

Synthesis of Dendritic-Linear Block Copolymers by Atom Transfer Radical Polymerization

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Abstract: The dendritic polyarylether 2-bromoisobutyrate as the macromolecular initiator for the controlled free radical polymerization of styrene was investigated. The polymerization was carried out with CuBr/2,2'-bipyridine catalyst at 110°C. It is found that the hybrid dendritic-linear block copolymers possess well-defined molecular weights and low polydispersities.

Keywords: Atom transfer radical polymerization, dendrimer, polystyrene, block copolymer.

Polymers and copolymers with complex, yet well-defined architectures are drawing significant attentions in the search for materials with excellent properties. Of these macromolecular structures, dendritic-linear block copolymers consisting of covalently bound linear and dendritic segments have shown interesting solution, solid-state, and interfacial properties. As a novel polymerization approach, atom transfer radical polymerization (ATRP) has been attracting increasing interest recently, since it furnishes control over the resulting polymers. Up to now, ATRP has been successfully applied to the synthesis of well-defined macromolecular architectures such as comb, gradient, star, and dendritic macromolecules¹.

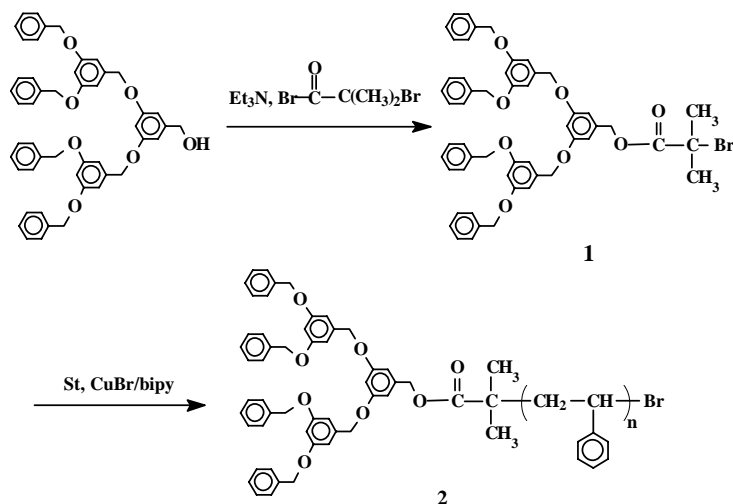
Experimental

The second-generation polyarylether dendron bearing a hydroxyl group at the focal point was prepared and purified according to the literature². The dendritic 2-bromoiso-butyrate **1** prepared by reaction of the dendrimer with 2-bromoisobutyryl bromide and triethylamine was employed as an initiator for the controlled/"living" ATRP of styrene. The bulk polymerization was conducted at 110°C in a sealed glass tube. A representative feed was [St]:[initiator]:[CuBr]:[bipy]=100:1:1:2. The molecular weight and molecular weight distribution were determined by GPC using polystyrene standards.

Results and discussion

The reaction scheme for the synthesis of well-defined dendrimer-polystyrene block

Scheme 1



copolymers is shown in **Scheme 1**. In the course of polymerization, the linear relationship between conversion and polymerization time is preserved until a higher conversion of 80-90% is reached, which suggests that the polymerization kinetics is of first-order nature. Meanwhile, it is found that the plot of molecular weight against polymerization conversion is almost a linear relationship and in excellent agreement with the calculated value. As shown in **Table 1**, even at high conversions, the resulting copolymers still possess predetermined molecular weights and low polydispersities ($M_w/M_n < 1.2$). This result shows that the polymerization process is controllable and of a living polymerization nature.

Table 1 ATRP of styrene initiated by Dendron/CuBr/bipy at 110°C

Run	time (hr)	conversion (%)	M_n (calc.)	M_n (found)	M_w/M_n
1	4	18.4	2500	3600	1.20
2	8	33.2	4400	5100	1.16
3	16	64.9	7700	8400	1.08
4	25	95.0	10800	11200	1.17

References and Notes

1. M. R. Leduc, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Sci.*, **1996**, *118*, 11111.
2. C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Sci.*, **1990**, *112*, 7638.
3. Compound **1**: a colorless glass; $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 7.29-7.42 (m, 20H, PhH), 6.56-6.67 (m, 9H, ArH), 5.12 (s, 2H, ArCH₂), 5.01 (s, 8H, PhCH₂), 4.96 (s, 4H, ArCH₂), 1.93 (s, 6H, CH₃); IR (KBr disc, cm^{-1}): 3033, 2931, 2874, 1736, 1597, 1498, 1453, 1375, 1296, 1160, 1057, 738, 697; Anal. Calcd for $\text{C}_{53}\text{H}_{49}\text{BrO}_8$: C 71.15, H 5.48, Br 8.93; Found: C 71.19, H 5.49, Br 8.93; MALDI-TOF: 915.34 ($[\text{M}+\text{Na}]^+$), 931.30 ($[\text{M}+\text{K}]^+$).

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