Polymer Vol. 36 No. 21, pp. 4155–4157, 1995

0032-3861/95/\$10.00+0.00

Synthesis of star polymers by organized polymerization of macromonomers

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Vinylbenzyl-terminated polyisoprene (PI) macromonomers were synthesized by the coupling reaction of the corresponding living anions with *p*-chloromethylstyrene. PI stars were prepared by the free-radical crosslinking of PI macromonomers with divinylbenzene (DVB) in n-heptane. No macrogelation was observed during polymerization. The radical copolymerization of PI macromonomer with DVB led to microgelation in micelles formed by PI macromonomers in the selective solvent (organized polymerization). The arm number of star polymers depended strongly on the concentration ratio of DVB to macromonomer ends.

(Keywords: macromonomer; star polymer; micelle)

Introduction

Star-branched or radial polymers have the structure of linked linear polymers with a core of small molecular weight. Generally, a star polymer has smaller hydrodynamic dimensions than a linear polymer with identical molecular weight. Interest in star polymers arises from their compactness and from their enhanced segment density.

Star polymers are best prepared by coupling of anionic living polymers with multifunctional electrophilic coupling agents. The coupling agents are either multifunctional chloromethylated benzene derivatives or multifunctional chlorosilane compounds. In general, with these compounds it is difficult to extend the functionality of the stars. However, Roovers and coworkers[1,2] have recently reported the synthesis of polybutadiene (PB) stars with 64 and 128 arms from the coupling of living PB lithium with dendrimers having chlorosilane bonds at the surface. At present, the most convenient way to prepare star polymers possessing more than 10 arms is to crosslink monocarbanionic chains with divinylbenzene (DVB)[3–5]. However, this crosslinking sometimes leads to macrogelation, and the stars produced do not have a narrow molecular weight distribution.

More recently, we have established a novel architecture for $(AB)_n$ star block copolymers by means of organized polymerization in micelles formed by diblock macromonomers possessing a vinylbenzyl group at the terminal end[6,7]. In the copolymerization of vinylbenzyl-terminated polyisoprene (PI) macromonomer with DVB, the primary copolymer radicals composed of PI and a few units of DVB or ethylstyrene (mixture in DVB commercial reagent) resembling block copolymer may be produced in the initial reaction stage. Such primary copolymer radicals can be expected to form micelles in a selective solvent such as aliphatic hydrocarbon at more than the critical micelle concentration. So, the styryl-type radicals on DVB or ethylstyrene sequences apparently take the concentrated state in micelles, as shown in *Figure 1*. In this organized assembly a star polymer will be formed by means of microgelation between macromonomer and a low-molecular-weight difunctional unsaturated compound such as DVB.

In this communication, vinylbenzyl-terminated PI macromonomers were synthesized by the coupling reaction of corresponding living anions with *p*-chloromethylstyrene (CMS). PI stars were prepared by the free-radical crosslinking of PI macromonomers with DVB in n-heptane. We discuss the star formation of the organized polymerization using PI macromonomers.

Experimental

Synthesis and characterization of macromonomers. Vinylbenzyl-terminated PI macromonomers were synthesized by the coupling reaction between poly(isoprenium) lithium end-capped with α-methylstyrene (MS) and CMS in a benzene–tetrahydrofuran (THF) mixture[8]. Details concerning the synthesis and characterization have been given elsewhere[8]. The characteristics of PI macromonomer IM1 used in this work are as follows: the number-average molecular weight $(\bar{M}_n) = 1.02 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.06$, vinylbenzyl group = 0.97 (number/1-polymer).

Synthesis and characterization of star polymers. Star polymers were prepared by crosslinking PI macromonomers with a small amount of DVB (Tokyo Kasei Ind. Ltd; 55% *m*-/*p*-isomer = 2, and 45% mixture of ethylstyrene and diethylbenzene) initiated by 2,2′-azobisisobutyronitrile (AIBN) in n-heptane at 60°C, or by 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70: Wako Pure Chemical Ind. Ltd) in benzene at 40°C.

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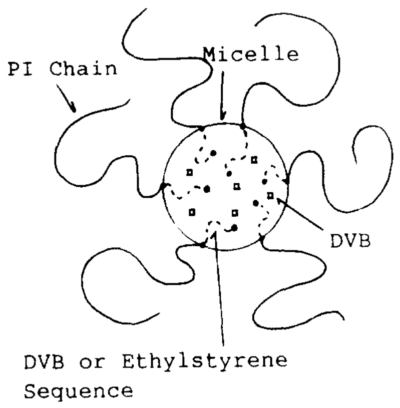

Figure 1 Schematic presentation of organized polymerization in micelles formed by primary copolymer radicals

After 72 h of polymerization, the reaction was stopped by introducing the viscous solution into an excess of methanol.

The weight-average molecular weight ($\bar{M}_w$) of star polymers was determined by gel permeation chromatography (g.p.c.). G.p.c. measurements were carried out with a Tosoh HLC-802A, equipped with a low-angle light-scattering (LS) detector (LS-8, He–Ne laser with detection angle of 5°) and refractive index (RI) detector, which was operated on a TSK GMH column with THF as eluent. The conversions were determined by the ratio of the peak area of PI star to the total peak area of the polymerization product in g.p.c. charts. The concentration of the sample injected was kept small, typically less than 0.1 wt%, to minimize the concentration effect in the detected scattered light intensity. The $\bar{M}_w$ of PI stars can be calculated from the peak area of LS and RI detectors as follows[9]:

$$\bar{M}_w = (k_1/k_2K)(A^{LS}/A^{RI}) \qquad (1)$$

where A^{LS} and A^{RI} are the peak areas of star polymers taken with LS and RI detectors, respectively. The constants k_1, k_2 and K are the proportionality constants defined by

$$h_i^{RI} = k_1 C_i$$

and

$$h_i^{LS} = k_2 R_\theta = k_2 K C_i M_i \qquad (2)$$

where h_i^{RI} and h_i^{LS} are the intensities at the elution volume i detected by RI and LS, respectively. M_i and C_i are the molecular weight and concentration of the solute corresponding to the elution volume i, and R_θ is the Rayleigh ratio. Then $\bar{M}_w/\bar{M}_n$ is calculated using equations (1) and (3):

$$\bar{M}_n = \sum_i h_i^{RI} / \sum_i (h_i^{RI}/M_i) \qquad (3)$$

The product k_1/k_2K, the instrument constant, was determined with PI macromonomer precursor, varying the polymer concentration.

Results and discussion

In the synthesis of IM1 macromonomer, the conversion of monomer to polymer was almost 100% within experimental error. The g.p.c. profile showed that IM1 macromonomer had a single and narrow molecular weight distribution. In a previous article[10], we reported that direct coupling of poly(styrene-*b*-isoprene) diblock living anions with CMS caused the formation of some dimeric block copolymer by electron transfer. In the termination reaction of the IM1, the end of PI living anions was capped with MS units. As a result, the end-group functionality of the IM1 macromonomer was determined to be unity by using g.p.c. calibration.

Tsukahara *et al.*[11] have investigated the radical polymerization behaviour of polystyrene (PS) macromonomers. They have made clear that the $\bar{M}_w$ of branched PS formed was very small at macromonomer concentration [ME] less than $\sim 2 \times 10^{-2}$ mol l^{-1}. Beyond this concentration, the molecular weight of branched PS rapidly increased to a great extent with an increase of [ME]. On the other hand, in the copolymerization of vinylbenzyl-terminated PI macromonomer with DVB, the primary copolymer radicals composed of PI and a few units of DVB or ethylstyrene resembling block copolymer may be produced in the initial reaction stage. Such primary copolymer radicals are able to form micelles in a selective solvent such as n-heptane, because n-heptane works well for PI segments but is a non-solvent for DVB or ethylstyrene sequences. So, we carried out the radical crosslinking of IM1 macromonomer with DVB in n-heptane in the range of [ME] near 0.5×10^{-2} mol l^{-1} (polymer concentration, 5.1 wt%).

Table 1 lists radical crosslinking conditions and results of IM1 macromonomer with DVB in n-heptane (SH series) and in benzene (SB series). It can be seen from this table that no crosslinking (SB-1) occurs in benzene at [ME]= 0.50×10^{-2} mol l^{-1}. Beyond [ME]= 1.75×10^{-2} mol l^{-1}, radical crosslinking (SB-2) occurs in benzene, but both the arm number ($n = 18$) and its molecular weight distribution are relatively low. These crosslinking systems correspond to polymerization in non-ordered isotropic solutions. On the other hand, crosslinking

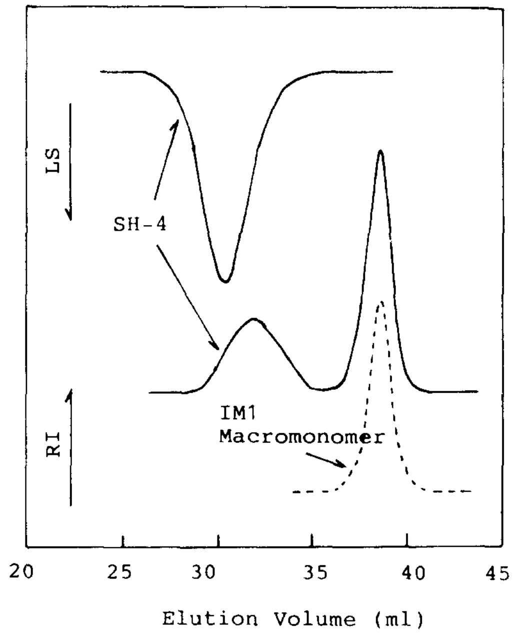

Figure 2 G.p.c. profiles of SH-4 and its PI precursor

Table 1 Radical crosslinking conditions and results of IM1 macromonomer with divinylbenzene

	Feed concentration			Star polymer			
Run no.[a]	$10^2 \times [\mathrm{ME}]^b$ ($\mathrm{mol\ l^{-1}}$)	$10^2 \times [\mathrm{DVB}]$ ($\mathrm{mol\ l^{-1}}$)	[DVB]/[ME] ($\mathrm{mol\ mol^{-1}}$)	Conversion[c] (%)	$10^{-6} \times \bar{M}_w{}^d$	$\bar{M}_w/\bar{M}_n{}^d$	n^e
SH-1	0.50	1.50	3	22.9	0.44	1.20	43
SH-2	0.50	2.50	5	33.9	1.55	1.24	152
SH-3	0.50	3.00	6	33.2	1.53	1.37	150
SH-4	0.50	4.00	8	31.6	4.32	1.28	423
SH-5	0.50	5.00	10	36.1	16.0	1.78	1569
SH-6	1.00	2.50	2.5	38.0	15.9	1.53	1560
SB-1	0.50	3.00	6	0[f]	–	–	–
SB-2	1.75	2.50	1.4	13.9	0.18	1.15	18

[a] SH-1–SH-6: polymerized in n-heptane initiated by AIBN at 60°C; SB-1 and SB-2: polymerized in benzene initiated by V-70 at 40°C
[b] IM1 macromonomer concentration ($\bar{M}_n = 1.02 \times 10^4$)
[c] Evaluated from g.p.c.
[d] Determined by g.p.c. with RI and LS double detectors
[e] Arm number
[f] No polymerization

occurs in all of the SH series (n-heptane solvent) even at $[\mathrm{ME}] = 0.50 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$.

Figure 2 shows typical g.p.c. profiles of SH-4 taken with RI and LS detectors. The g.p.c. distribution has a bimodal pattern. The first peak at lower elution volume in an RI chart corresponds to the PI star. The g.p.c. elution pattern of the second peak is identical with that of the IM1 macromonomer. The $\bar{M}_w$ (4.32×10^6) of this star can be calculated from the peak area of LS and RI detectors. The polydispersity ($\bar{M}_w/\bar{M}_n = 1.28$) is not so narrow. However, the conversion of star polymer (SH-4, 32%) is higher than that of the SB series. All of the experimental SH series maintained the solution state during copolymerization. This phenomenon suggests that free-radical crosslinking of IM1 macromonomer with DVB leads to microgelation in micelles formed by the primary copolymer radicals (ordered anisotropic solution).

We discussed the effects of the arm number n or polydispersity $\bar{M}_w/\bar{M}_n$ on the feed ratio of [DVB]/[ME], under the condition that the feed IM1 concentration is constant ($[\mathrm{ME}] = 0.50 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$). The arm number increases rapidly with an increase of [DVB]/[ME]. On the other hand, $\bar{M}_w/\bar{M}_n$ increases slightly with an increase of [DVB]/[ME]. Moreover, the narrowness of $\bar{M}_w/\bar{M}_n$ is worth noting for a radical polymerization. We may conclude that there was no single-chain crosslinking nor any transfer reactions in such organized polymerization. In the experimental SH-5, the arm number is evaluated to be more than 10^3. This star seems to exhibit the structure of a crosslinked poly(divinylbenzene) core with a highly branched PI shell. In the experimental SH-6 ($[\mathrm{ME}] = 1.00 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$, $[\mathrm{DVB}]/[\mathrm{ME}] = 2.5\ \mathrm{mol\ mol^{-1}}$), the arm number increases greatly (about 36-fold) compared to that obtained in the experimental SH-1. These results indicate that the arm number can be controlled by changing not only the feed ratio of the [DVB]/[ME] but also the feed PI macromonomer concentration [ME].

In conclusion, we could obtain PI stars with arbitrary arm number by means of organized polymerization of PI macromonomers with DVB in n-heptane as solvent.

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