Preparation and Characterization of α -Benzyl- ω -vinylbenzyl Polystyrene Macromonomer

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ABSTRACT: α -Benzyl- ω -vinylbenzyl polystyrene macromonomers of different molecular weights were prepared by the living anionic polymerization of styrene with *n*-BuLi/tetramethylethylenediamine/toluene ligand complex as an initiator followed by termination with vinylbenzyl chloride. Characterization of the end group of the macromonomer by ¹H NMR showed quantitative introduction of the α - and ω -end groups. Anionic polymerization of the macromonomer with *s*-BuLi provided poly(macromonomer)s of a narrow molecular weight distribution. The central backbone as well as the branch chain ends of the obtained poly(macromonomer)s have similar chemical structure to that of the constitutional repeating unit of the polystyrene chain and there is no unlike unit in the polymer structure. Thus, the macromonomer can provide useful model branched polystyrene of the regular structure.

KEY WORDS Polystyrene Macromonomer / Macromer / End Group / Living Anionic Polymerization / Poly(macromonomer) / Branched Polymer / Star Polymer / Comb Branched Polymer / Chain End Effect /

Contrary to the traditional point of view on a monomer unit as the basic unit, in polymeric materials designs, many workers have recently begun to regard the reactive oligomers or polymers as the basic unit, functional unit or reaction unit. Recent increased study on the synthesis and the application of macromonomers as well in the materials design is understandably in line with this thought.¹⁻⁴

On the other hand, polymerization of macromonomers provides regular multibranched polymers with high branching density. Such poly(macromonomer)s have the molecular shape intermediate between star polymers and comb branched polymers depending on

the chain length ratio of the branch and the central backbone which is controlled by the molecular weight of the macromonomer and the polymerization conditions.^{5,6}

In this paper, we report preparation and characterization of α -benzyl- ω -vinylbenzyl polystyrene macromonomers, in which the chemical structure of the chain ends are similar to that of the constitutional repeating unit of the polystyrene chain. Thus, the polymerizations of this macromonomer give multibranched polystyrenes without any unlike structural unit. In addition, the living anionic polymerization of this macromonomer might be possible to produce the poly(macromono-

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mer)s with narrow molecular weight distribution. Therefore, the obtained poly(macromonomer)s might be useful model branched polystyrenes for the study of branched polymers.

EXPERIMENTAL

α -Benzyl- ω -vinylbenzyl polystyrene macromonomers of different molecular weights were synthesized by living anionic polymerization of styrene monomer with *n*-BuLi/tetramethylethylenediamine (TMEDA)/toluene ligand complex as an initiator followed by termination with vinylbenzyl chloride after the con-

sumption of the monomer as shown in Scheme 1. The *n*-BuLi/TMEDA/toluene complex was prepared by the addition of TMEDA into the *n*-BuLi/toluene solution ($[\text{TMEDA}]/[\text{BuLi}] = 1.2$) and the initiation was carried out at given polymerization temperatures.⁷ The polymerizations were terminated with tetrahydrofuran (THF) solution of vinylbenzyl chloride (VBCl) at -78°C ($[\text{VBCl}]/[\text{BuLi}] = 3.0$) and stirred several hours at room temperature. Termination with methanol/HCl was also carried out to produce polystyrene (PSt) homopolymers for comparison as shown in Scheme 1. The products were precipitated into large amount of methanol and dried under vacuum at room

Scheme 1.

Table I. Preparation and characterization of α -benzyl- ω -vinylbenzyl polystyrene macromonomers and polystyrene homopolymers

Run	[Styrene] mmol	[BuLi] mmol	[Styrene] [BuLi]	[TMEDA] ^a mmol	[VBCl] mmol	Polymerization		Yield %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	F (%) ^b	
						Temp	Time				NMR	M.C. ^c
						$^\circ\text{C}$	h					
H-1	9.62	0.641	15	0.767	—	50	1	100	1670	1.15	—	—
H-2	9.62	0.128	75	0.153	—	50	1	100	6710	1.18	—	—
H-3	9.62	0.0641	150	0.0767	—	50	1	100	15500	1.13	—	—
H-4	9.62	0.0641	150	0.0767	—	0	1	80	13400	1.10	—	—
H-5	9.62	0.0641	150	0.0767	—	0	3	100	16800	1.07	—	—
M-1	128	14.3	9	17.1	43.0	50	1	100	1100	1.20	91	96
M-2	298	19.0	15	23.0	57.0	30	2	100	1200	1.19	91	99
M-3	484	10.0	48	12.0	29.0	30	3	100	4850	1.12	92	95
M-4	242	4.9	49	6.3	15.0	30	2	100	4770	1.12	—	97

^a $[\text{TMEDA}]/[\text{BuLi}] = 1.2$, $[\text{BuLi}]$ was determined by titration and then the concentration change during the storage was corrected by the DP value of the polymerization product of styrene directly initiated by *n*-BuLi.

^b F : ω -End group functionality.

^c M.C. = Maximum conversion.

temperature for 48 h, then, freeze dried with benzene. The preparation conditions of the macromonomers and the polystyrenes are shown in Table I.

The end groups of the macromonomer were characterized with ^1H NMR using Varian VXR500 in CDCl_3 at 55°C . The maximum conversions were also estimated in the radical copolymerizations of the macromonomers with methyl methacrylate (MMA) in benzene at 60°C to confirm the introduction of polymerizable end group. The number average molecular weight ($\bar{M}_n$) and the polydispersity index ($\bar{M}_w/\bar{M}_n$) of the macromonomers were determined by gel permeation chromatography (GPC) using Tosoh HLC802UR on THF with two Tosoh-GMH6 columns at 40°C with the calibration curve of polystyrene (PSt) standards. The characteristics of the macromonomers are shown in Table I.

Anionic polymerizations as well as radical polymerizations of the macromonomer were carried out with *s*-BuLi and azobis(isobutyronitrile) (AIBN), respectively. The anionic polymerizations were carried out in benzene at 40°C as well as room temperature under high

vacuum. The macromonomers were dissolved in benzene and the solutions were dried with CaH_2 and filtrated with a G-4 glass filter. The solutions were, then, freeze dried several times with purified benzene under high vacuum. The radical polymerizations were carried out in benzene at 60°C under N_2 atmosphere.

The weight average molecular weight ($\bar{M}_w$) and the $\bar{M}_w/\bar{M}_n$ of obtained poly(macromonomer)s were determined by GPC equipped with a low angle laser light scattering detector (Tosoh-LS8).⁹ The instrument optical constant was determined with linear polystyrene standards of different molecular weights. The average value was used for the calculation of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$. Conversion of the macromonomer in the polymerizations were determined from the peak area ratio of the unreacted macromonomer to the poly(macromonomer) in GPC with a UV detector. For this purpose, the UV absorption coefficients at 254 nm of each macromonomer and polystyrene in THF solution were measured using UV spectrometer (Shimadzu MPS-2000). The GPC peak area of the unreacted macromonomer was corrected by the ratio of the UV

Table II. Anionic and radical polymerizations of polystyrene macromonomer

Run	Macro- monomer ^a [M] mmol l ⁻¹	<i>s</i> -BuLi [I] mmol l ⁻¹	[M]/[I]	Temp. °C	Time h	Conversion ^b %	$\bar{M}_w^c$ × 10 ⁴	$\bar{M}_w/\bar{M}_n^c$	DP ^{c,d}
Living anionic polymerization									
1	19.0	1.7	11.1	40	3	91	9.5	1.09	17.6
2	19.0	1.7	11.1	40	24	92	9.0	1.12	16.6
3	51.5	2.0	25.8	25	3	89	18.3	1.15	33.7
4	20.6	0.8	25.8	25	3	83	13.5	1.15	24.8
5	51.5	1.2	42.9	25	3	38	36.8	1.53	67.7
Radical polymerization									
6	82.5	16.4 ^e	5.9	60	24	87	31.6	1.51	58.1
7	76.9	32.8 ^e	2.3	60	24	48	3.0	1.52	5.5
8	128	32.8 ^e	3.9	60	24	50	7.8	1.12	14.4

^a VB-PSt-Bz4850 ($\bar{M}_w = 5430$, $\bar{M}_n = 4850$, $\bar{M}_w/\bar{M}_n = 1.12$).

^b Determined by GPC with a UV detector.

^c Determined by GPC with a low angle laser light scattering detector.

^d Degree of polymerization.

^e 2,2'-Azobisisobutyronitrile (AIBN).

absorption coefficient of the macromonomer to that of the polystyrene. The details of the polymerization conditions of the macromonomers and the results are shown in Table II.

RESULTS AND DISCUSSION

n-BuLi in toluene in the presence of TMEDA gives benzyl anion by the anion transfer reaction *via* complexation of two nitrogen atoms of TMEDA with Li⁺. The bidentate nitrogen compound like TMEDA interacts with alkyllithium much stronger than the other tertiary amines like triethylamine.¹⁰ The produced benzyl anion initiates the living anionic polymerization of styrene monomer in toluene.⁷ When TMEDA added into *n*-BuLi/toluene solution, the solution showed dark red color which is the indication of the formation of the benzyl anion. The color became stronger gradually and almost saturated in *ca.* 10 min. The initiator was placed in a polymerization vessel about 10 min after the preparation of the initiator.

Termination of the living polymerization with MeOH/HCl produced polystyrene H-1—H-5 in Table I. The molecular weight of H-1—H-5 except H-4 are almost identical to the calculated values from $[M]/[I]$ which might indicate almost 100% initiator efficiency. Yields are 100% except for H-4 where the polymerization was done at 0°C for 1 h. This indicates that the polymerization rate is not fast at 0°C. The GPC peak shapes of H-1—H-5 are very sharp, the peak widths of which seem to be narrower than those of the commercial PSt standard samples except the slight tailing toward the low molecular weight direction.

¹H NMR spectrum of H-1 is shown in Figure 1(a). It is seen that there is no peak at 0.5—0.8 ppm corresponding to the methyl protons of the initiator residue of *n*-BuLi. This again indicates the initiation by the benzyl anion. ¹H NMR spectra of H-2—H-5 showed also no peak for the methyl protons showing

Figure 1. ¹H NMR spectra of a) α -benzyl polystyrene (H-1), b) α -benzyl- ω -vinylbenzyl polystyrene macromonomer (M-2), and c) α -*s*-butyl- ω -methacryloyl polystyrene macromonomer ($\bar{M}_n = 1730$, $F = 0.96$). The spectra were taken using Varian VXR500 in CDCl₃ at 55°C.

that the quantitative introduction of the benzyl group at α -chain end can be achieved.

Figure 1(b) shows the ¹H NMR spectrum of the polystyrene macromonomer M-2. The NMR spectrum of α -*s*-butyl- ω -methacryloyl polystyrene macromonomer obtained by the previous report⁵ is also shown in (c) for comparison. It is seen again in Figure 1 that the methyl proton peaks of the butyl group at α -chain end observed at 0.5—0.8 ppm in (c) are almost not detected in the spectrum in (b).

The small peaks at 5—5.6 ppm in Figures 1(b) and (c) correspond to the vinyl protons at the ω -end group. The end group functionality (*F*) of the α -*s*-butyl- ω -methacryloyl polystyrene macromonomers is normally estimated by the peak intensity ratio of the ω -end group to the α -end group without the $\bar{M}_n$ value obtained by other methods. However, the proton peaks of α -end group of α -benzyl- ω -vinylbenzyl polystyrene macromonomers is

Figure 2. GPC curves of (a) the macromonomer M-3, (b) living anionic polymerization product, and (c) radical polymerization product, respectively. GPC curves were taken on THF at 40°C at flow rate = 1.0 ml min⁻¹. The polymerization conditions are shown in Table II.

not discriminated from the large phenyl proton peaks of styrene repeating units, thus, F in Table I was estimated by comparing the molecular weight determined from the peak intensity ratio of the phenyl protons to those of vinyl protons and that determined by GPC using PSt standard calibration curve. The maximum conversion in the radical copolymerization with MMA also indicates the high end group functionality at ω -chain end as shown in Table I.

Figure 2 shows comparison of the GPC curves of (a) macromonomer M-3, $\bar{M}_n$ of which is 4850, (b) the product of the living anionic polymerization, and (c) of the radical polymerization, respectively. The right large peaks in (b) and (c) correspond to the poly(macromonomer)s, while the small peaks at the left side correspond to the unreacted macromonomer. It is seen that the peak shape of the poly(macromonomer) in (b) is much sharper than that in (c). The degree of polymerization (DP) and $\bar{M}_w/\bar{M}_n$ determined by GPC with a low angle laser light scattering detector for the anionically polymerized macromonomer (run 2) are 17 and 1.12, while those for the radical polymerization product are 58.1 and 1.58, respectively. The polymerization conditions and, DP and $\bar{M}_w/\bar{M}_n$ of poly(macromonomer)s

are shown in Table II. As seen in Table II, it was rather difficult to obtain the poly(macromonomer)s having large DP so far, probably because the difficulty of the purification of the macromonomers. Thus, further refinement is necessary to produce the large molecular weight poly(macromonomer)s by the living anionic polymerization. Takaki *et al.* pointed out that 1,1,4,4-tetraphenyl-2-butene-1,4-diyl dilithium is useful for the purification of PSt macromonomers having the same polymerizable end group.¹¹

When the purified 2-vinylpyridine monomer was added to the reaction mixture after the polymerizations of the macromonomer M-3 and M-4 with *s*-BuLi, the weak yellow color changed to red one. Figure 3 shows the GPC curves of the poly(M-4) precursor and the product after the addition of 2-vinylpyridine in which the new large peak corresponding to poly(M-4)-*block*-poly(2-vinylpyridine) appears at higher molecular weight side of the poly(macromonomer) precursor. These might also indicate the living anionic character of the polymerization.

It should be noted finally about the worth of the variation of the end groups of macromonomers. The polymerization products of macromonomers, *i.e.*, poly(macromonomer)s,

Figure 3. GPC curve of the living anionic polymerization precursor of M4 and that of the product after the addition of 2-vinylpyridine. GPC curves were taken on THF at 40°C at flow rate = 1.0 ml min⁻¹.

are regarded as the regular multibranched polymers with very high branching density. Since the branch length is controlled by the molecular weight of the macromonomer and the branch number can be controlled by the feed macromonomer concentration under the knowledge of the diffusion control effect,⁹ the branch length and number are regular. The branching period is also regular because the every constitutional repeating unit in the central backbone chain has one branch chain at all times. Furthermore, the chemical structure of the branch chain ends as well as the branching points, *i.e.*, the central backbone, can be varied by changing the α - and ω -end group of the macromonomer. This make it possible to investigate the effects of the chain ends as well as branching points on solution and bulk properties of branched polymers.⁵

For examples, the poly(macromonomer)s of α -benzyl- ω -vinylbenzyl polystyrene macromono-

mer in this study possess a benzyl group at every branch chain end, while those of α -*s*-butyl- ω -vinylbenzyl polystyrene macromonomer prepared according to Asami and Takaki^{8,11} possess a *s*-butyl groups at every branch chain end but the same chemical structure for the central backbone. Therefore, one can investigate the chain end effect on the glass transition temperature and the tensile strength as the bulk properties by comparing the results for these poly(macromonomer)s.^{5,12}

Furthermore, the replacement of *s*-butyl group with benzyl group in polystyrene macromonomers by the method in this work makes it possible to analyze the pyrolysis fragment from *s*-butyl end group of α -*s*-butyl- ω -methacryloyl polystyrene macromonomers in the end group analysis by the pyrolysis gas chromatography.¹³

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