# Characterization of *p*-t-butylstyrene–dimethylsiloxane triblock copolymers in solution

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(*Received 4 April 1989; revised 1 June 1989; accepted 6 June 1989*)

Anionically synthesized poly(*p*-t-butylstyrene)-*b*-poly(dimethylsiloxane)-*b*-poly(*p*-t-butylstyrene) block copolymers containing about 28% by weight *p*-t-butylstyrene were characterized by using differential refractometry, light scattering and viscosity methods in a good solvent, benzene, and in a selective solvent, methyl ethyl ketone. The unperturbed chain dimensions were estimated. Results were discussed with regard to the conformation of block copolymers in solution.

**(Keywords: poly(*p*-t-butylstyrene)-*b*-poly(dimethylsiloxane)-*b*-poly(*p*-t-butylstyrene); intrinsic viscosity; light scattering; unperturbed chain dimensions; short-range interactions; long-range interactions)**

## INTRODUCTION

There have been many studies on the synthesis and characterization of block copolymers. ABA-type triblock copolymers in which the centre block (B) is rubbery show useful thermoplastic elastomeric properties. The dilute-solution properties of these novel block copolymers have also been widely investigated. Some studies showed that block copolymers in dilute solution assume a segregated structure in which heterocontacts are few[1–3]. In some others, however, it has been suggested that the dissimilar chains are interpenetrating, giving rise to numerous heterocontacts, which cause the expansion of the copolymer molecule[4,5]. Within the wide field of block copolymers, siloxane-containing ones are of special interest due to their stability at elevated temperatures. Studies on siloxane-containing polymers are rather few[6–10] and they are mostly concerned with their surfactant properties.

In this article we present our results on the characterization of poly(*p*-t-butylstyrene)-*b*-poly(dimethylsiloxane)-*b*-poly(*p*-t-butylstyrene) (BS-DX-BS) triblock copolymers by light scattering and viscometric studies to obtain insight into the conformational behaviour of triblock copolymers.

## EXPERIMENTAL

### *Materials*

The ABA-type triblock copolymers of *p*-t-butylstyrene and dimethylsiloxane (BS-DX-BS-*n*, $n=2$–5) and the diblock copolymer sample (BS-DX-1) were synthesized using an anionic polymerization technique. t-Butylstyrene monomer was a mixture containing 95% *para* and 5% *ortho* isomer. Hexamethylcyclotrisiloxane was used as the siloxane monomer. The initiator was s-butyllithium. t-Butylstyrene was first completely polymerized for 24 h in benzene solution at 25°C. Then siloxane monomer in tetrahydrofuran (THF) solution was introduced into the reactor and completely polymerized for 24 h at 25°C. Finally, the stoichiometric amount of dimethyldichlorosilane was added to couple the living chains of diblock copolymers. Details of the synthesis of ABA triblock copolymers with sequential monomer addition and coupling was described elsewhere[11]. The resultant ABA block copolymers contained 4–10% diblock impurities. They were purified by fractional precipitation from dilute benzene solutions. Size exclusion chromatography (s.e.c.) traces of sample BS-DX-BS-2 before and after fractionation are given in *Figure 1*. The polydispersity of the samples was measured using s.e.c. A universal calibration method was used to evaluate $M_w/M_n$ ratios.

Benzene and toluene used for dilute-solution measurements were pure analytical-grade materials. Methyl ethyl ketone (MEK) was reagent-grade and further purification by drying and fractional distillation was carried out before use.

### *Methods*

The number-average molecular weights ($M_n$) were determined using a Hewlett–Packard 503 membrane osmometer with S and S-08 membranes.

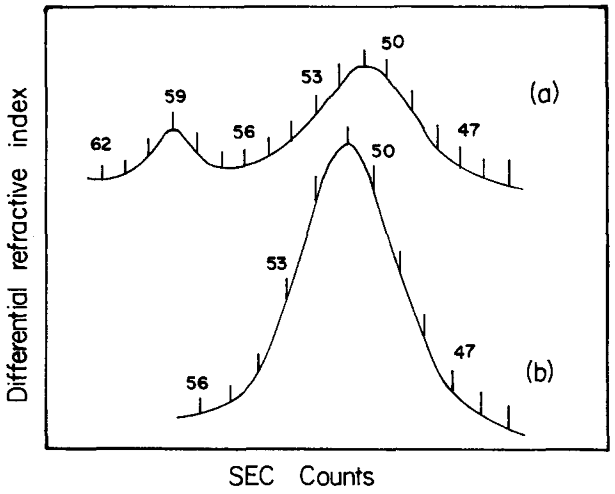

**Figure 1** S.e.c. chromatograms of BS-DX-BS-2: (a) before fractionation and (b) after fractionation

0032-3861/90/020379-04$03.00

**Table 1** Characteristics of block copolymer samples

| Sample no. | $M_n \times 10^{-3\,a}$ | $M_w/M_n{}^b$ | $W_{PTBS}{}^c$ | $\nu_{meas}$ | $\nu_{calc}$ | $[\eta]^d$ |
|---|---|---|---|---|---|---|
| BS-DX-1[e] | 39.8 | 2.33 | 0.296 | −0.053 | −0.052 | 0.197 |
| BS-DX-BS-2 | 70.2 | 1.64 | 0.297 | −0.052 | −0.052 | 0.278 |
| BS-DX-BS-3 | 151 | 1.93 | 0.294 | −0.058 | −0.053 | 0.533 |
| BS-DX-BS-4 | 294 | 2.82 | 0.273 | −0.059 | −0.056 | 1.01 |
| BS-DX-BS-5 | 555 | 2.32 | 0.270 | – | −0.053 | 1.51 |

[a] Determined by membrane osmometry
[b] Determined by s.e.c.
[c] Weight fraction of *p*-t-butylstyrene in block copolymer as determined by n.m.r.
[d] In benzene at 35°C
[e] Diblock copolymer sample

**Table 2** Weight-average molecular weights determined by $M_n$ and $M_w/M_n$ ratio and apparent molecular weights, apparent radii of gyration and apparent second virial coefficients determined by light scattering in toluene at 30°C

| Sample no. | $M_w \times 10^{-3}$ | $M_{app} \times 10^{-3}$ | $\langle S^2 \rangle_{app}$ (nm$^2$) | $A_{2,app} \times 10^4$ (cm$^3$ mol g$^{-2}$) |
|---|---|---|---|---|
| BS-DX-1 | 92.7 | 108 | – | 4.23 |
| BS-DX-BS-2 | 115 | 122 | – | 3.24 |
| BS-DX-BS-3 | 291 | 263 | 272 | 2.56 |
| BS-DX-BS-4 | 829 | 793 | 650 | 2.10 |
| BS-DX-BS-5 | 1287 | – | – | – |

Light scattering measurements were performed with a Brice–Phoenix light scattering photometer with unpolarized light of wavelength 436 nm. Solvent and solutions were directly injected into the cell by filtration through Millipore membrane filters of mean pore sizes 0.25 or 0.45 nm.

The refractive index increments were measured with a Brice–Phoenix model BP-2000 V differential refractometer at 436 nm wavelength. During light scattering and refractive index increment measurements, the temperature was controlled to ±0.1°C using a circulating water thermostat. Viscosity measurements were carried out in benzene and in methyl ethyl ketone (MEK) by using Ubbelohde dilution viscometers having negligible kinetic energy corrections. Intrinsic viscosities $[\eta]$ were obtained by extrapolating plots of $\eta_{sp}/c$ *versus* $c$ and $\ln \eta_{rel}/c$ *versus* $c$ to zero concentration.

## RESULTS AND DISCUSSION

*Table 1* summarizes the characteristics of the samples. One diblock copolymer sample (BS-DX-1) was also characterized to compare its properties with that of the triblock copolymers.

In order to remove homopolymer and diblock impurities, fractionation was carried out for triblock copolymer samples.

S.e.c. chromatograms showed that the fractionation was successful (*Figure 1*). The $M_w/M_n$ ratios after fractionation are listed in *Table 1*. The composition of the samples was kept constant (~28% by weight) during the synthesis. Exact compositions were determined by n.m.r. studies and are also listed in *Table 1*.

Based upon these compositions, we tested the following equation proposed for binary copolymers in single solvents[12,13]:

$$\nu = W_A \nu_A + (1 - W_A)\nu_B$$

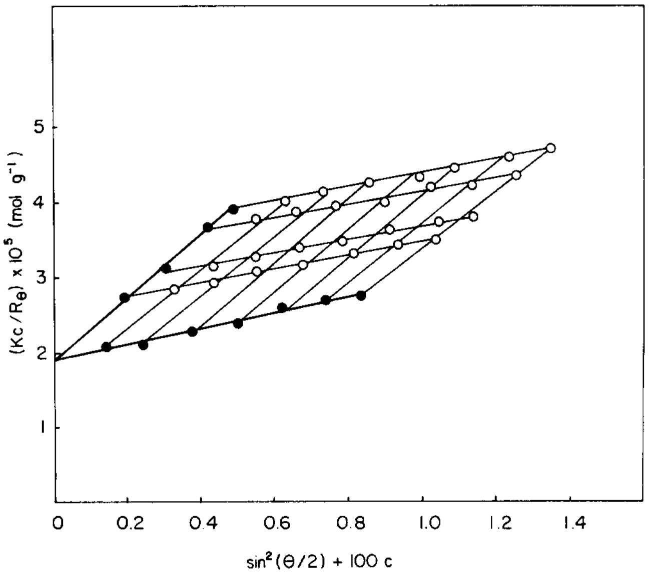

**Figure 2** Zimm plot for triblock copolymer BS-DX-BS-4 in toluene at 30°C

where $\nu$, $\nu_A$ and $\nu_B$ denote the refractive index increments of the copolymers and homopolymers A and B respectively, and $W_A$ indicates the weight fraction of component A in the copolymer. Values calculated from this equation are listed in *Table 1* together with the measured values in toluene at 30°C and 436 nm wavelength. For refractive index increments of homopolymers, the following values given for the same solvent, temperature and wavelength are used:

| | |
|---|---|
| for poly(*p*-t-butylstyrene)[14] | $\nu_A = +0.0669$ |
| for poly(dimethylsiloxane)[15] | $\nu_B = -0.1027$ |

It is seen in *Table 1* that the agreeement between the calculated and measured refractive index increments of block copolymer samples is good.

*Table 2* summarizes the results of light scattering measurements in toluene at 30°C together with weight-average molecular weights ($M_w$) calculated from $M_n$ and $M_w/M_n$ ratios from *Table 1*. The light scattering data were treated according to the Zimm model. A typical Zimm plot is given in *Figure 2*.

In a study of the light scattering behaviour of styrene–siloxane ABA block copolymers, Davies and Jones[16] observed marked curvature and distortion of the Zimm plots, although there were no micelle formation and dissymmetry effects. Zimm plots for our siloxane-containing block copolymer samples showed no distortion,

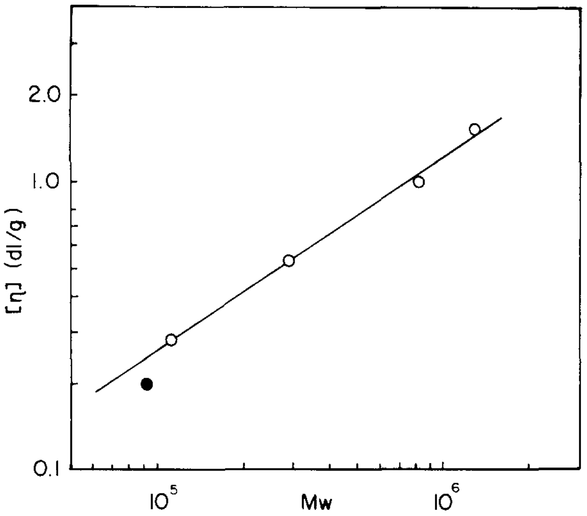

**Figure 3** Double logarithmic plot of $[\eta]$ *versus* $M_w$ for triblock copolymers (○) in benzene at 35°C and for diblock copolymers (●) in benzene at 35°C

probably because refractive index increments in toluene were sufficiently high.

The apparent molecular weight $M_{app}$ of a two-component copolymer determined by light scattering is given by[17]:

$$M_{app} = M_w + 2P[(\nu_A - \nu_B)/\nu] + Q[(\nu_A - \nu_B)/\nu]^2$$

where $P$ and $Q$ are parameters related to the compositional heterogeneity of the copolymer[17]. It is known that theoretically it is possible to evaluate the true weight-average molecular weight $M_w$ and the parameters $P$ and $Q$ from light scattering experiments in at least three solvents by solving three equations simultaneously[17]. But the error in $M_w$ thus determined can be too high because of the accumulation of experimental errors[18–20]. Our attempt to get true $M_w$ by doing light scattering in two more solvents (MEK and dioxane) has also failed. However, it can be seen in *Table 2* that $M_{app}$ values determined in toluene are close to $M_w$ calculated from osmometry and s.e.c. studies. Therefore, the compositional heterogeneity of these samples was low. We used $M_w$ values (not $M_{app}$) in evaluating viscosity data.

Intrinsic viscosities were measured in benzene at 35°C and in MEK at 15, 20 and 31°C. Benzene is a good solvent for both of the parent homopolymers, whereas MEK is a $\theta$ solvent for the centre block (poly(dimethylsiloxane)), the $\theta$ temperature being 20°C[21].

The following Kuhn–Mark–Houwink–Sakurada (KMHS) equations were obtained from the linear regression analysis of viscosity data, excluding the diblock sample, which deviates from linearity:

$$[\eta] = 5.89 \times 10^{-4} M_w^{0.50} \quad \text{(in MEK at 15°C)}$$

$$[\eta] = 4.05 \times 10^{-4} M_w^{0.54} \quad \text{(in MEK at 20°C)}$$

$$[\eta] = 1.93 \times 10^{-4} M_w^{0.61} \quad \text{(in MEK at 31°C)}$$

$$[\eta] = 1.54 \times 10^{-4} M_w^{0.66} \quad \text{(in benzene at 35°C)}$$

The KMHS plot in benzene at 35°C is given in *Figure 3*. KMHS plots in MEK were given in the previous study, which was on the $\theta$ behaviour of these block copolymers. The unperturbed dimension was estimated from intrinsic viscosities under $\theta$ conditions (in MEK at 15°C) in that study[22].

In the present study, in order to obtain short-range and long-range interaction parameters and the unperturbed dimensions from intrinsic viscosities determined under non $\theta$ conditions, we employed the Burchard-Stockmayer-Fixman (BSF) extrapolation procedure[23,24]. The BSF relation is given as:

$$\frac{[\eta]}{M_w^{1/2}} = K_\theta + 0.51 B \phi_0 M_w^{1/2}$$

$$K_\theta = \phi_0 A^3 \qquad A = \left(\frac{\langle r^2 \rangle_0}{M_w}\right)^{1/2}$$

where $\phi_0$ is the Flory–Fox viscosity constant (the most commonly employed value being $\phi_0 = 2.5 \times 10^{21}$ when $[\eta]$ is in dl g$^{-1}$ (refs. 25, 26)). $A$ and $B$ are the short-range and long-range interaction parameters and $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance of the polymer chain.

Plots of $[\eta]/M_w^{1/2}$ against $M_w^{1/2}$ for the block copolymer samples above the $\theta$ condition are given in *Figure 4*. These plots obey the BSF equation.

*Table 3* summarizes the conformational and thermodynamic parameters estimated from BSF plots (*Figure 4*). The long-range interaction parameters ($B$) were

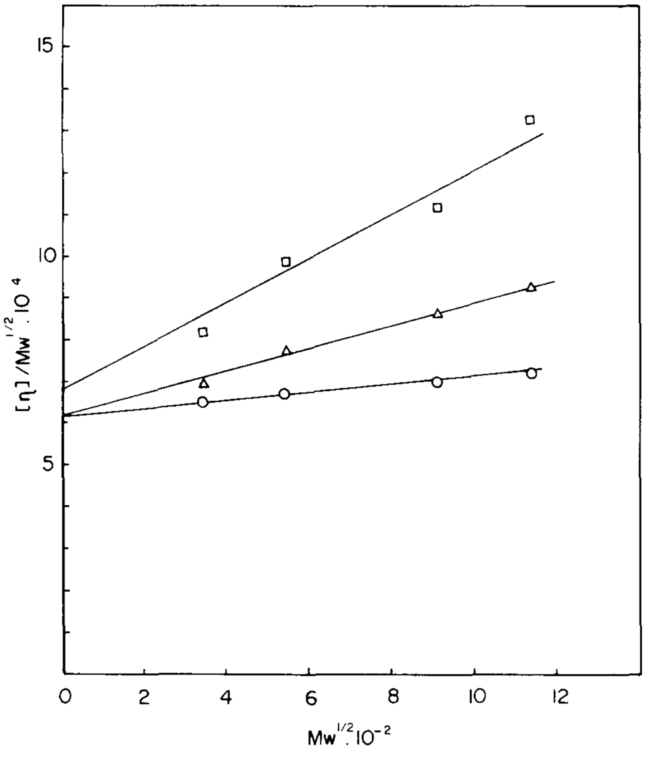

**Figure 4** Burchard–Stockmayer–Fixman plots for triblock copolymers in benzene at 35°C (□), in MEK at 20°C (○) and in MEK at 31°C (△)

**Table 3** Short-range and long-range interaction parameters from BSF plots for two solvents and four temperatures[a]

| | Benzene 35°C | MEK 31°C | MEK 20°C | MEK 15°C |
|---|---|---|---|---|
| $K_\theta \times 10^4$ (dl g$^{-3/2}$ mol$^{1/2}$) | 6.8 | 6.2 | 6.2 | 5.9 |
| $B \times 10^{28}$ (cm$^3$) | 3.8 | 2.1 | 0.60 | 0 |
| $A \times 10^9$ (cm) | 6.5 | 6.3 | 6.3 | 6.2 |
| $(\langle r^2 \rangle_0 / M) \times 10^3$ (nm$^2$) | 4.2 | 4.0 | 4.0 | 3.8 |

[a] Values estimated using KMHS equation at $\theta$ temperature[22]

obtained from the slopes of the lines in *Figure 4*. This parameter shows a normal behaviour in the sense that $B$ is higher in the better solvent (benzene) and becomes nearly zero when the $\theta$ condition is approached.

The $K_\theta$ value obtained from BSF plots in MEK at 20 and 31°C is close to the $K_\theta$ obtained under $\theta$ conditions, that is in MEK at 15°C where the viscosity exponent is 0.50[22] (*Table 3*). But in the good solvent, benzene, a higher value for $K_\theta$ is obtained from *Figure 4*.

For a binary copolymer chain obeying Gaussian statistics at the $\theta$ state, Stockmayer *et al.*[27] proposed the following equation for the unperturbed chain dimension:

$$\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{copolymer}} = W_{\text{A}}\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{A}} + (1-W_{\text{A}})\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{B}}$$

where A and B designate the parent homopolymers. The following values for the unperturbed dimensions of parent homopolymers were employed:

for poly(dimethylsiloxane)[21]

$$\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{PDMS}} = 4.6 \times 10^{-3}\,\text{nm}^2$$

for poly($p$-t-butylstyrene)[14]

$$\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{PTBS}} = 3.8 \times 10^{-3}\,\text{nm}^2$$

By using the equation given above for block copolymers having 28% by weight poly($p$-t-butylstyrene) (PTBS), it was found that:

$$\left(\frac{\langle r^2\rangle_0}{M}\right)_{\text{copolymer}} = 4.4 \times 10^{-3}\,\text{nm}^2$$

*Table 3* shows that the value of $\langle r^2\rangle_0/M$ for block copolymers determined from BSF plots in benzene ($4.2 \times 10^{-3}$ nm) is close to the calculated value within the experimental errors. In the selective solvent, MEK, slightly lower values were found from both the BSF method (present study) and the KMHS plot at the $\theta$ temperature[22].

These results indicate that, for $p$-t-butylstyrene–dimethylsiloxane ABA-type triblock copolymers in a good solvent, the conformation is more or less like a random-coil conformation. The interaction beween unlike segments does not cause any detectable coil expansion. But in the poor solvent of the centre block (MEK), there may be some segregation of blocks, leading to smaller overall dimension.

## ACKNOWLEDGEMENT

This work was partly supported by the Turkish Scientific and Technical Research Council, TUMKA.

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