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Novel synthesis of highly branched comb-like polymers by coupling reaction of polystyryllithium with 1,1-diphenylethenyl-functionalized polystyrene

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Abstract

Well-defined highly branched comb-like polystyrenes (PS) having one branch in each repeating unit have been successfully synthesized by the coupling reaction of living PS anions with 1,1-diphenylethenyl (DPE) groups along PS backbone prepared via atom transfer radical polymerization. When excess polystyryllithium (PSLi) was used, the quantitative grafting efficiency was achieved. The resulting polymers were characterized by NMR, IR, GPC, and SLS in detail.

Keywords: Atom transfer radical polymerization; Living anionic polymerization; Highly branched comb-like polymer

1. Introduction

Comb-like polymers have attracted much attention because of their exhibiting physical properties distinct from the linear homologues in solution and melt states [1–3]. In general, these comb-like polymers have been synthesized via anionic polymerization techniques. Three methodologies have been developed including 'grafting-onto', 'grafting-from', and 'macromonomer' [4,5]. However, synthesis of highly branched comb-like polymers, having one or more branches in each repeating unit, seems difficult by these three methods. The polymers obtained by 'grafting-from' method are usually less branched due to uncontrolled initiation efficiency, and the molecular weight distributions are usually broad. When 'macromonomer' method is used, the conversion of macromonomers and the molecular weight of poly(macromonomer)s are often low [6,7]. There are problems of competitive side reactions and grafting efficiency for 'grafting-onto' method [8–10].

To overcome these difficulties, the grafting-onto methodology using the special coupling reaction under appropriate conditions has been recently explored. Deffieux and Schappacher successfully prepared well-defined comb-like polymers by coupling PSLi with the poly(2-chloroethyl vinyl ether)s obtained by living cationic polymerization[11]. This is the first highly branched polymers with one branch per repeating unit synthesized by grafting-onto method. Soon after, Hirao [12–14] and Hadjichristidis [15] successfully synthesized the similar well-defined high-density branched polymers by coupling living polymer anions with the poly(chloromethyl styrene)s. More recently, the coupling reaction of PSLi with epoxy-functionalized PS has been used to prepare highly branched polymers [16]. Unfortunately, only a few reliable synthetic examples have so far been reported.

We herein report on the possible synthesis of such highly branched comb-like polymers by another type of linking reaction of PSLi with 1,1-diphenylethenyl (DPE) groups along PS backbone prepared via atom transfer radical polymerization, since it is well-known that DPE reacts with living polymer anion quantitatively and is widely used as the end-capping agent [17].

2. Experimental part

2.1. Materials

Styrene (St) was purified by distillation over calcium hydride. Tetrahydrofuran (THF) was refluxed with Na–K alloy and benzophenone until a characteristic violet colour was evident. Sodium hydride (NaH, >60% in solid paraffin) was washed by pentane before use. Methyltriphenylphosphonium

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iodide was prepared using triphenylphosphine and methyl iodide in dry benzene.

2.2. Synthesis of 4-vinylbenzyloxy benzophenone (Sc)

To a 250 ml three-necked flask, 11.5 g (58 mmol) 4-hydroxybenzophenone, 8.9 g (58 mmol) 4-vinylbenzyl chloride, 4.9 g (58 mmol) sodium bicarbonate, and 50 ml of *N*,*N*-dimethylformamide (DMF) was added. The reaction was carried out at 105 °C for 3 h with stirring under nitrogen flow. Upon cooling, the red-brown reaction mixture was poured into 250 ml of water, followed by extraction with 250 ml dichloromethane. After recrystallization from petroleum ether, white crystal was obtained in 70% yield. ^{1}H NMR ($CDCl_3$): $\delta = 5.13$ (s, 2H, –CH_2O–), 5.25, 5.28 (d, 1H, CH_2=CH–), 5.74, 5.79 (d, 1H, CH_2=CH–), 6.69~6.71 (q, 1H, CH_2=C*H*–). IR (KBr): 1640 cm^{-1} (C=O), 1604 cm^{-1}, 1503 cm^{-1} (aryl), 1250 cm^{-1}, 1173 cm^{-1} (–CH_2O–), 1604 cm^{-1}, 1015 cm^{-1} (vinyl).

2.3. Atom transfer radical polymerization (ATRP)

To an ampole charged with nitrogen, Sc, $PhCH_2Cl$, CuCl, 2,2′-bipyridine, and diphenyl ether were added. After three freeze–vacuum–thaw cycles, the ample was sealed under vacuum. The reaction was performed at 130 °C for 24 h and terminated by liquid nitrogen. The polymer was isolated by precipitation into methanol and was dissolved/precipitated with dichloromethane/methanol three times. The final product (PSc) was dried under vacuum at 50 °C for 12 h.

2.4. Wittig reaction

5.89 g (15 mmol) Methyltriphenylphosphonium iodide and 0.35 g (15 mmol) sodium hydride were suspended in 150 ml anhydrous THF, and the mixture was refluxed for 12 h under argon. Thereafter, the solution of 2.50 g (8 mmol) PSc in 30 ml THF was added dropwise at 0 °C. After refluxing for 12 h, the reaction was terminated by acetone. After filtration, the liquid was concentrated, and precipitated into methanol. The polymer (PSe) was dissolved/precipitated with dichloromethane/methanol three times and dried under vacuum at 50 °C for 12 h.

2.5. Coupling reaction

The anionic polymerization of St was performed at −78 °C using *n*-BuLi as an initiator and THF as a solvent. In half an hour, an aliquot of polymer solution was taken out for gel permeation chromatography (GPC) measurement. Subsequently the living PS was introduced quickly into the solution of PSe. The coupling reaction was carried out for 1 h and terminated by addition of degassed methanol. The polymer was isolated by precipitation into methanol.

2.6. Measurements

^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal reference. IR spectra were recorded on a 20SX spectrometer using KBr pellets. GPC measurements were carried out in THF (1 ml/min) at 35 °C using a Waters 515 liquid chromatography equipped with three styragel columns and a refractive index detector. Monodisperse PS samples were used as standards for calibration. Static light scattering (SLS) measurements were performed with an ALV5000 instrument using 633 nm in toluene at 25 °C. For light scattering detection d*n*/d*c* of the graft copolymers was determined in toluene with a laser source operating at 633 nm at 25 °C.

3. Results and discussion

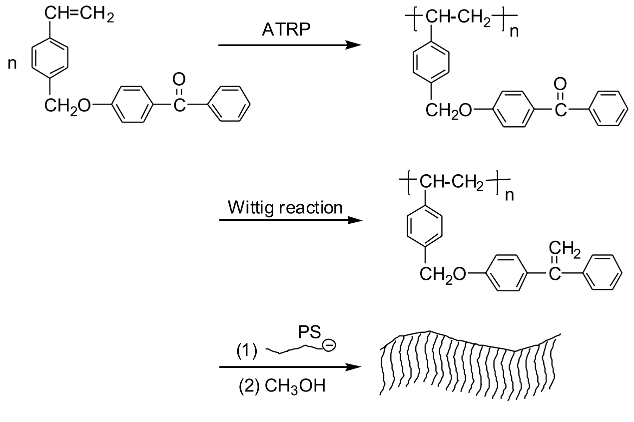
Scheme 1 illustrates our strategy for the preparation of the highly branched comb-like PS. Atom transfer radical polymerization (ATRP) of Sc leads to PSc with benzophenone pendant groups. This precursor is then converted to the corresponding PSe bearing 1,1-diphenylethenyl pendant groups via Wittig reaction and used as a polymer backbone. Finally the linking reaction of living PSLi with C=C group of PSe is carried out to form the highly branched comb-like PS.

3.1. ATRP of Sc

Owing to the existence of the nucleophilic addition reaction of *n*-BuLi onto carbonyl group of Sc monomer, the anionic polymerization of Sc cannot proceed to obtain the precisely controlled polymers. This problem can be overcome by means of ATRP method. The carbonyl groups may remain unchanged during ATRP process.

The ATRP of Sc was carried out in diphenyl ether at 130 °C using $PhCH_2Cl$ as an initiator and CuCl/2,2′-bipyridine complex as a catalyst. As expected for a living-type polymerization, the number average molecular weight of PSc determined by GPC ($M_{n,GPC} = 6970$), is in good agreement with the theoretical one ($M_{n,th} = 6970$), and the molecular weight distribution is also narrow ($M_w/M_n = 1.20$).

Fig. 1(a) shows the IR spectrum of PSc. The strong peak at 1650 cm^{-1} attributes to carbonyl groups, indicating that carbonyl groups leave unattacked. The peaks at 1600 and 1250 cm^{-1} attribute to benzene ring and –CH_2–O–, respectively.



Scheme 1. Synthetic route to highly branched comb-like polystyrene.

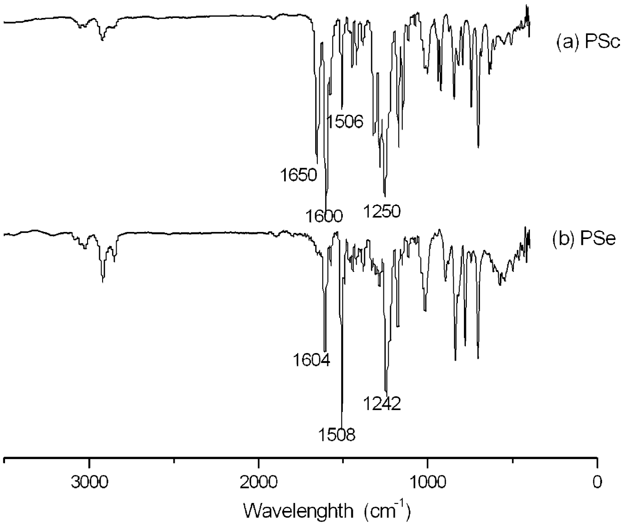


Fig. 1. IR spectrum of PSc before (a) and after (b) Wittig reaction.

3.2. Synthesis of well-defined PSe

Because Wittig reaction is a very effective reaction for carbonyl alkenation, we apply it to convert benzophenone pendant groups of PSc into DPE groups and use DPE-functionalized PS as a backbone polymer. The carbonyl alkenation reaction was performed in THF using ylid generated from methyltriphenylphosphonium iodide and NaH.

Fig. 2 shows the ^{1}H NMR spectrum of PSe. The peak at 5.29 ppm ascribes to the vinyl protons of DPE groups. Moreover, we found the integrated area of this peak is equal to that of the peak at 4.91 ppm corresponding to methylene protons, indicating the conversion of C=O to C=C is nearly quantitative. This is also supported by the complete disappearance of the peak at 1650 cm^{-1} corresponding to C=O in the IR spectrum of PSe (Fig. 1(b)). The GPC profiles of the polymers before and after Wittig reaction were very similar in shape and retention time, suggesting the side reaction such as chain degradation did not occur during the reaction.

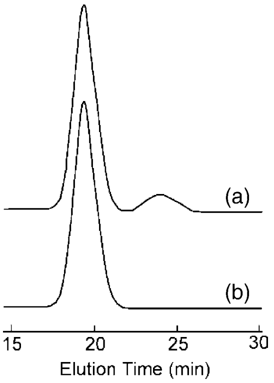


Fig. 3. GPC curves of comb-like polymer before (a) and after (b) fractionation.

3.3. Synthesis of highly branched comb-like polymer

PSLi was prepared in THF at −78 °C using *n*-BuLi as an initiator. The coupling reaction was achieved by adding quickly the PSLi solution into a known amount of PSe, previously vacuum dried and dissolved in dry THF. At the beginning of the PSLi addition, a rapid colour change from orange red to deep red was observed, indicting the formation of diphenylmethyl anion took place very fast. This reaction was complete within one hour based on sample analysis.

To achieve high grafting efficiency, a slight excess of PSLi toward DPE function of PSe ($[\mathrm{PSLi}]_0/[\mathrm{DPE}]_0 = 1.2$) was used. Fig. 3(a) shows the GPC profile of crude comb-like polymer. The first peak at higher molecular weight is ascribed to the comb-like polymers. As it may be seen, the peak is sharp monodal and very narrow ($M_w/M_n = 1.14$), suggesting a homogeneous and clean grafting. The second peak at lower molecular weight is ascribed to the polystyrene branch since its M_n and M_w/M_n are identical to those of the initial living PS. This formation is likely due to the PSLi excess and some deactivation of polystyryl carbanions by the impurities remaining in the PSe solution. The homopolymer PS was isolated by fractional precipitation using cyclohexane/hexane [15] to obtain pure highly branched comb-like PS (Fig. 3(b)).

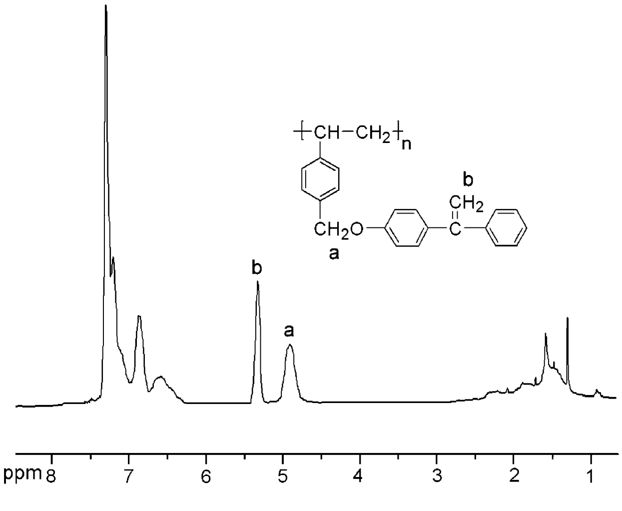


Fig. 2. ^{1}H NMR spectrum of PSe.

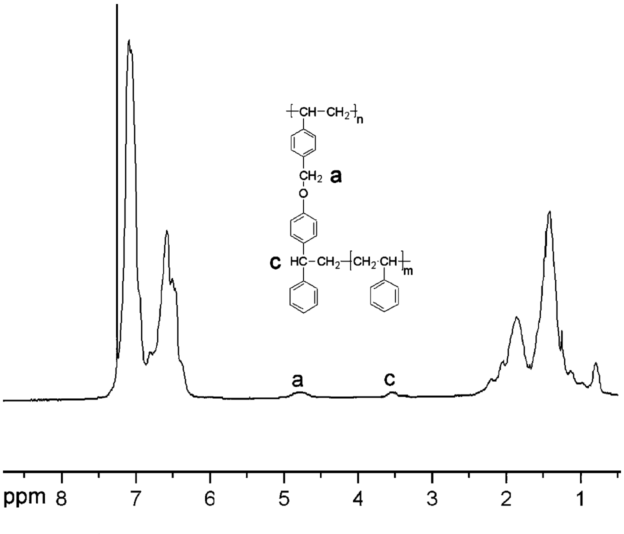


Fig. 4. ^{1}H NMR spectrum of fractionated comb-like polystyrene.

Table 1
Characteristics of highly branched comb-like polymer by coupling reaction of PSLi with PSe in THF at −78 °C

DPE groups (mmol)[a]	$[PSLi]_0/[DPE]_0$	Living PS M_w[b]	Comb-like polymer				
			$M_w \times 10^3$			M_w/M_n[b]	GE(%)[c]
			Theo.[d]	SLS	GPC		
1.92	0.7	7400	124.0	113.3	39.9	1.14	65.5
1.60	1.0	4500	108.8	101.0	29.3	1.18	92.8
0.96	1.2	4200	102.1	102.6	42.0	1.14	100

[a] Molecular weight of PSe: $M_n = 6970$, $M_w/M_n = 1.20$.
[b] Determined by GPC.
[c] Grafting efficiency (GE) based on the molecular weight determined by SLS.
[d] Calculated assuming all PSLi was coupled with DPE groups of backbone.

Fig. 4 shows the ^{1}H NMR spectrum of above-mentioned fractionated branched PS. The resonance at 5.29 ppm corresponding to vinyl protons disappeared completely. Instead, a new signal was observed at 3.52 ppm for the terminal methine proton in the coupling product; integration of the area of this signal relative to the area of the resonances at 4.91 ppm corresponding to the methylene protons adjacent to the ether linkage gave a value of 1:2.04 (theoretical value 1:2), suggesting the nearly full addition of DPE groups by the polystyryl anions.

In order to study the effect of feed molar ratios on grafting efficiency (GE), different molar ratios of $[PSLi]_0/[DPE]_0$ were used. Table 1 lists the experimental results with adding a less, equal, and excess of PSLi toward DPE function. It can be found that the GE increases from 65.5–100% with the rising of $[PSLi]_0/[DPE]_0$ ratio. This also implies that the coupling reaction had proceeded quantitatively until all the DPE groups were consumed by PSLi.

It should be noted that the apparent molecular weight of the highly branched PS determined by GPC was not reliable due to its branching structure. The absolute molecular weight of the graft copolymer was therefore determined by SLS measurement, after measuring the specific dn/dc values of different graft polymers. These values were very close to the corresponding theoretical ones calculated assuming all the living chains were coupled with DPE groups. This supports that the grafting is nearly complete. Therefore, this proposed method affords the synthesis of highly branched PS with precisely controlled molecular weight and one branch in each repeating unit.

4. Conclusion

In conclusion, a new route for the preparation of highly branched comb-like polymers by the coupling reaction of polystyryllithium with DPE pendant groups was investigated. We have successfully demonstrated that this method proposed here is very effective for the synthesis of well-defined highly branched polymers having one branch in each repeating unit.

Since the resulting diphenylmethyl carbanion is able to further initiate other monomers such as methyl methacrylate, vinyl pyridine, new centipede-like copolymers are presently synthesized. Details on these researches will be reported in the near future.

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References

[1] Nemoto N, Nagai M, Koike A, Okada S. Macromolecules 1995;28:3854–9.
[2] Terao K, Nakamura Y, Norisue T. Macromolecules 1999;32:711–6.
[3] Lohse DJ, Datta S, Kresge EN. Macromolecules 1991;24:561–6.
[4] Rempp P, Franta E, Herz J-E. Adv Polym Sci 1988;86:145–73.
[5] Pitsikalis M, Pispas S, Mays JW, Hadjichristidis N. Adv Polym Sci 1998;135:1–137.
[6] Heroguez V, Gnanou Y, Fontanille M. Macromolecules 1997;30:4791–8.
[7] Mecerreyes D, Dubois P, Jérôme R. Macromol Chem Phys 1999;200:156–65.
[8] Altares T, Wyman Jr DP, Allen VR. J Polym Sci, Part A 1965;3:4131–51.
[9] Takaki M, Asami R, Ichikawa M. Macromolecules 1977;10:850–5.
[10] Gauthier M, Möller M. Macromolecules 1991;24:4548–53.
[11] Schappacher M, Deffieux A. Macromol Chem Phys 1997;198:3953–61.
[12] Ryu SW, Hirao A. Macromolecules 2000;33:4765–71.
[13] Ryu SW, Hirao A. Macromol Chem Phys 2001;202:1727–36.
[14] Hirao A, Kawano H, Ryu SW. Polym Adv Technol 2002;13:275–84.
[15] Tsukatos T, Pispas S, Hadjichristidis N. Macromolecules 2000;33:9504–11.
[16] Hirao A, Shimohara N, Ryu SW. Macromol Symp 2004;217:17–28.
[17] Quirk RP, Yoo T, Lee Y. Adv Polym Sci 2000;153:67–162.