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Synthesis and characterization of polyfunctional star-shaped macromonomers

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Abstract

Functional polyisoprene stars were prepared by copolymerization of polyisoprenyl lithium with divinylbenzene in *n*-heptane, where the polyisoprene arm was prepared by anionic polymerization using [2-[*N*,*N*-dimethylamino)methyl]phenyl]lithium as the initiator. The star polymer was removed from the unreacted arms. These functional stars were converted by quaternization with *p*-chloromethylstyrene into polyisoprene star-shaped macromonomers having ca. one vinylbenzyl group at each arm end. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyisoprene; Functional initiator; Star-shaped macromonomer

1. Introduction

Star-shaped polymers are characterized as structures in which all the chains of a molecule are linked together to a small-molar-mass core. The interest in star polymers arises not only from the fact that they are models for branched polymers but also from their enhanced segment densities. More recently, we reported on the dilute-solution properties of polyisoprene (PI) stars (arm number $n = 43 \sim 237$) prepared by copolymerization of PI-lithium with divinylbenzene (DVB) in *n*-heptane [1]. It could be concluded that the non-uniformity of the number of arms in PI stars was relatively narrow due to the organized copolymerization of ω-functional PI-lithium with DVB in uniform micelles. The ratio of the radius of gyration over the Stokes radius (R_G/R_H) in cyclohexane decreased gradually and approached unity as n became large. Even PI stars with multiarms did not behave as neat hard spheres but as soft spheres which in good solvents were penetrable near the edges.

Stars with multiarms (the critical number of arms is estimated to be of the order of 10^2) are expected to form a crystalline array near the overlap threshold (C*) [2]. Willner et al. [3,4] investigated the ordering phenomena of stars around C* by means of small-angle neutron scattering (SANS). They showed that ordering was very weak for 8- and 18-arm polymers but became stronger with increasing arm numbers. We also investigated in detail the structural ordering of such stars by means of small-angle X-ray scattering (SAXS) [5]. PI stars ($n >$ ca. 90) formed a body-centred cubic (BCC) structure near C*. This structure changed to a mixed lattice of BCC and face-centred cubic (FCC) structures with increasing polymer concentration. The nearest-neighbour distance of the spheres (D_0) decreased continuously with an exponential function increasing the polymer concentration. It was found, moreover, that from the double-logarithmic plot of D_0 as a function of polymer concentration, the measured D_0 was proportional to the $-1/3$ power of the polymer concentration. This fact means that the spherical particles of PI stars lead to isotropic shrinkage increasing the polymer concentration around high polymer concentration.

We reported the architecture of a polymeric superstructure film formed by locking the cubic lattice of the core-shell polymer microspheres in poly(methyl methacrylate) (PMMA) [6]. In short, after the microspheres formed a cubic lattice such as a BCC structure in methyl methacrylate (MMA) monomer, the polymeric superstructures were constructed by locking a permanently ordered lattice into a solid matrix by means of the free radical polymerization of MMA. Therefore, star polymers with multiarms could be expected to construct polymeric superstructures by molecular design of locking as well as of core-shell microspheres. After the PI stars ($n >$ ca. 90) revealed a superlattice of BCC structure in vinyl monomers (MMA, styrene and *t*-butyl acrylate), the superstructures were constructed by locking

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Table 1
Characteristics of polyisoprene arm precursors

Code	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [b]	Micro structure [c] (%)		
			3,4-	1,2-	*cis*- and *trans*-1,4-
PI1	7200	1.14	71.8	21.3	6.9
PI2	9400	1.16	72.3	22.2	5.5

[a] Determined by vapour pressure osmometry.
[b] Determined by g.p.c.
[c] Determined by ^{1}H-n.m.r. in $CDCl_3$.

the ordered superlattice into a solid matrix by means of free radical polymerization of the vinyl monomers [7]. The morphologies of the polymerization-induced phase separation depended strongly on the arm number, the propagation rate of vinyl monomers, and the addition of chain transfer or crosslinking agents. However, PI stars could be locked microscopically with the shape of unimolecular micelles in a polymer matrix under some polymerization conditions. From the results obtained in such work, it was expected that one of the best methods for the locking of a lattice is one in which the star polymers themselves play the role of the crosslinker.

In this article, we mention the synthesis of functional PI stars having a vinylbenzyl group at each arm end. Functional PI stars were prepared by copolymerization of polyisoprenyl lithium with DVB in *n*-heptane, where the PI arm anion was prepared by anionic polymerization using [2-[(*N*,*N*-dimethylamino)-methyl]phenyl]lithium as the initiator. These functional stars were converted into polyfunctional PI star-shaped macromonomers with *p*-chloromethylstyrene by quaternization.

2. Experimental

2.1. Synthesis of star-shaped macromonomers

Antonietti et al. were the first to describe the synthesis of a polystyrene (PS) macrozwitterion. By means of the anionic polymerization technique, using [2-[(*N*,*N*-dimethylamino) methyl]phenyl]lithium as the initiator and 1,3-propanesultone as the terminating reagent, a bifunctional PS was obtained which could be quaternized and converted into the α,ω-macrozwitterion by ultrafiltration [8]. α,ω-Macrozwitterion block copolymers were also obtained using the same procedure [9].

Herein, we use the same initiating system for the preparation of the functional polyisoprenyl (PI)-lithium monoanion. The synthesis of the functional initiator was carried out at room temperature under high vacuum using the break-seal method. *N*,*N*-dimethylbenzylamine (DMB) was dissolved in a mixture of diethyl ether and cyclohexane. An *n*-butyl lithium (*n*-BuLi) was then added and the solution allowed to stand for 72 h. Under these conditions, DMB was converted into a functional initiator by metalation. The resulting white precipitate was filtered off, washed with cyclohexane, and dissolved in tetrahydropyran (THP), using pure and carefully dried reagents and solvents.

PI anions were prepared by living anionic polymerization techniques in *n*-heptane under a pressure of 10^{-6} mmHg (1 mmHg $\approx$ 133 Pa). Details of the synthesis and purification of such PI anions have been given elsewhere [10,11].

Functional star polymers were prepared by copolymerization PI monoanions with a small amount of divinylbenzene (DVB, Tokyo Kasei; 65 vol%, *m*-/*p*-isomer = 2, 35 wt%, ethylstyrene) in *n*-heptane. The resulting solution was stirred at 20°C for 48 h. Polymerization was stopped by introducing the viscous solution into an excess of methanol. The star polymer was extensively fractionated in a benzene/methanol mixture at 20°C in order to remove the unreacted arm. The turbidity of the PI precursor was measured beforehand at a wavelength of 500 nm (Hitachi Perkin-Elmer 139 UV-VIS spectrometer).

Subsequently, the quaternization of functional PI stars was carried out as follows. Typically, the functional PI star SI1 ($\bar{M}_w = 1.22 \times 10^5$, $n = 17$; 7.0 g) was dissolved in a mixture of 1,4-dioxane (20 ml) and methanol (10 ml). *p*-Chloro-methylstyrene (CMS; 1 ml) and a small amount of hydroquinone (polymerization inhibitor) were added to this solution. The resulting mixture was stirred at 40°C for 24 h. After reaction, the polymer solution was poured into an excess of methanol. The product was purified three times by reprecipitation from benzene solution with methanol.

2.2. Characterization

The number average molecular weight ($\bar{M}_n$) of the PI precursor was determined by vapour pressure osmometry (v.p.o.) on a Corona NA 117 vapour pressure osmometer in benzene. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined by gel permeation chromatography (g.p.c.; Tosoh HLC-8020 high speed liquid chromatograph) with tetrahydrofuran (THF) as eluent at 38°C, using a TSK gel GMH_{XL} column and a flow rate of 1 ml min^{-1}, with the distribution function improved by the reshaping method [12].

The microstructure of PI was determined by ^{1}H nuclear magnetic resonance (n.m.r.; 500 MHz, JEOL GSX-500 n.m.r. spectrometer) in $CDCl_3$.

The weight average molecular weight ($\bar{M}_w$) of PI stars was determined by static light scattering (SLS) in cyclohexane at 23°C, on a Photal TMLS-6000HL (Otsuka Electronics) with a He–Ne laser ($\lambda_0 = 632.8$ nm) in the Zimm mode [13]. The scattering angles were in the 30–150° range. Samples were filtered through membrane filters with a nominal pore size of 0.2 μm before measurement. Solutions were measured in the 0.6–6.2 g l^{-1} concentration range.

The hydrodynamic radius (R_H) of the star polymers was determined using dynamic light scattering (QELS;

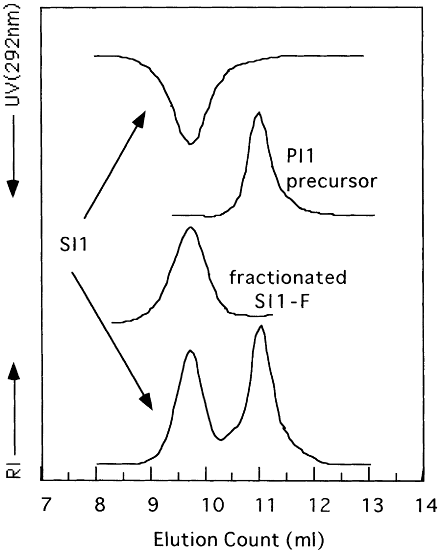

Fig. 1. G.p.c. profiles of SI1, fractionated functional PI star (SI1-F) and PI1 precursor.

scattering angle = 90°, Otsuka Electronics) in 0.1 wt% cyclohexane (viscosity $\eta = 0.898$ cp, $n_D = 1.4262$) solution at 23°C.

The degree of quaternization of functional PI stars (corresponding to the content of vinylbenzyl groups) was determined by Volhard's titration.

3. Results and discussion

3.1. Synthesis of PI arm precursors

Table 1 lists the characteristics of the PI arm precursors. The conversion for both series was almost 100% within experimental error. The g.p.c. profile of the PI1 precursor has a single and relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.14$; see Fig. 1). Fig. 2 shows the ^{1}H-n.m.r. spectrum of the PI1 precursor in $CDCl_3$. In addition to the signal of phenyl protons (7.2 ppm) of the functional initiator, the spectrum exhibits absorptions assignable to 3,4- (4.8 ppm), 1,2- (5.0 and 5.8 ppm) and *cis*- and *trans*-1,4- (5.3 ppm) addition protons of PI. The percentage of microstructure is also listed in Table 1. It is found that these polymerization systems formed mainly 3,4-additions of PI due to the presence of a small amount of polar solvent such as THP in the medium. Moreover, it was indicated that the content of functional initiator was unity from the peak ratio integrated phenyl protons to 1,4-, 1,2- and 3,4-addition protons of PI. The accuracy of n.m.r. measurements of the contents of the microstructure and terminal initiator group was within 0.5%.

3.2. Synthesis of functional star polymers

We synthesized PI stars by varying the concentration ratio of DVB to polyisoprenyl monoanions ([DVB]/[LE]) and the initial concentration of polyisoprenyl monoanions. Table 2 lists the experimental conditions and results for PI star formation. A typical g.p.c. profile of SI1 is shown in Fig. 1. The g.p.c. distribution is bimodal according to the refractive index (RI) monitor but unimodal according to the u.v. monitor. The u.v. wavelength is set at 292 nm, i.e. at the characteristic absorption wavelength of the vinylbenzyl group of DVB. In the RI chart, the low molecular weight fraction was in agreement with elution patterns of the PI precursor. Therefore, the polymerization product is a mixture of PI star and its precursor. In the u.v. chart, the unreacted PI precursor has no absorption at 292 nm (see Fig. 1). This fact indicates that all of the feed DVB is consumed in the core formation of the star polymers. Moreover, macrogelation was not observed in either experiment during polymerization. The polymerization yields are in the 39 ~ 45% range. However, the polymerization yields in a good solvent system, as reported by Fetters [14], were usually close to 90%. With regard to these results, it can be speculated as follows. As compared with free radical

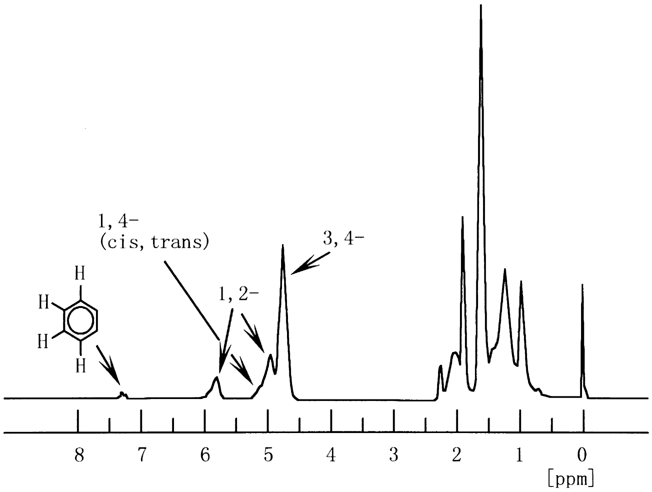

Fig. 2. ^{1}H-n.m.r. spectrum of polyisoprene PI1.

Table 2
Experimental conditions and characteristics of polyisoprene stars

No.	PI arm		$[DVB]/[LE]^b$ (mol mol^{-1})	Star polymer				
	Code	$10^3[LE]^a$ (mol l^{-1})		Yield[c] (wt%)	$10^{-5}\bar{M}_w{}^d$	n^e	$R_H{}^f$ (nm)	$R_c{}^g$ (nm)
SI1	PI1	7.2	1.90	45.3	1.22	17	8.3	1.40
SI2	PI2	15.7	1.17	38.7	1.59	17	8.5	1.26

[a] Concentration of PI anions.
[b] Mole ratio of divinylbenzene/PI anions.
[c] Determined by g.p.c.
[d] Determined by SLS.
[e] Arm number per macromolecule.
[f] Hydrodynamic radius determined by QELS.
[g] Radius of DVB core.

copolymerization of vinylbenzyl-terminated macromonomers, the PI chain is fitted rapidly with DVB. Therefore, part of the feed PI anions would form linear PI macromonomers possessing terminal pendant double bonds at the initial stage of the reaction. These macromonomers would form uniform micelles in a selective solvent, such as an *n*-heptane. As a result, core formation by crosslinking may proceed within such micelles. In such copolymerization systems, the residual PI anions unfitted with DVB cannot penetrate into the DVB core of star molecules due to high segment density.

After precipitation fractionation, we performed a characterization of the fractionated PI stars. The g.p.c. profile of the high molecular weight fraction SI1-F (PI star) is shown in Fig. 1. Table 2 also lists the characteristics of PI stars. The yield of PI stars was estimated by their g.p.c. distribution. The values of $\bar{M}_w$ of PI stars in cyclohexane were derived from Zimm plots. The arm number n of the star polymers was equal for both SI1 and SI2 series. The arm number seemed to depend on the feed ratio of [DVB]/[LE] and initial concentration of PI monoanions, as the aggregation number of PI micelles depends strongly on both parameters. All of the PI stars prepared apparently had a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.13 \sim 1.15$) from g.p.c. measurements.

As mentioned earlier, all of the feed DVB were consumed in core formation of the star polymers. It is possible to estimate the core radius (R_c) of PI stars because the yield of star and feed amounts of DVB are known. R_c is calculated from the equation: $n = [4\pi/(3P_E)]R_c^3\rho N_A$, assuming that the core is spherical, where n is the arm number, ρ is the density of the DVB core (1.01×10^4 mol m^{-3}) [15], N_A is Avogadro's number and P_E is the number of monomeric units (mixture of DVB and ethylstyrene) fitted at the arm PI chain. The calculated R_c is also listed in Table 2. As a matter of course, the values of R_c are small compared to the corresponding R_H values for PI stars.

Polyfunctional star-shaped PI macromonomers were converted from the quaternization of corresponding PI stars having tertiary amino groups at each arm end. Quaternization of functional SI1-F stars with CMS was carried out in a mixed solvent of 1,4-dioxane and methanol with the addition of hydroquinone. It was found from Volhard's titration that the degree of quaternization achieved was 87.2%. From this result, the number of vinylbenzyl groups of star-shaped PI macromonomers (SI1-FM; arm number $n = 17$) is estimated to be 15 per molecule. It is necessary to introduce quantitatively the vinylbenzyl groups into the tertiary amino groups at arm ends, choosing various reaction conditions.

It will be of interest to investigate the architecture of a polymeric superstructure formed by locking the cubic lattice of PI star-shaped macromonomers with multiarms into some kind of polymer matrix. The information obtained will be reported on in the near future.

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