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Novel synthesis and characterization of cyclic polystyrenes

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To overcome some experimental difficulties, a new approach to cyclic polystyrenes with narrow molecular weight distribution is proposed. The well-defined α,ω-dibromobutyl polystyrene was prepared by direct coupling of the polystyryl dianion with a large excess of 1,4-dibromobutane. End-to-end ring closure of the α,ω-dibromobutyl polystyrene was performed by interfacial condensation between the aqueous phase (hexamethylene diamine) and the organic toluene phase (polystyrene precursor). The limited field of reactions such as at the interface was very effective for ring closure. The conversion of cyclic polymers was very high (more than 80%) at polystyrene precursor concentration of 10^{-3} M. The hydrodynamic size of the cyclic polymers was substantially less than that of the corresponding linear precursor. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyclic polymer; ring closure; interfacial condensation)

INTRODUCTION

Cyclic polymers are interesting materials because, in contrast to linear polymers, all structural units of the chain are chemically and physically equivalent. Two main synthetic methods are presently known for the preparation of cyclic polymers. The first method is based on simultaneous formation (step-growth polymerizations) in some macromolecular systems exhibiting ring–chain equilibrium[1]. The synthesis of cyclic polymers is related to a favourable competition of an intramolecular reaction over the intermolecular reaction. The fraction of ring formation will depend only on the relative probability of finding the end of the chain in the reaction volume over that of finding any other chain end, following Jacobson and Stockmayer[2]. The second method concerns polymers with carbon–carbon linkages in the backbone (chain-growth polymerizations). Usually, this type employed the end-to-end ring closure of a living α,ω-dicarbanion with difunctional electrophile reagents under a very low carbanion concentration of *c.* 10^{-5}–10^{-7} M (refs 3–6). More recently, a new route to cyclic polymers was achieved by the direct end-coupling of an α,ω-heterodifunctional polymer after the appropriate activation under highly dilute conditions of one of its two end-functions[7]. In any case, the unsolved problem with these routes remains that the solvent medium should be a highly dilute solution.

On the other hand, the phase segregation properties of cyclic block copolymers have been investigated using the theory of Leibler[8], ignoring the topological constraints specific to cyclic polymers[9]. It was predicted that, in the strongly segregated state, the wavelength of lamellar domains composed of rings is 0.63 times that of linear diblock lamellae with the same molecular weight. Yin and Hogen-Esch[10] synthesized polystyrene–poly(dimethylsiloxane) cyclic block copolymers by the end-to-end ring closure of the corresponding α,ω-dicarbanion with a difunctional electrophile reagent. However, the quantitative nature of the predictions has never been examined in detail for neat copolymers.

In this work, the well-defined α,ω-dibromobutyl polystyrene (PSB) was prepared by direct coupling of the living polystyryl anion with a large excess of 1,4-dibromobutane (DBB). End-to-end ring closure of the PSB precursor was performed by interfacial condensation, i.e. dissolution of the reactants in a pair of immiscible liquids, one of which is water and the other an organic solvent. The aqueous phase contained hexamethylene diamine (HMDA), while the organic solvent (toluene) contained PSB precursor. The conversion of cyclic polystyrene (PS) was determined by gel permeation chromatography (g.p.c.) as a function of PSB concentration. The solution properties of cyclic PS were also studied in detail.

EXPERIMENTAL

Synthesis and characterization of α,ω-dibromobutyl polystyrene

PSBs were synthesized by the coupling reaction of the poly(styrylsodium) living dianion initiated by α-methylstyrene (MS) tetramer sodium with an excess amount of DBB in a benzene–tetrahydrofuran (THF) mixed solvent[11–13]. Styrene and DBB were dried over a mixture of calcium hydride/lithium aluminium hydride and then distilled under vacuum. Subsequently, styrene was purified with triphenylmethyl sodium in vacuum. The DBB was also purified with n-butyl lithium (n-BuLi). Benzene was dried over sodium metal and then purified

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Table 1 Characteristics of α,ω-dibromobutyl polystyrene

Code	$\overline{M}_n \times 10^{-3}$ (g mol^{-1})[a]	$\overline{M}_w/\overline{M}_n$ [b]	Bromine groups[c] (number/1-polymer)
PSB-1	7.0	1.08	2.0

[a] Determined by v.p.o.
[b] Determined by g.p.c.
[c] Determined by Volhard's titration

with n-BuLi under vacuum. THF was distilled from its solution of MS tetramer sodium anion under vacuum. The product was purified three times by reprecipitation from benzene solution with methanol.

The number-average molecular weight ($\overline{M}_n$) of difunctional PSB was determined by vapour pressure osmometry (v.p.o.) on a Corona NA 117 vapour pressure osmometer in benzene. The polydispersity ($\overline{M}_w/\overline{M}_n$) was determined by g.p.c. (Tosoh HLC-8020 high-speed liquid chromatograph with THF as eluent at 38°C, a TSK gel GMH$_{XL}$ column and a flow rate of 1.0 ml min^{-1}), with distribution functions improved by the reshaping method[14].

Terminal bromine groups were determined by Volhard's titration, after the reaction of PSB with an excess amount of sodium naphthalene in THF[11-13]. The characteristics of PSB are listed in *Table 1*.

Cyclization of α,ω-dibromobutyl polystyrene by interfacial condensation

Interfacial polymerization is the term used to describe step-reaction polymerization carried out at the interface between two immiscible liquid phases. In this work, an organic phase [mixture of toluene and dimethyl sulfoxide (DMSO)] contained the difunctional PSB and an aqueous phase contained a mixture of HMDA and sodium hydroxide (NaOH) as an acid accepter. In the interfacial method factors such as purity and stoichiometry are not nearly as critical as in high-temperature melt processes. These two heterogeneous phases were maintained at 80°C under rapid stirring. After the reaction, the organic phase was separated using a separating funnel. The organic solution was concentrated by evaporation and the polymer was recovered by precipitation in methanol.

Characterization of cyclic polystyrene

The yield of condensation and the conversion of cyclization were determined by g.p.c. under the same measurement conditions as described above. Then, precipitation fractionation was carried out in the benzene–methanol system at 20°C in order to separate the cyclic polymer, while the turbidity of the PSB precursor was measured beforehand at a wavelength of 500 nm (Hitachi Perkin–Elmer 139 u.v.-vis. spectrometer).

The radii of gyration (R_g) of cyclic PS and PSB precursor were determined by small-angle X-ray scattering (SAXS). The SAXS intensity distribution $I(q)$ was measured with a rotating-anode X-ray generator (Rigaku Denki Rotaflex RTP 300 RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized Cu K_α ($\lambda = 1.54$ Å) radiation. In the measurement of a toluene solution (3 wt%) of the sample, we used the cell sandwiched between mica plates as a holder vessel. The value of R_g is estimated by Guinier's method from the following equation[15]

$$\ln I(q) = \text{const} - (1/3)\langle R_g^2 \rangle q^2 \qquad (1)$$

where q is the scattering vector.

The intrinsic viscosities ($[\eta]$) of linear and cyclic polymers were measured by a Ubbelohde viscometer in THF at 38°C.

RESULTS AND DISCUSSION

Synthesis of linear difunctional polymers

Table 1 lists characteristics of the difunctional PSB. The conversion was almost 100% within experimental error. The g.p.c. profile of PSB-1 had a single and narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.08$). The direct coupling of polystyryl anion with DBB formed the functional polymer possessing α,ω-dibromobutyl groups at both terminal ends.

Cyclizations

Table 2 lists the reaction conditions and results of interfacial condensations of difunctional PSB and HMDA, varying the condensation time. In these reaction systems, we employed toluene as the organic phase. The aqueous phase contained 50 wt% NaOH as an acid acceptor. Typical g.p.c. profiles of RP11 and RP13 are shown in *Figure 1*. It is found for both condensation products that the elution count of the main peak shifts to the side of low molecular weight compared with PSB precursor. Generally, the cyclic polymer has a smaller hydrodynamic volume than the linear precursor. It is therefore suggested that these products are a mixture of cyclic PS and PSB precursor. The molecular weight distribution of cyclic PS can be separated from the reshaped g.p.c. of the condensation product by subtracting the known

Table 2 Reaction conditions and results of interfacial condensations of difunctional PSB with HMDA[a]

	Toluene phase	Aqueous phase[b]			
Code	PSB (mol l^{-1})	HMDA (mol l^{-1})	Time (h)	Yield of condensation (wt%)	Conversion of cyclization (%)
RP11	6.67×10^{-3}	6.67×10^{-3}	3	80	~ 100
RP12			6	81	~ 100
RP13			12	91	~ 100

[a] Interfacial condensations were carried out at 80°C
[b] 50 wt% aqueous NaOH solution as acid acceptor

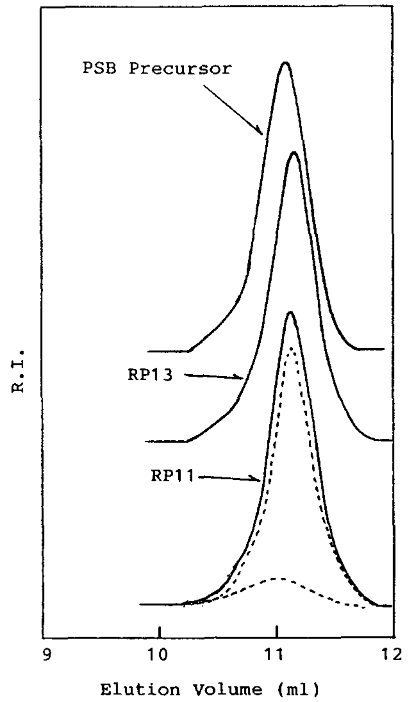

Figure 1 G.p.c. profiles of RP11, RP13 and PSB precursor

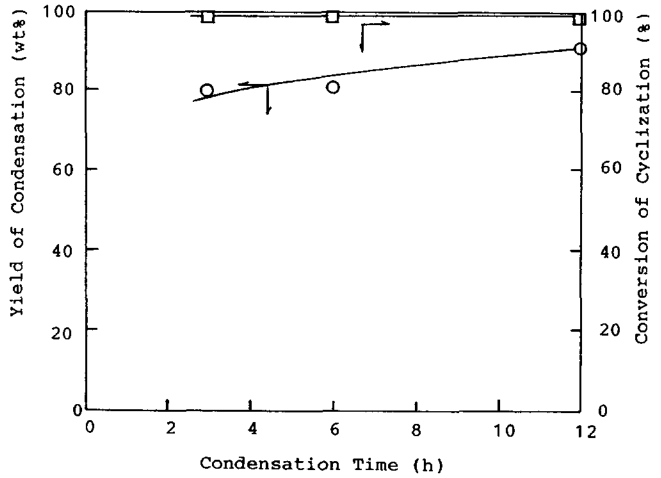

Figure 2 Relationship between yield of condensation or conversion of cyclization and condensation time

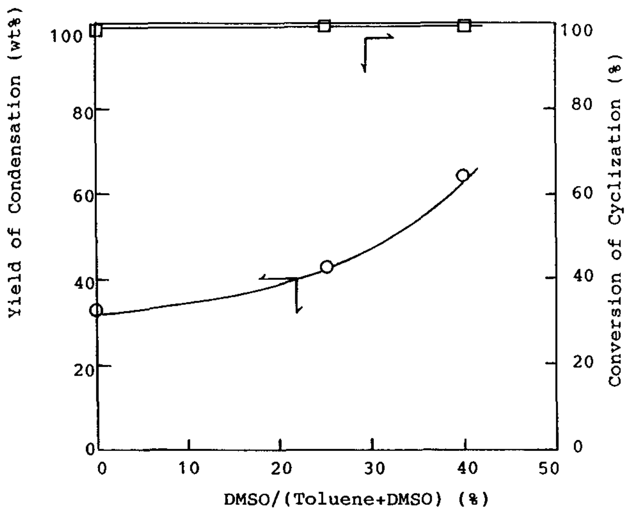

Figure 3 Relationship between yield of condensation or conversion of cyclization and solvent composition of DMSO in organic phase

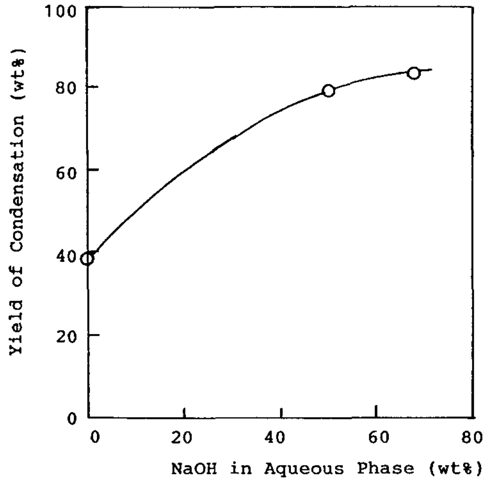

Figure 4 Relationship between yield of condensation and feed amount of NaOH in aqueous phase

distribution function of the PSB precursor on a personal computer. G.p.c. distribution functions of RP11 after curve resolution are also shown in *Figure 1* (dotted lines). It is recognized from these profiles that RP11 is a mixture of cyclic PS and unreacted PSB precursor. The yield of condensation and the conversion of cyclization [cyclization/(cyclization + polycondensation)] can be estimated by the g.p.c. profiles as shown in *Table 2*. The errors in the estimates of the cyclic polymer yields through such computer analysis were within a few percent. *Figure 2* shows the relationship between the yield of condensation or the conversion of cyclization and condensation time. After 3 h of condensation, the yield of condensation reaches ~ 80%. Moreover, the conversion of cyclization of each product was close to 100%. Usually, the end-to-end ring closure of living α,ω-dicarbanions with difunctional electrophile reagents (homogeneous condensation) is achieved under a very low concentration $(10^{-5}\text{–}10^{-7}\,\mathrm{mol\,l^{-1}})$[3-6]. It is remarkable that polycondensation (intermolecular condensation) took place scarcely in RP11–RP13 (PSB concentration $= 6.7 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$). Interfacial condensation is thus a most useful method for end-to-end ring closure, due to the dissolution of the reactants in a pair of immiscible liquids.

Next, we examined the effect of organic/aqueous solvent phases on the interfacial condensation. This series of experiments was carried out at 80°C for 6 h under the condition of $6.67 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ of difunctional PSB in the toluene/DMSO/H_2O ternary system. The acid acceptor (NaOH) was not added in these experiments. *Figure 3* shows the relationship between the yield of condensation or the conversion of cyclization and volume fraction of DMSO in the organic phase. The yield of condensation increases with increasing volume fraction of DMSO. The condensation product of each experiment was almost cyclic polymer. DMSO is miscible with both toluene and water. Therefore, the addition of DMSO was speculated to promote dissolution of the

Table 3 Reaction conditions and results of interfacial condensations of difunctional PSB with HMDA, varying PSB concentration[a]

	Toluene phase	Aqueous phase[b]		
Code	PSB ($mol\,l^{-1}$)	HMDA ($mol\,l^{-1}$)	Yield of condensation (wt%)	Conversion of cyclization (%)
RP31	6.7×10^{-4}	6.7×10^{-4}	79	~ 100
RP32	6.7×10^{-3}	6.7×10^{-3}	81	~ 100
RP33	3.0×10^{-2}	3.0×10^{-2}	97	22

[a] Interfacial condensations were carried out at 80°C for 6 h
[b] 50 wt% aqueous NaOH solution as acid acceptor

reactants in the immiscible toluene/water mixed solvent as well as the effect of phase transfer catalysis.

We examined the effect of acid acceptor (NaOH) on the interfacial condensations. These experiments were carried out at 80°C for 6 h under the condition of $6.67 \times 10^{-3}\,mol\,l^{-1}$ of difunctional PSB in toluene/aqueous phases. *Figure 4* shows the relationship between the yield of condensation and feed amount of NaOH in the aqueous phase. It is found from this plot that the yield of condensation increases with increasing NaOH concentration and reaches > 80% beyond 50 wt% aqueous NaOH solution. The excess of alkaline promoted the incorporation of HMDA into the organic layer. Similar results were reported in the synthesis of polyamines by interfacial polymerization of phenylsulfonylamine with dihalide compounds in the two-phase system of benzene/50 wt% aqueous NaOH solution[16,17]. It was concluded from the preliminary experiments described above that the additions of DMSO and acid acceptor (NaOH) were effective for cyclization in the interfacial condensations.

It was mentioned previously that the concentration of difunctional PSB is the most important factor for cyclization in the interfacial condensation method. Generally, the condensation of difunctional PSB with HMDA proceeds competitively with cyclization (intramolecular condensation) and polycondensation (intermolecular condensation). *Table 3* lists the reaction conditions and results of interfacial condensations of PSB with HMDA, varying the PSB concentration. The experiments RP31–RP33 were carried out at 80°C for 6 h in toluene/aqueous (50 wt% NaOH) phases. Typical g.p.c. profiles of RP31 and RP33 are shown in *Figure 5*. The RP31 product ($PSB = 6.7 \times 10^{-4}\,mol\,l^{-1}$) was a mixture of cyclic polymer and PSB precursor. In the g.p.c. profile of RP33 product ($PSB = 3.0 \times 10^{-2}\,mol\,l^{-1}$), a large, new main peak appears on the side of high molecular weight. It is suggested that RP33 is a mixture of polycondensation product, cyclic polymer and PSB precursor. The yield of condensation and the conversion of cyclization are summarized in *Table 3*. *Figure 6* shows the relationship between the yield of condensation or the conversion of cyclization and PSB concentration for RP31–RP33. Beyond PSB concentration of $10^{-2}\,mol\,l^{-1}$, the conversion of cyclization decreased sharply regardless of the high yield of condensation, due to the formation of polycondensation product. It is remarkable that in the interfacial condensation method, the end-to-end ring closure of α,ω-difunctional polymers was achieved for high concentrations of PSB (such as $10^{-3}\,mol\,l^{-1}$) compared with the homogeneous system (very low concentration of 10^{-5}–$10^{-7}\,mol\,l^{-1}$).

Properties of cyclic polymers

In order to study the solution properties of cyclic PS, we carried out the large-scale interfacial condensation of difunctional PSB with HMDA. In this experiment

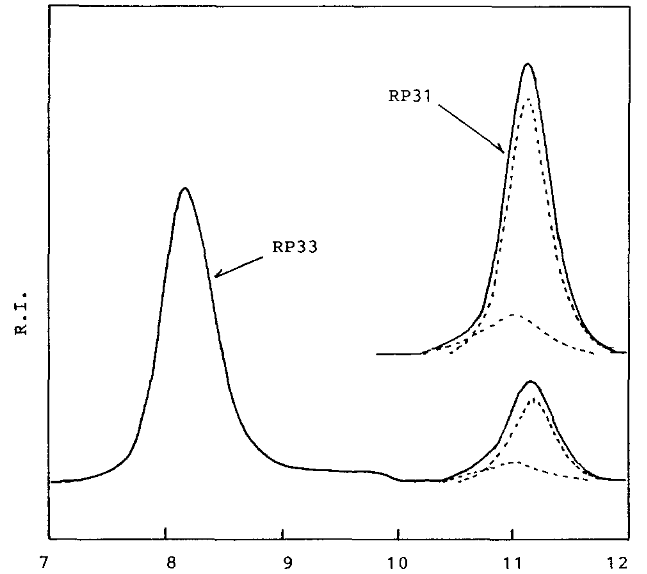

Figure 5 G.p.c. profiles of RP31 and RP33

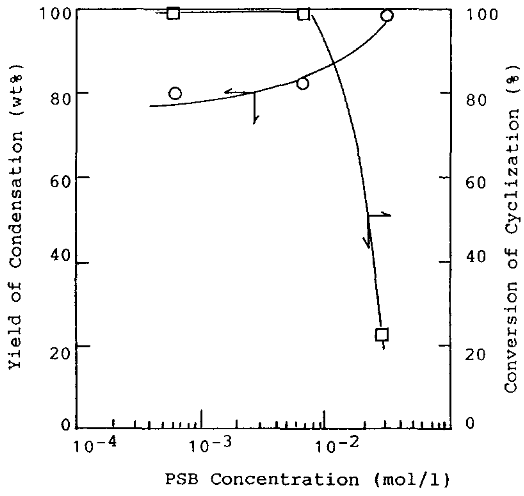

Figure 6 Relationship between yield of condensation or conversion of cyclization and PSB concentration

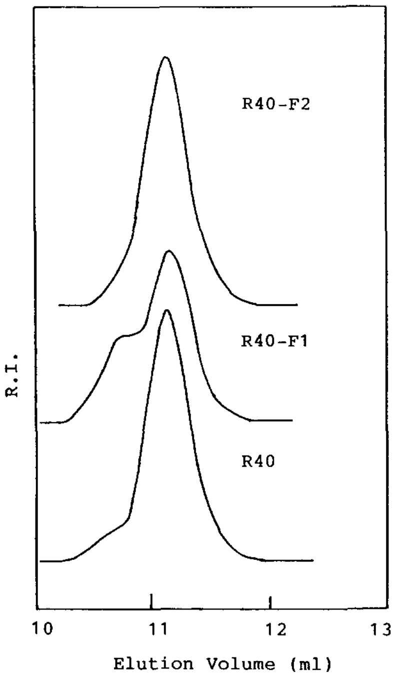

Figure 7 G.p.c. profiles of R40 before and after precipitation fractionation

(RP40), we employed the optimum conditions for ring formation, i.e. PSB $= 6.7 \times 10^{-4}$ mol l^{-1}, volume composition of DMSO $= 25\%$ in organic phase, 50 wt% aqueous NaOH solution, temperature $= 80$°C, condensation time $= 12$ h. *Figure 7* shows the g.p.c. profiles of R40 before and after precipitation fractionation (benzene–methanol system). It is found from these profiles that the fraction R40-F2 is removed from the PSB precursor by this fractionation and has a single and narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.06$).

We studied the solution properties of cyclic polymers. In order to study the ring dimensions, the shrinkage due to ring formation can be evaluated by means of the following dimensionless parameters

$$g = \langle R_g^2\rangle/\langle R_g^2\rangle_L \tag{2}$$

$$g' = [\eta]/[\eta]_L \tag{3}$$

where the subscript L refers to the properties of the linear polymer with identical molecular weight. The intrinsic viscosity of a single-cyclic polymer has been calculated by the method of Zimm[18,19]. The value of g' is 0.645 (non free-draining case) in the theta condition of the solvent. On the other hand, Fixman[20,21] has developed an ingenious method for treating the Oseen diadic tensor in the normal coordinate, without introducing the Kirkwood–Riseman approximation. This method can be applied to the cyclic polymer without any essential modification. Thus, in the diagonal approximation of Fixman, Fukatsu and Kurata[18] obtained g' to be modified as 0.648. *Table 4* lists the characteristics of cyclic polymer R40-F2. The value of g' was estimated to be 0.644 in THF as good solvent ($[\eta]_L = 8.85$ ml g^{-1}). This value is well in agreement with the theoretical one ($g' = 0.645$) in theta solvent.

The value of g is predicted by statistical theories as follows[22-24]

$$g = 1/2[1 + (\pi/2)z + \ldots] \tag{4}$$

where z ($|z| < 0.15$) denotes

$$(3/2\pi b^2)^{3/2}\beta N^{1/2}$$

N and b are the total number of segments in the molecule and the root-mean-square length of a segment vector, respectively, and β is the excluded volume for any pair of segments.

Figure 8 shows Guinier's plot of cyclic polymer R40-F2. The observed R_g values of cyclic and precursor polymers are listed in *Table 4*. The value of g determined by SAXS is 0.514. Moreover, the value of g can be estimated by the universal calibration on g.p.c. Equation (5) is written for linear polymers as the Flory–Fox equation[25]

$$[\eta]_L = \Phi\langle R_g^2\rangle_L^{3/2}/M_w \tag{5}$$

where Φ is a universal constant independent of the nature of the macromolecule and independent of the solvent medium.

Grubisic *et al.*[26] made clear using this equation that all linear polymers confirmed the relationship of $\log[\eta]_L M_w$ *versus* elution volume on g.p.c., regardless of their chemical species. Therefore, the value of g can be estimated from the relationship between this universal calibration and the elution peak counts of PSB precursor and cyclic polymer R40-F2. Values of g are collected in *Table 4*. Both values of g determined by SAXS and g.p.c. are slightly larger than 0.5. Considering the self-avoiding chain in a good solvent, the obtained g may be suitable for the shrinkage due to ring formation. It is thus plausible that the time-averaged shape of the cyclic polymer is not spherical but ellipsoidal.

We are investigating the synthesis of cyclic diblock and

Table 4 Characteristics of cyclic polystyrene

						g^f	
Code	$\overline{M}_n$[a]	$\overline{M}_w/\overline{M}_n$[b]	$[\eta]^c$ (ml g^{-1})	$\langle R_g\rangle^d$ (nm)	g'^e	SAXS	g.p.c.
R40-F2	7000	1.06	5.70	2.10	0.644	0.514	0.523

[a] Determined by v.p.o.
[b] Determined by g.p.c. distribution function
[c] Measured in THF at 38°C
[d] Radius of gyration of cyclic PS determined by SAXS in toluene
[e] $g' = [\eta]/[\eta]_L$, $[\eta]_L = 8.85$ ml g^{-1}
[f] $g = \langle R_g^2\rangle/\langle R_g^2\rangle_L$, $\langle R_g\rangle_L = 2.93$ nm in toluene

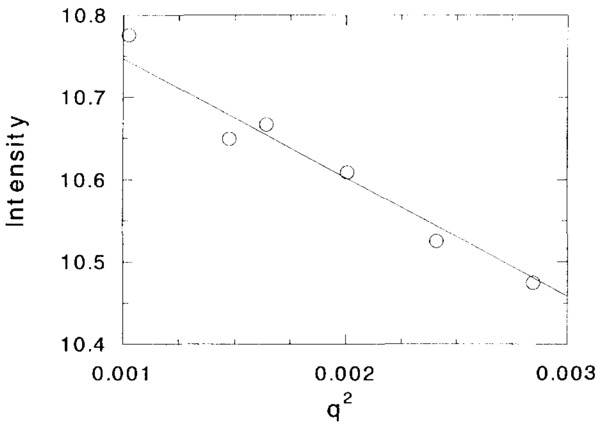

Figure 8 Guinier's plot of cyclic polymer R40-F2

multiblock copolymers using the interfacial condensation method. The results obtained for their phase separation behaviours will be reported in the near future.

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