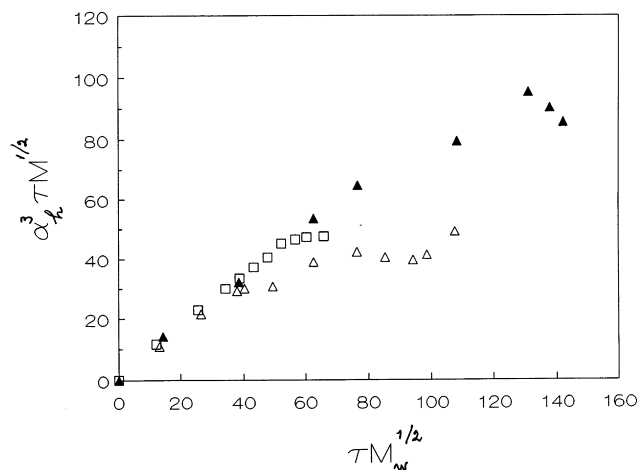

Figure 5 Scaled expansion factor of hydrodynamic size $\alpha_H^3 \tau M_w^{1/2}$ *versus* $\tau M_w^{1/2}$ where $\alpha_H = R_H(T)/R_H(\theta)$ and $\tau = \theta - T/\theta$; PPCS-225, △, PCS-232, ▲, and viscosity data ([12]),□

however dramatic differences in master curves of PCS-232 and PPCS-225 showed that more precise determination of θ temperature for poly(chlorostyrene), PCS-232 in *n*-propylbenzene is required.

We observed a limited contraction of PPCS coils below θ temperature. The results are consistent with the previous observations such as poly(α-methylstyrene) in cyclohexane which exhibits slight shrinkages in the sub-θ region[29].

POCS/2-butanone (POCS-1032 and POCS-430/MEK) systems

The poly(2-chlorostyrene) (POCS)/2-butanone system exhibits LCST behaviour. It was previously reported that there was a considerable solvent effect in this system for which θ temperature was found to be 25°C[15,20]. Since investigations of halogen derivatives of polystyrene with LCST behaviour have seldom been made, it was thought useful to obtain information on the chain dimensions of POCS both above and below θ temperature.

For these two samples of POCS, the hydrodynamic radius as a function of temperature is shown in *Figure 6*. It is remarkable that R_h decreases drastically just above the θ temperature (25°C). This decrease in size is more pronounced for higher molecular weight (10.32 $\times$ 10^6 g mol^{-1}) of POCS. After the first sharp decrease of size to (α_h = 0.810) which occurs in a quite narrow temperature range ($\sim$5°C) for POCS-1032, there appears to be a plateau region before further contraction and final precipitation. Dilute polymer solution ($C = 11.6 \times 10^{-6}$ g/ml) was brought from 25°C to the designated temperatures
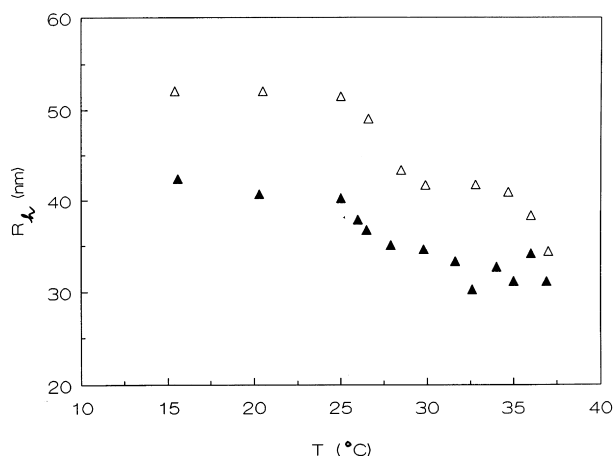
and R_h was then determined. R_h at 25°C was found to be 51.5 nm (M_z/M_w = 1.6) and 40.3 nm (M_z/M_w = 1.2) for POCS-1032 and POCS-430 respectively. For the POCS-1032/MEK system it is interesting to note that when the temperature was increased to 29.9°C, the normalized variance μ_2/Γ^2 and M_z/M_w also decreased. The behaviour of the R_h at 25 and 29.9°C is shown clearly in *Figure 7*.

The decrease in the variance, expressed as apparent M_z/M_w ratios, from 1.60 to 1.10 might be due to the precipitation of high molecular weight POCS fractions leaving only the lower molecular weight fractions in solution with a lower R_h. However, since a decrease of the concentration in the scattering volume would accompany such a fractional precipitation, one would expect the decrease of the scattered light intensity to be even more dramatic[7,9]. Such a decrease of the scattered light intensity was not observed and the polydispersity (M_z/M_w) also remained constant ($\sim$1.10) after the first contraction. Therefore, we could say that the contraction of the chains having the higher molecular weights is more effective in terms of a decrease of R_h with temperature.

The highest accessible temperature was 37.0°C for both POCS systems before the onset of precipitation. At this temperature, R_h was found to be 34.5 nm, corresponding to 67% of the unperturbed θ state for POCS-1032 whereas for the lower molecular weight of POCS-430, R_h was found to

Figure 6 Hydrodynamic radius (R_H) *versus* temperature for POCS/MEK

Figure 8 Hydrodynamic radius of distribution of the same solution in *Figure 7* at theta conditions, 25°C ●, and 37.0°C ○
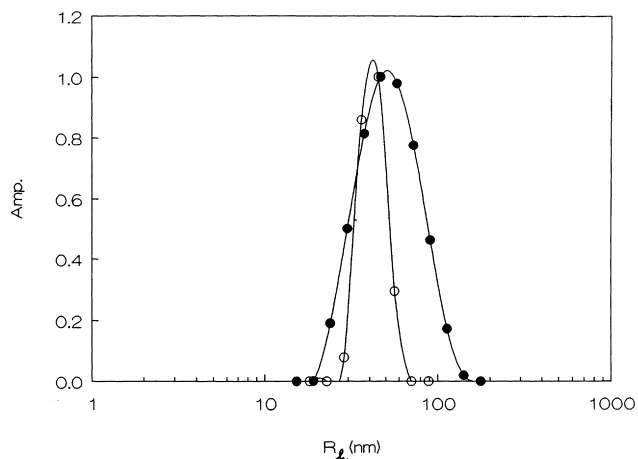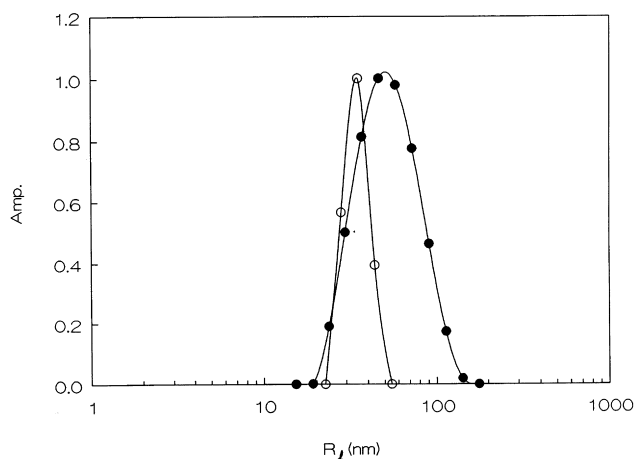
Figure 7 Typical hydrodynamic radius distribution of POCS-1032/MEK solution at theta conditions (25°C), ●, and poor solvent conditions (29.9°C), ○
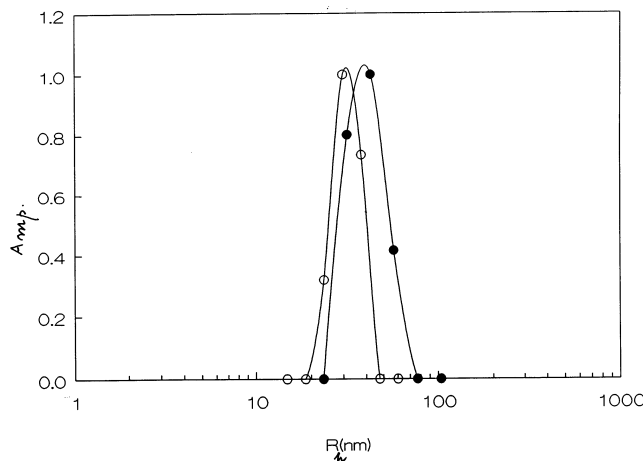
Figure 9 Hydrodynamic radius of distribution of POCS-430/MEK solution at 25°C (θ conditions) ●, and 37.0°C □
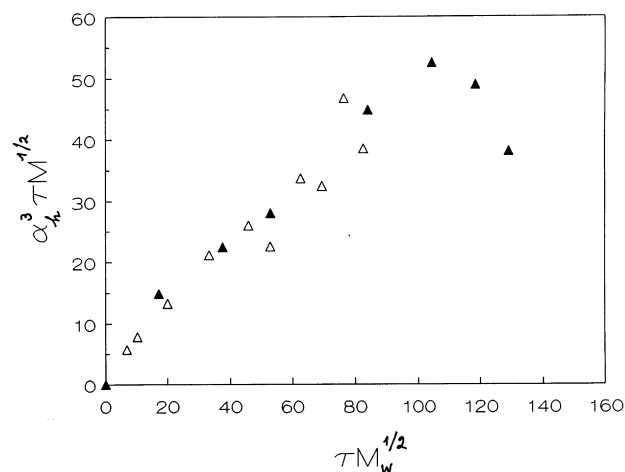
Figure 10 Scaled expansion factor $\alpha_H^3 \tau M_w^{1/2}$ of the hydrodynamic radius *versus* $\tau M_w^{1/2}$ for POCS/MEK systems, POCS-1032, ▲, and POCS-430, △

be 31.2 nm with a value of $\alpha_h = 0.77$. Precipitation was suddenly started at 37.9°C ($R_h \sim 144$ nm).

Typical R_h distributions at 25 and 37°C are given in *Figure 8* and *Figure 9* for POCS-1032 and POCS-430, respectively. This critical temperature (namely, precipitation temperature 37–38°C) is in agreement with the value calculated (~35°C) from the experimental data reported previously in the determination of the θ temperature for the POCS/2-butanone system[20].

Figure 10 shows the scaled expansion factor $\alpha_h^3 \tau M_w^{1/2}$ as a function of the scaled reduced temperature $\tau M_w^{1/2}$ for the POCS/MEK systems. $\alpha_h^3 \tau M_w^{1/2}$ value reaches a maximum value (51.2 $g^{1/2}$ $mol^{-1/2}$) and then decreases in the POCS-1032/MEK system. No plateau regions could be observed for both POCS-1032 and POCS-430 samples. Recently experimental results for poly(n-isopropyl acrylamide) with LCST behaviour in water have been reported in which an extended plateau was observed[10]. Although POCS-1032 used here has a high molecular weight (10.32 × 10^6 g mol^{-1}) and the polydispersity is particularly narrow, we could observe only limited chain collapse ($\alpha_h = 0.67$) before the system reached a thermodynamically unstable regime; i.e. phase separation and aggregation.

CONCLUSIONS

Coil–globule transition experiments were carried out for very dilute polystyrene solutions[1–11]. Various experimental methods such as static and quasi-elastic light scattering, small-angle neutron scattering, ulracentrifuge and viscometric measurements were used for the determination of linear polymer dimensions. Chain contraction reported for a polystyrene–cyclohexane system was only about 75% of the unperturbed state[4–6,11]. This small decrease in size has not justified a proper definition of a densely packed collapsed globule. Recently, Chu and coworkers reported two-stage kinetics of single-chain collapse for polystyrene in cyclohexane[7,8,30]. Time dependence of the hydrodynamic radius (R_h) of a single polymer chain in solution was investigated. Unperturbed R_h value of a single polystyrene molecule reduced first to 26% of a crumpled molecule, and in a second stage further reduced to a compact molecule indicating a total reduction to about 69% of its original radius. This observation was in accordance with an earlier theoretical prediction about two-stage kinetics[31,32]. However, the

possibility of chain clustering during the second stage of was taken into consideration by Raos and Allegra[33]. It was concluded that much smaller objects in the second stage of the collapse reported as 'compact globules' by Chu and coworkers under kinetic conditions were actually macromolecular clusters resulting from aggregation of a small number of polymer chains. Consequently, the initial contraction stage (about 25%) corresponds to the final equilibrium state for polystyrene in cyclohexane. A two-stage kinetics was not observed in this work. Although chain contraction values for poly(4-chlorostyrene) and poly(2-chlorostyrene) observed in this work exceed the contraction reported in earlier studies of the polystyrene/cyclohexane system, they are still not satisfactory for a single globule formation. Therefore, we may conclude that substitution of chlorine groups into polystyrene chains do not produce a dramatic effect on the sub-θ behaviour. However, it has been shown recently that contrary to polystyrene and substituted polystyrenes, certain poly(methyl methacrylate)/poor solvent systems exhibit about 85% contraction[34,35]. A chain dimension study of syndiotactic poly(methyl methacrylate) using dynamic light scattering and viscometry methods is now under progress in our laboratories.

REFERENCES

1. Adam, M. and Delsanti, M., *J. Phys.*, 1980, **41**, 713.
2. Perzynski, R., Adam, M. and Delsanti, M., *J. Phys.*, 1982, **43**, 129.
3. Vidakovic, P. and Rondelez, F., *Macromolecules*, 1983, **16**, 253.
4. Park, I. H., Wang, Q.-W. and Chu, B., *Macromolecules*, 1987, **20**, 1965.
5. Park, I. H., Wang, Q.-W. and Chu, B., *Macromolecules*, 1987, **20**, 2833.
6. Chu, B., Xu, R. and Zhuo, J., *Macromolecules*, 1988, **21**, 273.
7. Yu, J., Wang, Z.-L. and Chu, B., *Macromolecules*, 1992, **25**, 1618.
8. Chu, B., Ying, Q. and Grosberg, A. Y., *Macromolecules*, 1995, **28**, 180.
9. Kubota, K., Fujishige, S. and Ando, I., *J. Phys. Chem.*, 1990, **94**, 5154.
10. Wu, C. and Zhou, S., *Macromolecules*, 1995, **28**, 5388.
11. Baysal, B. M. and Uyanik, N., *Polymer*, 1992, **33**, 4798.
12. Williams, C. and Brochard, F., *Ann. Rev. Phys. Chem.*, 1981, **32**, 433.
13. Fujita, H., *Polymer Solutions*. Elsevier, Amsterdam, 1990.
14. Noguchi, Y., Aoki, A., Tanaka, G. and Yamakawa, H., *J. Chemical Physics*, 1970, **52**, 2651.
15. Izumi, Y. and Miyake, Y., *Polymer Journal*, 1973, **4**, 205.
16. Matsumura, K., *Die Makromolekulare Chemie*, 1969, **124**, 204.
17. Mohite, R. B., Gundiah, S. and Kapur, S. L., *Die Makromolekulare Chemie*, 1968, **116**, 280.
18. Chiba, A., Uzawa, S., Uda, M. and Doi, S., *Polym. Phys. Jap.*, 1974, **17**, 105.
19. Baysal, B. M. and Yilmaz, F., *Polymer International*, 1992, **27**, 339.
20. Matsumura, K., *Polymer Journal*, 1970, **1**, 322.
21. *The Aldrich Library of FT-IR Spectra*, ed.C. J. Pouchert, Edition I, Vol. 2. Aldrich Chemical Company Inc., 1985, 1207 C, 1207 B.
22. Simons, W. W. and Zanger, M., *The Sadtler Guide to the NMR Spectra of Polymers*. Sadtler Research Laboratories, Inc., 1973.
23. Brown, W. and Nicolai, T., in *Dynamic Light Scattering—The Method and Some Applications*, ed. W. Brown. Clarendon Press, Oxford, 1993.
24. Berne, B. J., Pecora, P., ed. *Dynamic Light Scattering*. Wiley, New York, 1976.

25. Provencher, S. W., *Makromol. Chem.*, 1979, **180**, 201.
26. Brown, J. C. and Pusey, P. N., *J. Phys. D.*, 1974, **7**, L31.
27. Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*, 73rd Edition, 1992–93.
28. Dwight, E. G., ed., *American Institute of Physics Handbook*, 3rd Edition. McGraw-Hill Book Company, 1972.
29. Li, J., Harville, S. and Mays, J. W., *Macromolecules*, 1997, **30**, 466.
30. Chu, B. and Qicong, Y., *Macromolecules*, 1996, **29**, 1824.
31. De Gennes, P.G., *J. Phys. Lett.*, 1985, **46**, L–639.3.
32. Grosberg, A. Yu., Nechaev, S. K. and Shakhnovich, E. I., *J. Phys. Fr.*, 1988, **49**, 2095.
33. Raos, G. and Allegra, G., *Macromolecules*, 1996, **29**, 8565.
34. Nakata, M., *Physical Review E*, 1995, **51**, 5770.
35. Baysal, B. M. and Kayaman, N., paper submitted to *J. Chemical Phys.*, 1997.