# Synthesis of Dendronized Poly(Methacrylates) and Their Diblock Copolymers by Atom Transfer Radical Polymerization

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**ABSTRACT:** Two kinds of dendronized polymers [poly((4-3,4,5)-12G1-CH$_2$MA) and poly(G2-CH$_2$MA)] were synthesized successfully by atom transfer radical polymerization (ATRP). The polymerization carried out with CuBr/ $N,N,N',N',N'$-pentamethyldiethylenetriamine (PMDETA) as catalyst/ligand system led to the polymers with narrow polydispersity (1.14 < $M_w/M_n$ < 1.35). The dendronized polymers obtained with retained reactivity at chain end were further utilized as macroinitiators to the chain exten-sive reaction of a second monomer (St) by ATRP, which resulted in the formation of a new type of linear–dendritic diblock copolymers. In addition, the polymers and their diblock copolymers were characterized by GPC and DSC. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2733–2737, 2004

**Key words:** atom transfer radical polymerization; dendrimers; diblock copolymers

## INTRODUCTION

Since Tomalia et al. disclosed the synthesis and characterization of the first family of dendrimers in 1984–1985,[1,2] some of the research interest in the area of dendrimers has been shifted to the use of dendrimers as building blocks for the design and synthesis of novel functional materials. Gitsov et al. first synthesized linear–dendritic copolymers by reacting one or both hydroxyl termini of poly(ethylene glycol) (PEG) chain with dendritic bromides.[3,4] Linear–dendritic copolymers have also been synthesized by other approaches.[5–10] In the synthesis of linear–dendritic copolymer mentioned above, a dendron of higher generation with a reactive group at the focal point was usually used as the dendritic segment to undergo the coupling reaction with a linear polymer segment,[11–14] or was modified to become macroinitiator for carrying out the copolymerization of a second monomer, usually by living polymerization or ring-opening polymerization.[15–25] So far, a way has not been found to use a dendronized (or dendron-jacketed) linear polymer as dendritic segment in the synthesis of the lin-ear–dendritic block copolymer. Meanwhile, it is well known that most of the dendronized polymers reported in literature were synthesized by the macromonomer approach developed by Percec and Schlüter.[18] In the macromonomer approach, a wide variety of polymerization techniques have been utilized, but few reports were found to utilize the living technique, such as the atom transfer radical polymerization (ATRP), for the preparation of dendronized polymer. More recently, Schlüter et al. briefly reported the polymerization of methacrylate-based macromonomer-bearing aromatic amide-type dendron of low generations by ATRP.[26]

In the present work, the ATRP of two kinds of methacrylate macromonomer-bearing pendant dendron [(4-3,4,5)-12G1-CH$_2$MA and G2-CH$_2$MA] were successfully performed. The dendronized polymers obtained by this living/controlled radical polymerization were demonstrated to possess narrow polydispersities. Meanwhile, the retained reactivity of polymer chain end can be further used as macroinitiator for the chain extensive polymerization reaction of a second monomer (St) by ATRP, resulting in the formation of a new class of linear-dendritic diblock copolymers.

## EXPERIMENTAL

### Materials

4-$N,N$-Dimethylaminopyridine (DMAP), methacrylic anhydride, methyl-3,4,5-trihydroxy benzo-ate, $N,N,N',N',N'$-pentamethyldiethylenetriamine

(PMDETA), and 2,2′-bipyridine (bpy) were products of Aldrich. St, CuBr, toluene, $CH_2Cl_2$, THF, $Et_2O$, and p-toluene sulfonyl were products of Beijing Chemicals Co., Beijing, China. St was distilled under reduced pressure after removal of the inhibitor and stored at low temperature. CuBr was purified by stirring in acetic acid, washed with ethanol, and then dried *in vacuo*. Toluene was dried over Na, distilled, and stored under $N_2$. $CH_2Cl_2$ was dried over $CaH_2$ and freshly distilled before use. THF and $Et_2O$ were refluxed over sodium ketyl until the solution turned purple and then distilled before use. *p*-Toluene sulfonyl chloride (initiator 1) was recrystallized from benzene/petroleum ether (1/20,v/v). Other reagents were of analytical grade and used as received.

## Characterization

$^1$H-NMR spectra were recorded with a Varian XL-300 NMR spectrometer by using tetramethylsilane (TMS) as internal standard at room temperature. The gel permeation chromatography (GPC) measurements were carried out on a Waters 201 with a $\mu$-styragel column and tetrahydrofuran as solvent, and the molecular weight was calibrated with standard polystyrene. Differential scanning calorimetry (DSC) was carried out on a DSC822$^e$ with a heating rate of 20°C/min under nitrogen atmosphere, relative to indium standards.

## Synthesis

Monomer 1 (G2-CH$_2$MA) was synthesized according to the literature.[27,28]

Monomer 2 [(4-3,4,5)-12G1-CH$_2$MA] was obtained by adding 20 mg DMAP to a solution of 12G1-CH$_2$OH (0.50 g),[29] triethylamine (0.12 g), and methacrylic anhydride (0.15 g) in 10 mL $CH_2Cl_2$. After stirring overnight at room temperature, a few drops of methanol were added to quench the reaction. The mixture was then portioned between $CH_2Cl_2$ and water. The organic layer was washed with dilute hydrochloric acid, aqueous solution of sodium bicarbonate, and brine, dried over MgSO$_4$, and further evaporated to dryness. The crude product was purified by silica gel chromatography, eluted with petroleum ether (60–90°C)/ ethyl acetate = 5/1 (v/v), and gradually increased to 3/1, to give monomer 2 a white solid (0.47 g, 89%) [melting point (m.p.) 41–42.5°C].
$^1$H-NMR (CDCl$_3$): δ 0.88 (t, 9H, $CH_3$), 1.26 (overlapped m, 54H, CH$_3$ ($CH_2$)$_9$), 1.78 (m, 6H, $CH_2$CH$_2$OAr), 1.95 (s, 3H, C ($CH_3$) =CH$_2$), 3.90–3.98 (overlapped t, CH$_2$$CH_2$OAr), 4.93 (s, 2H, Ar$CH_2$OAr, 4 position), 5.02 (s, 4H, Ar$CH_2$OAr, 3.5 position), 5.06 (s, 2H, Ar$CH_2$MA), 5.58 and 6.11 (s, 2H, =$CH_2$), 6.64 (s, 2H, ArH, o-CH$_2$MA), 6.76 (d, 2H, ArH, m-CH$_2$OAr 4 position), 6.90 (d, 4H, ArH m-CH$_2$OAr 3.5

position), 7.26 (overlapped d, 2H, ArH, o-CH$_2$OAr 4 position), 7.33 (d, 4H, ArH o-CH$_2$OAr 3.5 position).

Initiator 2 (2-bromo-2-methyl propionic acid phenyl ester) was prepared by slowly adding bromoisobutyryl bromide (11.5 mL, 0.07 mol) to a solution of phenol (6.60 g, 0.07 mmol), triethylamine (10 mL, 0.072 mol) in THF (150 mL); the reaction was left for 6 h with stirring over reflux. The insolubles were removed by filtration prior to removal of solvent by evaporating, leaving a yellow liquid. The product was dissolved by dichloromethane by washing with saturated Na$_2$CO$_3$ (aq), dilute HCl (aq), and distilled water. The dichloromethane solution was dried with MgSO$_4$ and the solvent was removed by rotary evaporation. On overnight cooling at −15°C, the product crystallized. The crude product was purified by silica gel chromatography, eluted with petroleum ether to give the initiator 2 a light yellow oily liquid (10.8 g, 63.5%) (m.p. below ambient).
$^1$H-NMR (CDCl$_3$): δ 7.12 (d, 2H, m-PhH), 7.25 (t, H, p-PhH), 7.40 (t, 2H, o-PhH), 2.05 (s, 6H, CH$_3$).

## Polymerization

The typical procedure was as follows: monomer (1 or 2), initiator (*1* or *2*), catalyst, and ligand were accurately weighed and placed into a dried glass tube, and a given amount of toluene was added. The polymerization mixture was degassed with freeze-evacuate-thaw cycle three times and sealed. Then the tube was heated to 80°C with stirring for a given time. The reaction mixture was dissolved in THF and passed through a short column on basic aluminum oxide to remove most of the Cu complex. The excess THF was evaporated under reduced pressure and the product was precipitated from a large amount of methanol, filtered, and dried under vacuum to constant weight.
$^1$H-NMR (CDCl$_3$): Poly(G2-CH$_2$MA): δ 0.85–2.01 (br, CH$_2$CH$_3$), 4.67–4.83 (br, 14H, ArCH$_2$O), 6.33–6.45 (br, 9H, ArH), 7.15–7.26 (br, 20H, PhH).
Poly(12G1-CH$_2$MA): δ 0.86−0.88 (br, $CH_3$), 1.24−1.25 (br, 54H, CH$_3$ ($CH_2$)$_9$), 1.43−1.72 (br, $CH_2$), 3.66−3.91 (br, 6H, CH$_2$$CH_2$OAr), 4.61−4.93 (br, 8H, Ar$CH_2$OAr), 6.49−6.64 (br, 8H, ArH), 6.98−7.17 (br, 6H, ArH).
$^{13}$C-NMR (75 MHz CDCl$_3$): Poly(G2-CH$_2$MA): δ 69.6, 70.0, 76.5, 76.9, 77.3, 101.5, 106.3, 127.4, 127.7, 127.9, 128.3, 128.5, 136.7, 139.1159.8. ANAL. calcd for PIV [C$_{10}$H$_{11}$O$_2$-(C$_{53}$H$_{48}$O$_8$)$_{11}$-Br]: C, 77.56; H, 5.87; Br, 0.87. Found: C, 77.51; H, 5.98; Br, 0.80.
Poly(12G1-CH$_2$MA): δ 14.0, 22.6, 26.1, 29.3, 29.7, 31.9, 68.0, 71.2, 74.9, 76.5, 76.9, 77.4, 113.7, 114.0, 114.4, 128.8, 129.1, 129.2, 129.6, 129.7, 129.8, 129.9, 130.2, 152.9, 158.7. ANAL. calcd for PVIII [C$_{10}$H$_{11}$O$_2$-(C$_{68}$H$_{100}$O$_8$)$_{18}$-Br]: C, 77.65; H, 9.50; Br, 0.41. Found: C, 77.62; H, 9.84; Br, 0.30.

## Block copolymerization

To a given amount of dendronized polymer (i.e., macroinitiator PII or PIX) obtained above, St, CuBr, PM-
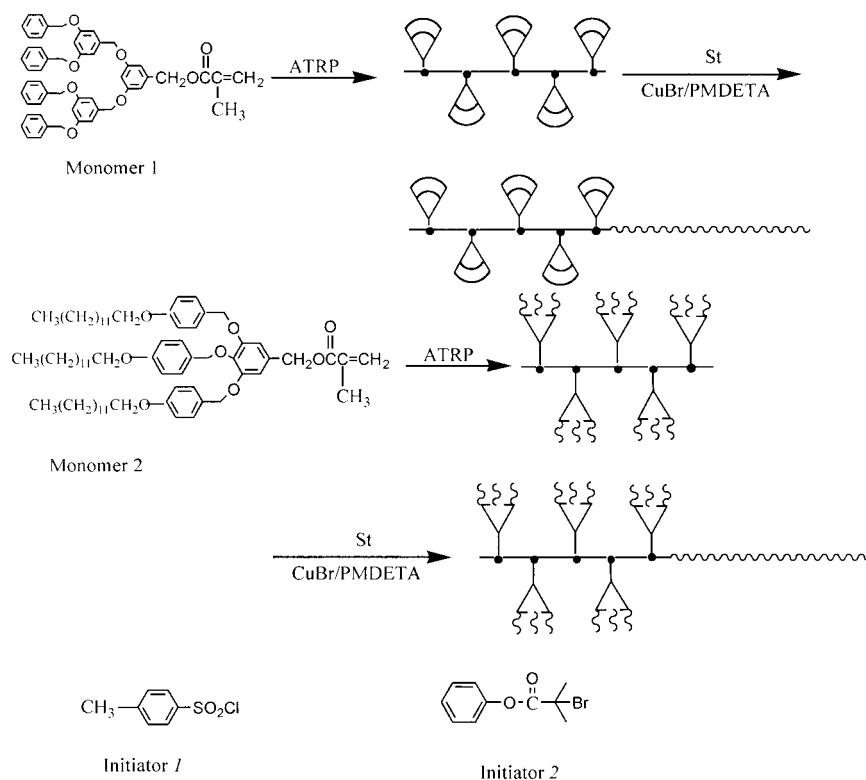
**Scheme 1** Synthetic routes of dondrimized poly(methacrylates) and their diblock copolymers.

DETA, and toluene was added to the polymerization tube in the order mentioned. The tube was then subjected to freeze-pump-thaw cycles three times and heated to 80°C for a given time. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral aluminum oxide to remove metal salt. The excess of THF was evaporated under reduced pressure. The resulting copolymers were precipitated in a large amount of methanol, filtered, and dried under vacuum to constant weight.

## RESULTS AND DISCUSSION

Initiators and the synthetic strategy followed for the preparation of polymers and AB-type block copolymers via the ATRP route are depicted in Scheme 1.

## Polymerization

The polymerizations of monomer 1 (G2-CH$_2$MA) and monomer 2 (12G1-CH$_2$MA) were carried out in toluene solution by using CuCl or CuBr as catalyst and bpy or PMDETA as ligand in the presence of initiator (1 or 2) at 80°C; the results are shown in Table I and Table II. It is found that both methacrylate monomers with bulky dendritic wedges can be polymerized successfully by ATRP to give the dendronized polymers with relatively narrow polydispersity ($1.07 < M_w/M_n < 1.35$). In the polymerization of monomer 1 (G2-CH$_2$MA) shown in Table I, the CuCl/bpy seems to be an unsuitable catalyst system and low conversion and low molecular weight is obtained. However, CuBr/PMDETA as a heterogeneous catalyst system proceeds in a controlled manner with a higher initiation effi-

**TABLE I**
**Syntheses of Poly(G2-CH$_2$MA) via ATRP Route (Temperature: 80°C, 0.4 ml Toluene/g Monomer)**

| Run | Initiator | Catalyst | Ligand | Time (h) | Conversion (%) | $M_{nGPC}$ (/10$^4$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| PI[a] | 1 | CuCl | bpy | 60 | 42.0 | 0.52 | 1.07 |
| PII[b] | 1 | CuBr | PMDETA | 60 | 92.2 | 0.84 | 1.12 |
| PIII[c] | 1 | CuBr | PMDETA | 60 | 98.4 | 1.37 | 1.35 |
| PIV[d] | 2 | CuBr | PMDETA | 60 | 89.0 | 0.92 | 1.16 |

[a] $[M]_0 : [I]_0 : [Cat.] : [Lig.] = 30 : 1 : 1 : 2.$
[b] $[M]_0 : [I]_0 : [Cat.] : [Lig.] = 30 : 1 : 1 : 4.$
[c] $[M]_0 : [I]_0 : [Cat.] : [Lig.] = 30 : 1 : 1 : 2.$
[d] $[M]_0 : [I]_0 : [Cat.] : [Lig.] = 30 : 1 : 1 : 4.$

**TABLE II**
**Syntheses of Poly(12G1-CH$_2$MA) via ATRP Route (Temperature: 80°C, 0.4 ml Toluene/g Monomer)**

| Run | Initiator | Catalyst | Ligand | Time (h) | Conversion (%) | $M_{n\text{GPC}}$ (/10$^4$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| PV[a] | 1 | CuCl | bpy | 60 | 25.0 | 0.75 | 1.06 |
| PVI[b] | 1 | CuBr | PMDETA | 60 | 39.7 | 3.18 | 1.28 |
| PVII[c] | 1 | CuBr | PMDETA | 60 | 49.7 | 3.21 | 1.29 |
| PVIII[d] | 2 | CuBr | PMDETA | 60 | 93.4 | 1.95 | 1.16 |
| PIX[e] | 2 | CuBr | PMDETA | 60 | 91.0 | 1.25 | 1.14 |

[a] $[M]_0:[I]_0:[Cat.]:[Lig.] = 30:1:1.5:2$.
[b] $[M]_0:[I]_0:[Cat.]:[Lig.] = 30:1:1.5:4$.
[c] $[M]_0:[I]_0:[Cat.]:[Lig.] = 30:1:1.5:2$.
[d] $[M]_0:[I]_0:[Cat.]:[Lig.] = 30:1:1.5:2$.
[e] $[M]_0:[I]_0:[Cat.]:[Lig.] = 30:1:1.5:4$.

ciency to be successfully used in conjunction with a halide-exchange technique to produce polymers. As shown in Table I, the polymers (PII–PIV) have higher molecular weights and higher conversion. In addition, the proper decrease of feed ratio of PMDETA might cause the increase of conversion and molecular weight of polymer, except for the polydispersity becoming broad. Similar results are observed by using initiator 1 and 2. In the case of monomer 2 (12G1-CH$_2$MA) (Table II), the ATRP by using initiator 2/CuBr/PMDETA system is obviously much better than by using initiator 1/CuCl/bpy or initiator 1/CuBr/PMDETA system in the polymerization conversion and polydispersity. However, the molecular weights of polymers (PVIII and PIX) are lower than that of PVI and PVII.

The measurement of molecular weight by GPC exhibits that the molecular weights of polymers obtained here are not high, but they are still acceptable and comparable with the molecular weights of similar polymers by conventional radical polymerization.[27–29] On the other hand, the actual molecular weights of polymers should be higher than those obtained from GPC because the hydrodynamic volumes of the polymers are not the same as those of linear PS standards; dendritic polymers are known to take a very compact molecular size in solution. Many researchers proved this by measuring molecular weights with small-angle laser light scattering.[30,31] In general, it is difficult to obtain high molecular weight polymers because of steric hindrance no matter how polymerization proceeds (ATRP or conventional radical polymerization). Schlüter et al.[32] and Percec et al.[33] re-

ported that a higher molecular weight polymer with reasonable distribution could be successfully obtained by introducing a shorter spacer between the vinyl group and the dendritic wedge.

## Block copolymerization

The syntheses of diblock copolymers consisting of PSt segment was performed by using the dendronized polymers obtained above (PII and PIX) as macroinitiators to initiate the polymerization of St via ATRP route. The conditions and results of polymerization are tabulated in Table III. The GPC traces of macroinitiators (PII and PIX) and their AB-type block copolymers (Copolymer 1 and Copolymer 2) are portrayed in Figure 1. The results indicate that the dendronized polymers were found to be efficient macroinitiators for St in ATRP. These copolymers were contaminated with a small amount of unreacted macroinitiator that could be easily removed via precipitation fractionation. As shown in Figure 1, the GPC traces for Copolymer 1 and Copolymer 2 reveal no trace of unreacted macroinitiator. The composition of block polymer estimated according to their molecular weights is P(G$_2$-CH$_2$MA)$_{10}$-b-PSt$_{89}$ for Copolymer 1 and P(12G$_1$-CH$_2$MA)$_{12}$-b-PSt$_{152}$ for Copolymer 2, respectively, in which the subscript number represents the average degree of polymerization. In addition, their polydispersities still remained narrow ($M_w/M_n = 1.12$ and 1.14). The results of DSC analyses indicate that there are two glass transition temperatures ($T_g$) for each block of copolymers as expected (i.e., 52.7 and 111.2°C for

**TABLE III**
**Synthesis of AB-Type Block Copolymers via ATRP Route (Temperature: 80°C, Ligand = PMDETA, Cat. = CuBr, [M]/[I]/[Cat.]/[Lig.] = 100:1:2:4, Monomer/Toluene = 6, v/v)**

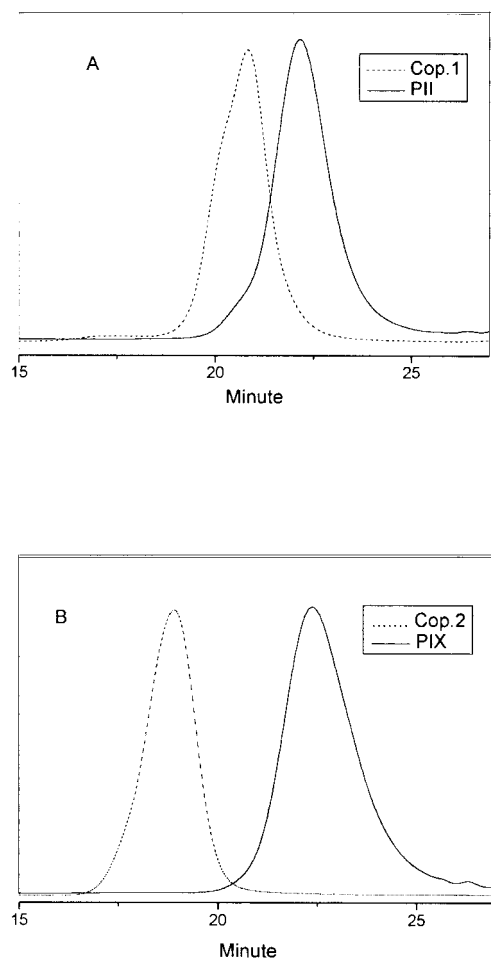| Copolymer | Monomer | Macroinitiator | Time (h) | Conversion (%) | $M_{n\text{GPC}}$ (/10$^4$) | $M_w/M_n$ | $T_{g1}$ (°C) | $T_{g2}$ (°C) |
|---|---|---|---|---|---|---|---|---|
| 1 | St | PII | 30 | 78 | 1.77 | 1.12 | 52.7 | 111.2 |
| 2 | St | PIX | 30 | 65 | 2.83 | 1.14 | 53.5 | 115.7 |

**Figure 1** A comparison of the GPC traces for (A) Copolymer 1 and PII and (B) Copolymer 2 and PIX.

Copolymer 1 and 53.1 and 115.7°C for Copolymer 2, respectively).

## CONCLUSION

Two kinds of methacrylate macromonomer-bearing pendant dendron (G2-CH$_2$MA and 12G1-CH$_2$MA) were successfully polymerized by ATPR. The dendronized polymers obtained were demonstrated to possess narrow polydispersities. The retained reactivity of polymer chain end can be further used as macroinitiator for the polymerization of a second monomer (St) by ATRP, resulting in the formation of a new class of linear–dendritic diblock copolymers.

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