

Synthesis of cyclic diblock copolymers by interfacial condensation

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(Received 5 September 1997; revised 8 December 1997; accepted 25 December 1997)

The well-defined α,ω -dibromopropyl polyisoprene-*block*-polystyrene-*block*-polyisoprene copolymer was prepared by coupling of corresponding triblock dianion end-capped with 1,2-diphenylethylene with a large excess of 1,3-dibromopropane. End-to-end ring closure of the α,ω -dibromopropyl triblock copolymer was performed by interfacial condensation between the aqueous phase (1,6-diaminohexane) and the organic phase (difunctional triblock copolymer). The limited field of reactions such as at the interface was very effective for ring closure. In the strongly segregated state, the lamellar domain spacing of cyclic diblock copolymer was smaller than that of linear A–B diblock copolymer with the same molecular weight. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: cyclic diblock copolymer; 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 equilibrium¹. The second method concerns polymers with carbon–carbon linkages in the backbone (chain-growth polymerizations)^{2–4}. End-to-end cyclization is based upon intramolecular coupling, for example, between the active chain ends of an α,ω -dicarbanionic polymer, using an appropriate difunctional electrophile, in stoichiometric proportions. As predicted by Jacobson and Stockmayer⁵, the probability of cyclic formation decreases with increasing chain length and polymer concentration. Usually the reaction is carried out at very low concentration (10^{-5} – 10^{-7} M) to favour cyclization with respect to intermolecular chain extension.

To avoid such problems, we proposed a new approach to cyclic polymers with narrow molecular weight distribution⁶. The well-defined halogen-terminated telechelic polystyrene (PS) was prepared by direct coupling of the polystyryl dianion with a large excess of alkyl dihalide. End-to-end ring closure of such telechelic PS was performed by interfacial condensation between the aqueous phase (1,6-diaminohexane) and the organic toluene phase (telechelic PS). The limited field of the reactions such as at the interface was effective for ring closure. The conversion of cyclic polymers was very high (more than 80%) at difunctional PS concentration of 10^{-3} M.

On the other hand, the phase segregation properties of cyclic diblock copolymers have been investigated using the

theory of Leibler⁷, ignoring the topological constraints specific to cyclic polymers⁸. 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. Recently, cyclic PS-*block*-poly(2-vinylpyridine) (P2VP) and PS-*block*-poly(dimethylsiloxane) (PDMS) copolymers have been synthesized by end-coupling their linear triblock precursors bis-anionic LiP2VP-*block*-PS-*block*-P2VPLi and LiPDMS-*block*-PS-*block*-PDMSLi with 1,4-bis(bromomethyl)benzene and $\text{Cl}_2\text{Si}(\text{CH}_3)_2$, respectively^{9–11}. Subsequently, Lescanec *et al.*¹² have investigated the effect of loops versus bridges on the morphological characteristics of microphase-separated block copolymer systems. Cyclic A–B diblocks only assume doubly looped chain conformations in the microphase-separated state, while their linear ABA triblock precursors are looped and bridged. They have directly observed the effect of looped *versus* bridged chain conformations in the microphase-separated state through an analysis of the relative domain spacings of the lamellae formed by the cyclic diblock and linear triblock systems. The presence of double loops in the A–B cyclic systems versus a mixture of single-loop and bridged conformations in the A–B–A triblock systems was argued to account for the observed behaviour.

In this article, we prepared α,ω -dibromopropyl polyisoprene (PI)-*block*-PS-*block*-PI triblock copolymer by coupling reaction of corresponding triblock dianion with a large excess of 1,3-dibromopropane. We present the cyclization of such α,ω -dibromopropyl triblock copolymers (organic 1,1,2-trichloroethane phase) by interfacial condensation. Triblock copolymer precursor was allowed to react with 1,6-diaminohexane (aqueous phase) at the interface between the organic phase and the aqueous phase as a function of end-functional concentration of triblock copolymer. Moreover, we discuss microphase separation of cyclic diblock lamella compared to linear diblock ones.

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EXPERIMENTAL

Synthesis and characterization of difunctional triblock copolymer

PI-*block*-PS-*block*-PI triblock dianion was synthesized by sequential anionic addition of styrene and isoprene initiated by lithium naphthalene in benzene/tetrahydrofuran (THF) (8/2, v/v) mixture. α,ω -Dibromopropyl triblock copolymer (XSI) was prepared by the coupling reaction of corresponding triblock dianion end-capped with 1,1-diphenylethylene (DPE) with an excess amount of 1,3-dibromopropane (DBP) in THF. The details concerning the synthesis and purification of such triblock dianions have been given elsewhere^{6,13}.

The number-average molecular weight (\bar{M}_n) of PS precursor was determined by gel permeation chromatography (g.p.c.: Tosoh HLC-8020 high-speed liquid chromatograph) with THF as eluent at 40°C, TSK gel G4000H_{XL}, G3000H_{XL} and G2000H_{XL} columns in series and a flow rate of 1.0 ml min⁻¹. \bar{M}_n of triblock copolymers was also determined by universal calibration¹⁴ ($\log[\eta]M$ versus elution volume) by g.p.c. The polydispersity (M_w/\bar{M}_n) was determined by g.p.c. using the reshaping method¹⁵ with a personal computer. The content of bromopropyl groups in the polymers was determined by Volhard's titration⁶. The content of PS blocks was determined by ¹H nuclear magnetic resonance (n.m.r.; 500 MHz, JEOL GSX-500 n.m.r. spectrometer) in CDCl₃. The characteristics of difunctional XSI are listed in Table 1.

Cyclization of difunctional triblock copolymer by interfacial condensation

An organic phase (1,1,2-trichloroethane (TCE) and *N,N*-dimethylformamide (DMF)) contained difunctional XSI, and an aqueous phase contained a mixture of 1,6-diaminohexane (DAH) and sodium hydroxide (NaOH) as an acid acceptor. These two heterogeneous phases were maintained at 100°C under rapid stirring for 48 h. 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 diblock copolymer

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 25°C in order to separate the cyclic diblock copolymer, while the turbidity of the XSI precursor was measured beforehand at a wavelength of 500 nm (Hitachi-Perkin-Elmer 139 u.v.-vis spectrometer).

\bar{M}_n of cyclic diblock copolymer was determined by vapour pressure osmometry (v.p.o.) on a Corona NA 117 vapour pressure osmometer in benzene.

Film specimens of the triblock and cyclic diblock copolymers for morphological observations were obtained

by cast from a dilute solution of toluene on a Teflon sheet for 5 days and dried under vacuum. These specimens were further annealed at 120°C for 1 week under vacuum, so as to have structures thermodynamically at equilibrium. These films were embedded in an epoxy resin and cut into ultra-thin sections (about 70–100 nm thick) using an ultra microtome equipped with cryosystem (Reichert-Nissei Co., Ultracut N). These specimens were exposed to a vapour of osmium tetroxide (OsO₄). Morphological results were obtained with transmission electron microscopy (TEM; Hitachi H-500 TEM) at 75 kV.

RESULTS AND DISCUSSION

Synthesis of difunctional triblock copolymer

Table 1 lists characteristics of the difunctional PI-*block*-PS-*block*-PI copolymer. The conversion was almost 100% within experimental error. The g.p.c. profile of XSI11 had a single and narrow molecular weight distribution ($M_w/\bar{M}_n = 1.03$). It was found from Volhard's titration that the XSI11 was a linear macromolecule carrying two equal functional endgroups.

Cyclizations

In order to check the condensation of difunctional XSI11 with 1,6-diaminohexane (DAH), preliminary experiment (CXB-10) was carried out in a homogeneous system. The reaction conditions were as follows. Difunctional XSI11 (concentration [XSI] = 5×10^{-3} mol l⁻¹) was allowed to react with DAH ([DAH] = 5×10^{-3} mol l⁻¹) at 100°C for 16 h in a mixture of TCE/DMF (10:4, v/v). A g.p.c. profile of CXB-10 is shown in Figure 1. In this chart, a large, broad main peak appears on the side of high molecular weight. On the other hand, the elution count of the right peak at the side of low molecular weight is in agreement with the XSI11 precursor. It is therefore suggested that this product is a mixture of polycondensation product and XSI11 precursor. The yield of condensation and the conversion of cyclization [cyclization/(cyclization + polycondensation)] can be estimated by the g.p.c. profiles.

The reshaping method¹⁵ employed in this work was a new one, solving Tung's diffusion equation for q.p.c. Tung observed that a monodisperse fraction gave an approximately Gaussian type of chromatograph on passage through a column of cross-linked PS gel¹⁶.

$$F(v) = \int_{v_a}^{v_b} W(y)(h/\pi)^{1/2} \exp\{-h(v-y)^2\} dy \quad (1)$$

This relates the observed chromatograph $F(v)$ to the distribution function $W(y)$ that would be obtained if axial diffusion effects were absent. Here v is the elution volume, v_a is the initial elution volume, v_b is the final elution volume, and h is a parameter characteristic of the columns used. Pierce and Armonas's method is based on the Fourier transform method for solving Tung's integral

Table 1 Characteristics of α,ω -dibromopropyl PI-*block*-PS-*block*-PI triblock copolymer

Code	\bar{M}_n ($\times 10^{-4}$) ^a		PS block (mol.%)		M_w/M_n ^a	Bromopropyl groups ^c (number/molecule)
	PS	Block copolymer	G.p.c. ^b	N.m.r.		
XSI11	1.1	2.0	44.4	44.9	1.03	2.0

^aDetermined by g.p.c.

^bEstimated from \bar{M}_n s of PS precursor and triblock copolymer

^cDetermined by Volhard's titration

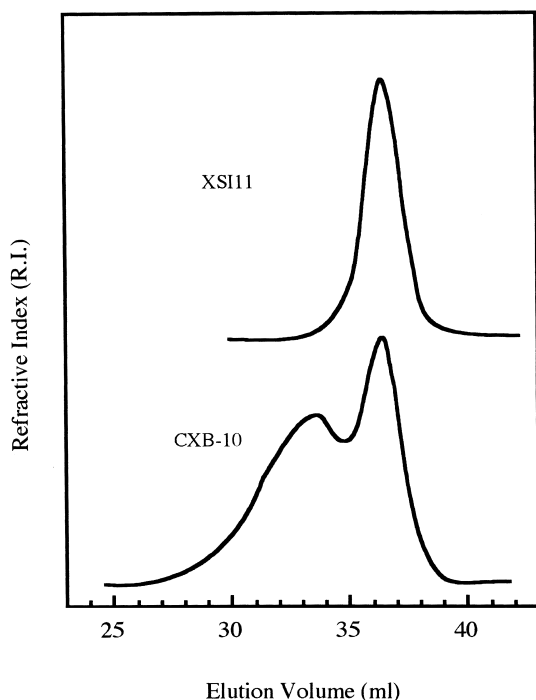


Figure 1 G.p.c. profiles of CXB-10 and XSI11 precursors

equation (equation (1)). As a result, taking the limit as $v \rightarrow v_0$ (v_0 , the arbitrary point of elution volume, $v_a < v_0 < v_b$) finally gives

$$W(v_0) = [h/(h-c)]^{1/2} F(v_0) \exp\{-b^2/4(h-c)\} \quad (2)$$

where $b = (\partial \ln F/\partial v)_{v_0}$ and $c = -1/2(\partial^2 \ln F/\partial^2 v)_{v_0}$.

This relatively simple expression involves the parameter h , which is a function of the set of columns used, and b and c , which are related to the first and the second logarithmic derivatives of $F(v)$ with respect to the elution volume v . The mathematical operations can be performed by a personal computer.

The errors in the estimates of the cyclic polymer yields through such a computer analysis were within a few percent. The yield of condensation in the experiment CXB-10 was 65 wt.%. The end-to-end ring closure of XSI was never achieved under such polymer concentration: $5 \times 10^{-3} \text{ mol l}^{-1}$.

Next, we examined the effect of organic/aqueous solvent phases on the interfacial condensation (CXB-21–CXB-24). This series of experiments was carried out at 100°C for 48 h under the condition of 10^{-4} – $10^{-2} \text{ mol l}^{-1}$ of the difunctional XSI11 in the TCE/DMF/water ternary system. DMF is miscible with both TCE and water. Therefore, the addition of DMF was speculated to promote dissolution of the reactants in the immiscible TCE/water mixed solvent as well as effect of phase transfer catalysis. The acid acceptor

(NaOH) was also added in these experiments. Table 2 lists the reaction conditions and results of interfacial condensation of difunctional XSI and DAH, varying the XSI concentration. Typical g.p.c. profiles of CXB-21 and CXB-24 are shown in Figure 2. G.p.c. profile of CXB-24 ($[\text{XSI}] = 1.2 \times 10^{-2} \text{ mol l}^{-1}$) is bimodal. A large, broad peak at the side of high molecular weight corresponds to polycondensation product. On the other hand, a small, narrow right peak shifts to the side of low molecular weight compared to that of the XSI precursor. It is suggested that CXB-24 is a mixture of polycondensation product and cyclic diblock copolymer. In the experiment CXB-21 ($[\text{XSI}] = 1.2 \times 10^{-4} \text{ mol l}^{-1}$), the condensation product is almost cyclic diblock copolymer.

Figure 3 shows the relationship between the yield of condensation or the conversion of cyclization and XSI concentration for CXB-21–CXB-24. It is found that the end-to-end ring closure proceeded quantitatively until XSI concentration of $10^{-3} \text{ mol l}^{-1}$. Beyond this concentration region, 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 diblock copolymer was achieved for high concentrations of XSI (such as $10^{-3} \text{ mol l}^{-1}$) compared with the homogeneous system.

These results can be explained as follows. In an interfacial condensation system, the first step reaction of difunctional XSI with DAH proceeds within the two-dimensional like interface formed by organic/water phases. Even if the organic solvent is not a non-solvent for the diblock copolymer, a thin film of cyclic diblock copolymers should form at the interface. Of course, TCE is a good solvent for cyclic diblock copolymers. Then, such heterofunctional pre-block copolymer may lead to ring closure near the interface region before the transfer to organic phase. Cyclic polymer continues to form at the interface until one of the reactants is used up. Cyclic diblock copolymers transferred into organic phase are inert. Rapid stirring of the system results in increased condensation rates because of the increase in interfacial surface area. Difunctional block copolymer concentration is lower than that in organic phase due to two-dimensional surface area. Therefore, the end-to-end ring closure seems to be performed apparently in high dilute solution such as the limited field of interfacial surface.

Morphology of cyclic diblock copolymer

In order to study the microphase separation of cyclic diblock copolymer, we carried out a large-scale interfacial condensation under the same conditions as CXB-22 ($[\text{XSI}] = 1.2 \times 10^{-3} \text{ mol l}^{-1}$). After precipitation fractionation, the characterization of cyclic diblock copolymer (CXB-F) was performed with v.p.o., g.p.c. and n.m.r. CXB-F had almost

Table 2 Reaction conditions and results of interfacial condensation of functional XSI11 with HMDA^a

Code	TCE phase ^b	Aqueous phase ^c	Yield of condensation (wt.%)	Conversion of cyclization (%)
	XSI11 (mol l^{-1})	HMDA (mol l^{-1})		
CXB-21	1.2×10^{-4}	1.2×10^{-4}	83	~100
CXB-22	1.2×10^{-3}	1.2×10^{-3}	90	~100
CXB-23	5.4×10^{-3}	5.4×10^{-3}	95	66
CXB-24	1.2×10^{-2}	1.2×10^{-2}	~100	20

^aInterfacial condensations were carried out at 100°C for 48 h

^bTen vol.% DMF was contained in TCE phase

^cFive wt.% aqueous NaOH solution as acid acceptor

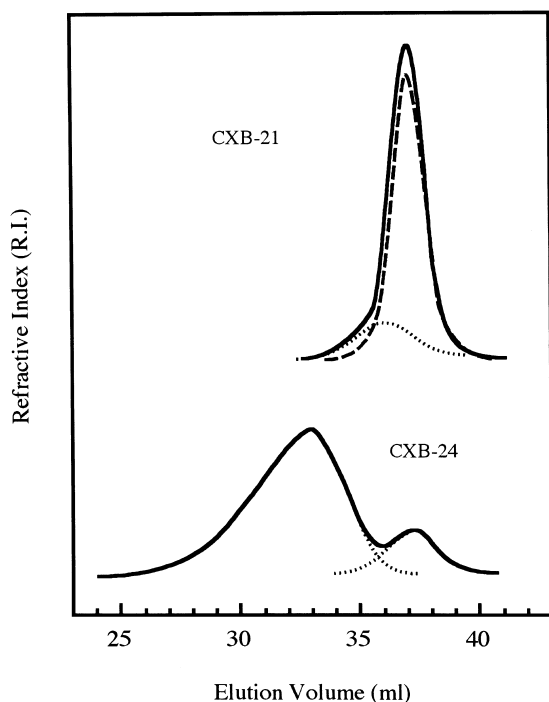


Figure 2 G.p.c. profiles of CXB-21 and CXB-24

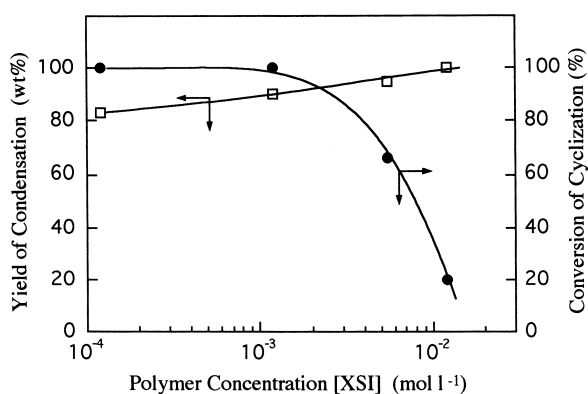


Figure 3 Relationship between yield of condensation or conversion of cyclization and XSI11 concentration for CXB-21-CXB-24

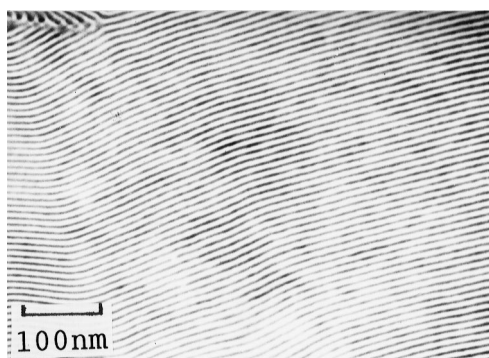


Figure 4 TEM micrograph of cyclic diblock copolymer CXB-F

the same molecular weight and composition ($\bar{M}_w/\bar{M}_n = 1.85 \times 10^4$, PS block = 44.8 mol% and $\bar{M}_w/\bar{M}_n = 1.02$) as those of triblock precursor and a narrow molecular weight distribution.

Figure 4 shows a TEM micrograph of cyclic diblock copolymer (CXB-F). The dark portions correspond to PI

domains selectively stained with OsO_4 . The texture shows alternating PS/PI lamellar structure. The periodic distance of lamellae was estimated to be 10.5 nm from the TEM micrograph. Triblock copolymer precursor (XSI11) showed also PS/PI lamellar morphology and had almost the same periodic distance as that of cyclic diblock copolymer specimen (CXB-F), judging from the TEM micrograph. Lescanec *et al.*¹² have discussed the ratio of the domain spacing of the cyclic diblock to its linear analogue, D_c/D_1 , to understand the origin of the observed dependence of D on architecture. For the cyclic diblock/linear triblock pairs, D_c/D_1 was in the range of 0.91–0.95 from TEM and small-angle X-ray scattering (SAXS) measurements. Since the microdomains formed by the triblock copolymers are composed of a mixture of looped and bridged chains, D_1 should always be larger than D_c because the cyclic system always has more loops per chain. In general, a TEM image is not sufficient to determine the value of the periodic distance of lamellae. In order to discuss it quantitatively, SAXS data for our samples will be necessary.

On the other hand, Marko⁸ calculated theoretically the domain spacing for symmetric, strongly segregated, lamellae-forming cyclic and linear A–B diblock copolymers. For a symmetric cyclic/linear diblock pair having the same molecular weight, this analysis predicts $D_0/D_1 \rightarrow 2^{-2/3} \cong 0.64$. Then, we focus the effect of loops on the morphological characteristics of cyclic/linear diblock pair. According to previous results¹⁶, the periodic distance of PS-*block*-PI diblock copolymer ($\bar{M}_n = 2.1 \times 10^4$, PS = 53 wt.%) was 17.2 nm in thermal equilibrium. So, the observed value for cyclic diblock copolymer (CXB-F) ($D_c/D_1 = 0.61$) is in good agreement with the predicted one within experimental error. Cyclic A–B diblocks only form doubly looped chain conformations in the microphase-separated state. This observation is attributed to the differences in architecture between the two systems.

It will be necessary to discuss quantitatively the microphase separation for the cyclic/diblock/triblock copolymer trio from SAXS data and TEM observations, varying the molecular weight and composition. The solution properties of cyclic diblock copolymers are also interesting. Moreover, we are investigating the synthesis of cyclic multiblock copolymers using the interfacial condensation method. The results will be reported in the near future.

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