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Synthesis of Well-Defined Dendritic-Linear Diblock and Triblock Copolymers by Controlled Free Radical Polymerization

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Abstract: The design and synthesis of novel dendritic-linear block copolymers were described. The copolymers were synthesized by atom transfer radical polymerization (ATRP) using dendritic polyarylether 2-bromoisobutyrate macroinitiator. ATRP carried out in bulk with CuBr/bipy catalyst at 120°C, yielded well-defined block copolymers with polydispersities less than 1.36.

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

Recently, significant progress has been made in the field of living free radical polymerization such as nitroxide-mediated stable free radical polymerization, atom transfer radical polymerization (ATRP), reverse ATRP and reversible addition-fragmentation chain transfer[1]. Among them, ATRP has been successfully applied to the synthesis of well-defined comb, gradient, star and dendritic macromolecules. Recent advances have been carried toward new initiators, metals and ligands.

As a new class of macromolecules, dendrimers have attracted much attention due to their potential applications in the fields such as diagnostics, host-guest chemistry, supramolecular chemistry and catalyst. The present interest has shifted to using dendrimers for the design and synthesis of novel functional materials[2]. In a previous paper, we reported the ATRP of N-phenylmaleimide and styrene using dendritic initiators[3]. In this letter, the dendritic polyarylether 2-bromoisobutyrate (G2-Br)[4] as a macroinitiator for the synthesis of diblock and triblock copolymers was investigated.

The polymerization of methyl methacrylate (MMA) can be well controlled with G2-Br/CuBr/bipy initiating system. MMA was polymerized in bulk at 120°C with the molar ratio of [MMA] : [G2-Br] : [CuBr] : [bipy] = 100:1:1:2. The plot of $\ln[M]_0/[M]$ *versus* time (Figure not shown) appeared as a straight line, indicating the first-order polymerization kinetics. From **Figure 1**, it can be seen that the measured molecular weight increased linearly with increasing conversion and was close to the calculated value. At low conversions, however, the measured value was obviously larger than the expected one, which can be ascribed to the unique macromolecular architecture.

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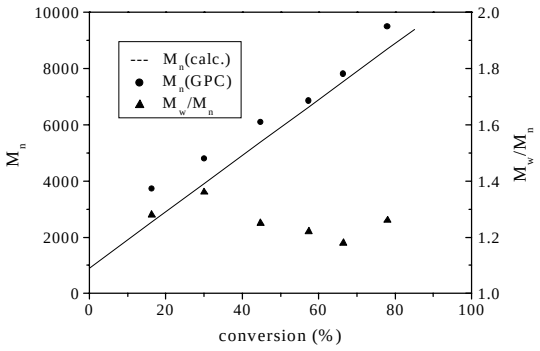
Meanwhile, the polydispersity of the resulting copolymer (G2-PMMA) was relatively narrow (less than 1.36). The above results reveal that the controlled free radical polymerization of MMA can be conducted with the G2-Br/CuBr/bipy initiating system.

Figure 1 Dependence of molecular weight and polydispersity on monomer conversion



Moreover, the diblock copolymer G2-PMMA with an -bromo in the chain end can be successfully used as a macroinitiator for the synthesis of triblock copolymers. When G2-PMMA (M_n(GPC) = 3640, M_w/M_n = 1.28) was applied to the bulk polymerization of styrene, the results are listed in **Table 1**. As compared with the macroinitiator, the resulting triblock copolymers possessed much higher molecular weight, while the polydispersity was still narrow. These results demonstrate the living nature of the reaction system.

Table 1 ATRP of styrene with G2-PMMA macroinitiator*

No.	Time (hr)	conversion (%)	M_n (calc.)	M_n (GPC)	M_w/M_n
1	2	31.6	6930	7800	1.32
2	3	44.8	8300	8960	1.27
3	4	55.7	9430	10800	1.25
4	6	72.4	11170	12400	1.24
5	10	85.3	12500	13640	1.25

* [St]:[G2-PMMA]:[CuBr]:[bipy] = 100:1:1:3, 120 C, bulk polymerization.

References and Notes

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5. Spectra data of **G2-PMMA**: ^{1}H NMR ($CDCl_3$, δ_{ppm}): 7.28 - 7.42 (m, PhH), 6.5 - 6.7 (br m, ArH), 5.06 (s, $ArCH_2O$), 4.98 (s, $PhCH_2O$), 4.92 (s, $ArCH_2O$), 3.75 (s, $COOCH_3$ of the end group), 3.58 (s, $COOCH_3$), 2.62 (s, CH_2 of the end group), 1.36 - 2.20 (br m, CH_2), 0.7 - 1.3 (br m, CH_3); IR (KBr, cm^{-1}): 3060, 3026, 2995, 2951, 2843, 1730, 1607, 1482, 1449, 1388, 1268, 1242, 1193, 1150, 1064, 990, 842, 752, 700.
6. Spectra data of **G2-PMMA-PSt**: ^{1}H NMR ($CDCl_3$, δ_{ppm}): 7.28 - 7.44 (m, PhH), 6.2 - 7.2 (br m, ArH), 5.04 (s, $ArCH_2O$), 4.96 (s, $PhCH_2O$), 4.92 (s, $ArCH_2O$), 4.2 - 4.5 (br m, CH(Ph)Br), 3.60 (s, $COOCH_3$), 0.7 - 2.4 (CH and CH_2); IR (KBr, cm^{-1}): 3060, 3026, 2995, 2951, 2840, 1731, 1598, 1493, 1450, 1387, 1269, 1242, 1193, 1150, 1067, 990, 842, 752, 699.

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