Synthesis of Isopropenylbenzyl-Terminated Macromonomers and Preparation of Polymer Brushes by Anionic Homopolymerization

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ABSTRACT: Isopropenylbenzyl-terminated polystyrene (PS) macromonomers were synthesized by anionic addition in a two-stage process using styrene and 1,4-diisopropenyl-benzene (DIPB) in benzene. The reaction products of polystyryl anions with DIPB provided PS macromonomer possessing less than two isopropenylbenzyl groups at the propagating end under the condition of being in hydrocarbon solvent at 25°C (ceiling temperature) because of the anionic equilibrium nature. Subsequently, anionic homopolymerization of such macromonomers was carried out in tetrahydrofuran (THF) at −78°C using anionic initiators to prepare the polymer brushes. The conversion of polymer brushes was very low (ca. 5%). Moreover, the degree of polymerization (DP) was less than 50. The low concentration of propagating chain ends seemed to affect the formation of polymer brushes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1790–1793, 2003

Key words: isopropenylbenzyl-terminated macromonomer; polymer brush

INTRODUCTION

It is well known that comb copolymers with densely grafted side chains in a good solvent can adopt a wormlike cylindrical brush conformation, in which the side chains are stretched in the direction normal to the backbone as a result of the excluded volume interaction. Polymerization of macromonomers provides regular multibranched polymers with dense branching. Because both degree of polymerization and length of the branches are varied, polymacromonomers, often called "polymer brushes," are interesting models for the study of branched polymers.[1–9] We previously reported on the synthesis and dilute-solution properties of diblock copolymer brushes composed of diblock branches.[10,11] These types of diblock copolymer brushes have the advantage of controlling the stiffness of the main chain parts by crosslinking internal block domains. Moreover, we synthesized alternating copolymer brushes by free-radical alternating copolymerization of binary macromonomers.[12–14] These alternating copolymer brushes formed prototype copolymer brushes because incompatible polystyrene (PS) and poly(ethylene oxide) (PEO) side chains align alternately and highly densely on the main chain.[13,14]

More recently, Matyjaszewski et al.[15] also synthesized diblock copolymer brushes with a relatively narrow molecular weight distribution (M_w/M_n = 1.2–1.4) by the graft-from approach using atom transfer radical polymerization (ATRP). In general, these polymer brushes exhibited broad molecular weight distribution because the free-radical polymerization of macromonomers. It can be expected that anionic polymerization of isopropenylbenzyl-terminated macromonomers will provide polymer brushes with narrow polydispersity because such anionic polymerization will proceed with the thermal equilibrium process.

Rempp et al.[16] reported the synthesis of isopropenylbenzyl-terminated PEO macromonomers, in which the double bond at the chain end was introduced either on initiation or on deactivation. They also reported the synthesis of polyvinylpyridine (PVP) macromonomer by the coupling of living PVP anions with *p*-bromomethyl α methylstyrene[17] (deactivation method). However, thus far anionic polymerization of such isopropenylbenzyl-terminated macromonomers has not been studied. On the other hand, we prepared diblock macromonomers possessing central vinylbenzyl groups by anionic addition in a three-stage process using styrene, 1,4-divinylbenzene (DVB), and *t*-butyl methacrylate monomers.[18] On the addition of DVB monomers to polystyryl anions in tetrahydrofuran (THF) at −78°C, aggregates of polystyryl anions were formed despite variation in the reaction time and feed mole ratio of the living ends to DVB. However, on reaction in toluene, linear polystyryl anions possess-

TABLE I
Reaction Conditions and Results for the Reaction M11–M13 and M2 of Polystyryl Anion with DIPB[a]

| Expt code | Polystyryl anion | | | DIPB/LE (molecule/molecule) | Reaction time (min) | Double bonds[e] (number/molecule) |
	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]	10^3 LE[d] (mol/L)			
M11					10	1.2
M12	5300	1.04	3.5	5.0	20	1.2
M13					120	2.0
M2	3400	1.13	5.6	5.0	10	1.1

[a] Polystyryl anion was reacted with DIPB in benzene at 25°C.
[b] Determined by VPO in benzene.
[c] Determined by GPC.
[d] [LE], concentration of polystyryl anion.
[e] Determined by ^{1}H-NMR in CDCl$_3$.

ing terminal vinylbenzyl groups were formed. Anionic propagation of t-butyl methacrylate monomers with linear polystyryl anions end-capped with DVB led to the formation of PS-*block*-poly(t-butyl methacrylate) diblock macromonomers possessing central vinylbenzyl groups.

The aim of the current study was to establish the method of synthesis of isopropenylbenzyl-terminated macromonomers by anionic addition in a two-stage process using styrene and 1,4-diisopropenylbenzene (DIPB). Subsequently, we performed equilibrium anionic polymerization of such macromonomers to prepare polymer brushes.

EXPERIMENTAL

Macromonomer synthesis and characterization

Styrene was first dried over a mixture of calcium hydride–lithium aluminum hydride and then purified with triphenylmethyl sodium *in vacuo*. Benzene was first dried over sodium metal and then purified with n-butyl lithium (n-BuLi) *in vacuo*. The anionic polymerization of isopropenylbenzyl-terminated polystyrene (PS) macromonomers was carried out by the two-stage addition of styrene and DIPB (both monomers were diluted with benzene) using n-BuLi as the initiator (polymerization of styrene: 4°C; reaction of polystyryl anion with DIPB: 25°C). After the polymerization of DIPB at the prescribed time, the polymerization product was purified twice by reprecipitation from benzene solution with methanol.

The number-average molecular weight (M_n) of the PS macromonomers was determined by vapor pressure osmometry on a Corona NA117 vapor pressure osmometer in benzene. The polydispersity (M_w/M_n) was determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph HLC-8020) using PS standard samples with tetrahydrofuran (THF) as the eluent at 38°C; two TSK gel columns, GMH$_{XL}$ and G2000H$_{XL}$ in series; and with a flow rate of 10.0 mL/min. The content of the isopropenylbenzyl

groups was determined by ^{1}H-NMR (500 MHz, JEOL GSX-500 NMR spectrometer) in CDCl$_3$.

Synthesis and characterization of polymer brushes

Anionic equilibrium polymerization of isopropenylbenzyl-terminated PS macromonomers was carried out in THF at −78°C in a sealed glass ampoule under high vacuum, using n-BuLi or sodium α methylstyrene (Na-MS) tetramers as the initiator. After polymerization the solution was poured into an excess of methanol.

A combination of GPC with a light-scattering (LS) detector is very useful for measuring the weight-average molecular weight (M_w) and molecular weight distribution of branched polymers such as polymer brushes because it is not necessary to have any isolation procedures to remove unreacted PS macromonomers. GPC measurements were also carried out, using an HLC-8020 equipped with a low-angle laser-light-scattering (LALLS) detector, an LS-8 (He-Ne laser with a detection angle of 5°), and a refractive index (RI). The conversion of polymer brushes was determined by the change in the ratio of the peak area of the polymer brush produced to the total peak area of the polymerization product in GPC charts. The details concerning the calculation method for M_w have been provided elsewhere.[19]

RESULTS AND DISCUSSION

In anionic polymerization the reactivity of the double bond (1-position) in DVB is 10-fold greater than the pendant double bond (4-position).[20] As noted above, the primary molecular structure of the reaction product of polystyryl anions with DVB in hydrocarbon solvent is linear PS macromonomers possessing terminal pendant double bonds.[18] Rempp et al.[21] studied anionic polymerization of DIPB in THF at −30°C. They obtained linear polydiisopropenylbenzene (PDIPB) in the early stage of the reaction. Conjugation should
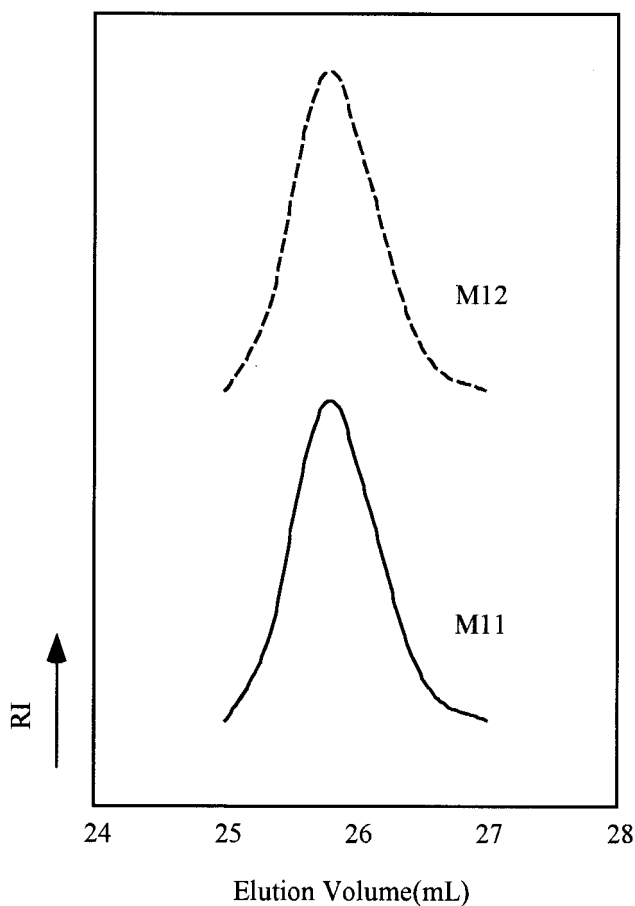
Figure 1   GPC profiles of macromonomers M11 and M13.

Figure 2 ^{1}H-NMR spectrum of macromonomer M11.

NMR spectrum of M11 is shown in Figure 2. The aromatic protons, methylene protons of the double bond, and methyl protons of the isopropenyl group are assignable to the signals at δ 6.3–7.6 (a and b), 5.0 and 5.3 (c and d), and 2.1 (g) ppm, respectively. The functionality was calculated from the integration ratio

also strongly affect the reactivities of the double bonds in DIPB as well as the polymerization of DVB. Therefore, it can be expected from the above results that the reaction product of polystyryl anions with DIPB would afford to PS macromonomers possessing fewer than two isopropenylbenzyl groups at the propagating end under the condition of being in hydrocarbon solvent at near–room temperature (ceiling temperature) because of the nature of anionic equilibrium.

At first, polystyryl anions were synthesized by anionic polymerization of styrene in benzene at 4°C initiated by *n*-BuLi. The preliminary experiments for the reactions of such polystyryl aniosn with DIPB were carried out in benzene at 25°C varying the reaction time. Table I lists the reaction conditions and results for the reactions M11–M13 of polystyryl anion with DIPB. The concentration of living anion ends (LE) was 3.5×10^{-3} mol/L. The feed ratio of DIPB–LE was 5.0 molecule/molecule. Figure 1 shows typical GPC profiles of the reaction products of M11 and M13. Both GPC curves are unimodal. The GPC elution patterns agreed well with that of the PS precursor. The molecular weight distribution of these reaction products is very narrow ($M_w/M_n = 1.04$). The GPC profile of M12 also showed the same elution pattern. A typical ^{1}H-
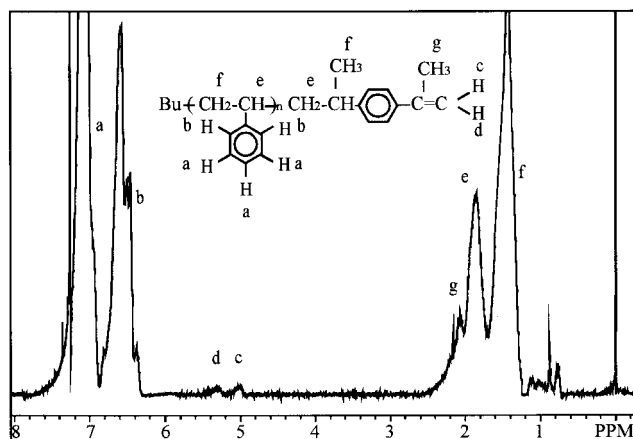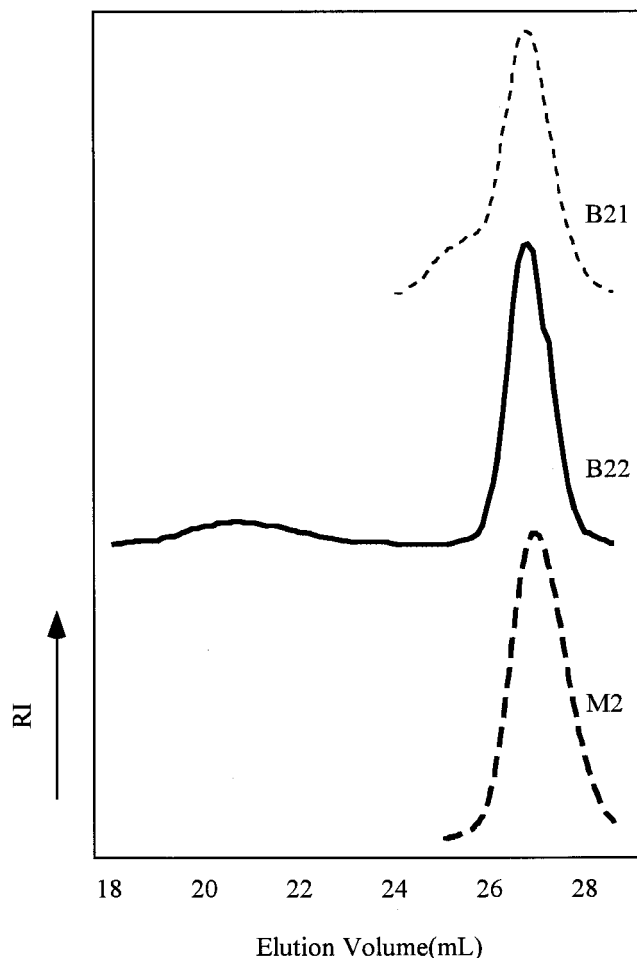

Figure 3   GPC profiles of homopolymerization products B21 and B22.

TABLE II
Reaction Conditions and Results for Anionic Polymerization of PS Macromonomer M2[a]

Expt no.	Macromonomer $10^3 M_0$ (mol/L)	Initiator		Time (day)	Polymer brushes			
		Code 10^5	I_0 (mol/L)		Conv[b] (%)	$10^{-4}\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[b]	DP
B21	6.6	n-BuLi	8.1	2	4.8	1.4	1.10	4
B22	6.9	Na-MS	1.4	6	5.0	17.1	1.28	50

[a] Polymerized in THF at −78°C.
[b] Determined by GPC (RI curve).
[c] Determined by GPC (LS and RI curves).

of the aromatic protons to the methylene protons of double bonds. These values are also listed in Table I. It was found that the functionality closed gradually from unity to 2 with an increment of reaction time. DIPB could not propagate more than two monomer units because the polymerization temperature employed was near the ceiling temperature. Moreover, DIPB monomers were not consumed by addition reactions within this reaction time (2 h). As a result, these reaction products have the primary molecular structure of a linear PS macromonomer, possessing terminal pendant double bonds.

Subsequently, we performed preparation of the polymer brushes using macromonomer M2 (M_n = 3400 and double bonds = 1.1 number/molecule; see Table I). The GPC profile of macromonomer M2 is shown in Figure 3. Anionic equilibrium polymerization was carried out in THF at −78°C initiated by n-BuLi (monofunctional initiator) and Na-MS (bifunctional initiator). Table II lists the polymerization conditions and results for homopolymerizations B21 and B22. Both GPC distributions for B21 and B22 are bimodal, as shown in Figure 3. The polymerization product was a mixture of the polymer brush and its precursor. The polymer brush B22-B was removed from the corresponding precursor by precipitation fractionation (benzene–methanol system). It was found from ^{1}H-NMR that such a precursor was unreacted PS macromonomer M2. The M_w (17 × 10⁴; DP = 50) of B22-B can be calculated from the peak areas of the LS and RI curves. The conversion of B22-B was 5.0% from RI curve of B22. On the other hand, the DP of polymer brush B21 was calculated to be 4. The molecular weight distribution of the polymer brushes obtained was not as narrow (M_w/M_n = 1.1–1.3). Anionic polymerization was very slow despite the presence of sufficient unreacted macromonomers. It is speculated that the reason for this phenomenon is that the concentration of propagating anion ends is extremely low. Moreover, these active sites on the backbone are hindered to an appreciable extent by the branched chains, and subsequent addition to macromonomer occurs less readily or not at all.

Tsukahara et al.[22] investigated the radical polymerization behavior of PS macromonomers. They made

clear that the M_w of polymer brushes formed was very small at macromonomer concentrations [M] less than 2×10^{-2} mol/L. Beyond this concentration, the M_w of polymer brushes rapidly increased to a great extent with an increase of [M]. In the radical polymerization system polymerization temperature is in the range of 60°C–80°C. So the segment migration also may have an effect on the formation of polymer brushes with a long aspect ratio. Radical polymerization is superior to the anionic technique for the preparation of polymer brushes.

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