Samarium enolate on crosslinked polystyrene beads: anionic initiator for well defined synthesis of polymethacrylate on a solid support

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A resin-supported samarium enolate successfully initiated the living anionic polymerization of methacrylates to afford the corresponding homopolymer as well as block copolymer with well-controlled molecular weights, which could be quantitatively isolated from the resin, so demonstrating the applicability of the present technique for solid supported construction of macromolecular architectures.

Polymer grafting on various organic and inorganic solid supports has been attracting significant attention as an effective technique for modification of functional materials.[1] Living polymerization is one of the most powerful tools for polymer grafting, because its capability in controlling the degree of polymerization together with end-functionalization and block copolymerization allows us to construct macromolecular architectures on solid supports in a well defined manner. Our research interest is in living polymerization of functional monomers on crosslinked polystyrene beads which have been widely applied as solid supports in solid phase organic syntheses which has brought about today's expanding development of combinatorial synthesis of chemical libraries.[2] Our approach would be a promising route to combinatorial synthesis of functional polymeric materials with defined structures. Since bead-supported photo-iniferter radical polymerization has been pioneered by Otsu *et al.*, only a few examples have been reported concerning controlled polymerization on polystyrene beads.[3] Here we describe the first example of living anionic polymerization of methacrylates on polystyrene beads.

Previously we have developed samarium(III) enolate mediated living anionic polymerization of methacrylates (Scheme 1).[4] Based on this technique, we have designed a novel grafting system involving (1) an easy access to immobilized samarium enolate through reduction of the corresponding bromoisobutyrate moiety by divalent samarium iodide (SmI_2), and (2) selective cleavage of the benzyl ester linkage between the formed poly(methacrylate)s and the beads, which enables the isolation of the formed polymer so allowing examination of the polymerization behavior in detail (Scheme 2).

The resin bearing 2-bromoisobutyrate moiety **1** was prepared by the condensation of 2-bromoisobutyric acid with Wang resin (crosslinked polystyrene containing hydroxymethyl groups, 0.68 mmol g^{-1}, 100–200 mesh) using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride as a dehydrating reagent. The condensation was repeated (usually twice) until

Table 1 Polymerization of MMA with various feed ratios

Entry	$[MMA]_0$/ $[Sm\text{-enolate}]_0$	M_n[a]	M_w/M_n[a]
1	20	3300	1.24
2	30	4400	1.21
3	50	7700	1.13

[a] Estimated by SEC [eluent: THF, poly(MMA) standards].

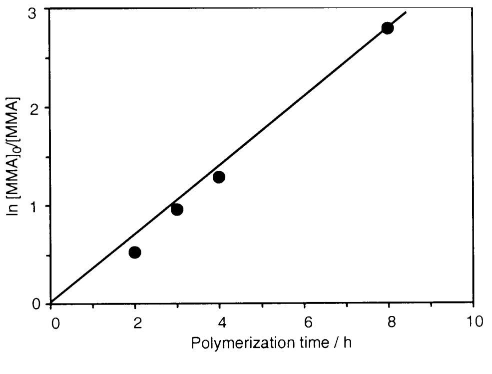
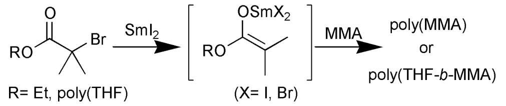
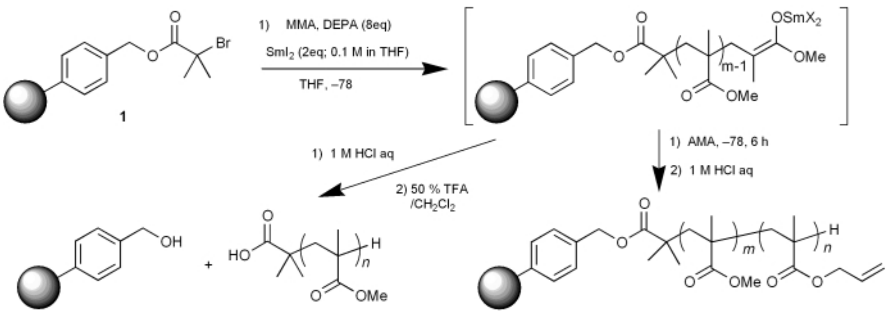


Fig. 1 $\ln[MMA]_0/[MMA]$ *vs.* polymerization time. $[MMA]_0$ = 5 mmol (50 eq. to Sm-enolate).



Scheme 1



Scheme 2

complete acylation was confirmed by the disappearance of IR absorption of hydroxy groups at 3500 cm^{-1}.

The polymerization of methyl methacrylate (MMA) was performed by the addition of SmI_2 (2.0 eq. to 2-bromoisobutyrate moiety) to **1** in the presence of *N*,*N*-diethylpivaloylamide (DEPA), which is essential to accomplish well controlled polymerization in a homogeneous system, with shaking at −78 °C for 12 h.[5] The dark blue reaction mixture arising from SmI_2 gradually turned into yellow during a few hours, indicating Sm(III) enolate formation. The polymerization was terminated by the addition of 1 M aqueous hydrochloric acid, and the resulting resin was filtered off and washed with appropriate solvents. No polymer was detected in the filtrate by size exclusion chromatography (SEC), while the resin, as expected, gained weight according to the amount of MMA fed. Formation of poly(MMA) on the resin was also confirmed by IR analysis of the resin, which showed strong absorption attributable to ester carbonyl groups at 1740 cm^{-1}. Treatment of the resin with trifluoroacetic acid (TFA, 50% in CH_2Cl_2) resulted in selective cleavage of benzyl ester linkers without cleavage of the methyl ester in the side chain, and consequently poly(MMA) was quantitatively obtained.[6] The presence of carboxylic acid at the chain end of the polymer was confirmed by TLC analysis: the obtained polymer was not eluted by chloroform–THF (9 : 1, v/v) while poly(MMA) having terminal ester groups eluted easily. Isolated poly(MMA) was analyzed by SEC to estimate its number- and weight-average molecular weights (M_n and M_W). Table 1 summarizes the results of the polymerization with various feed ratios. In each case, MMA was completely consumed to give quantitatively poly(MMA) with a narrow M_W/M_n. The M_n of the polymer increased linearly with the feed ratio, demonstrating the ability of the present polymerization system to control the molecular weights of the polymer. We next examined the polymerization process on the solid state. Fixing the feed ratio to 50, separate series of polymerization was carried out with various polymerization times. The monomer conversion was determined based on the weight increase of the resin. Fig. 1 depicts a semi-logarithmic kinetic plot ($\ln[MMA]_0/[MMA]$ *vs.* polymerization time), the linear relationship of which may suggest the living character of the polymerization. The M_n of isolated poly(MMA) increased with monomer conversion (23%: M_n = 1500, 50%: M_n = 4200, > 99 %: M_n = 7700).

Finally, the living character of the present polymerization was confirmed by block copolymerization of MMA with allyl methacrylate (AMA) as shown in Scheme 2. After the polymerization of MMA (20 eq. to the initiator) was complete, AMA (20 eq.) was added and the mixture shaken at −78 °C for 12 h. The resulting resin gained weight according to the total amount of methacrylates fed, and its treatment with TFA resulted in quantitative isolation of the block copolymer. The ^{1}H NMR spectrum of the block copolymer showed signals assignable to methoxy groups of poly(MMA) and allyl groups of poly(AMA), where the integration ratio was in good agreement with the feed ratio (Fig. 2). SEC analysis showed that the unimodal peak of poly(MMA) shifted toward a higher molecular weight region with a narrow molecular weight distribution being maintained after AMA addition, indicating the successful formation of the block copolymer (Fig. 3).

In summary, we have demonstrated a new solid-supported living anionic polymerization of methacrylates. The initiator samarium enolate was readily and effectively generated by SmI_2-induced reduction of bromoisobutyrate moieties, supported on polystyrene beads. Further applications of the present system to multi-block copolymerization of various functional methacrylates, together with subsequent chemical modifications of the resulting polymer on polymer supports, are now in progress.

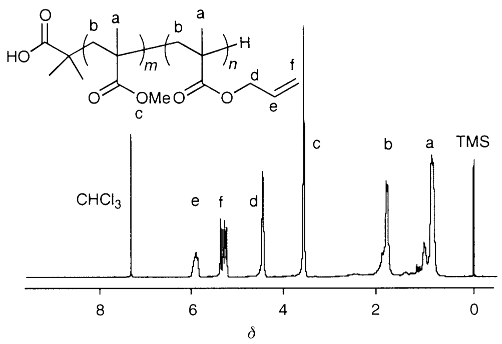


Fig. 2 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(MMA-*b*-AMA).

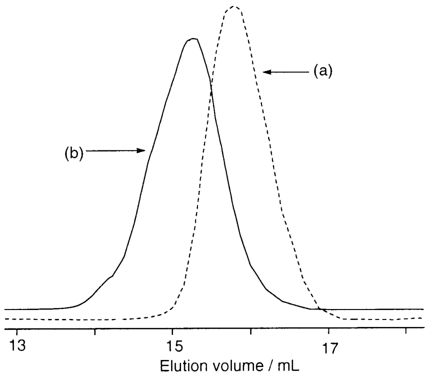


Fig. 3 SEC profiles of polymethacrylates obtained by block copolymerization: (a) poly(MMA) (M_n = 3,300, M_W/M_n = 1.24); (b) poly(MMA-*b*-AMA) (M_n = 6,800, M_W/M_n = 1.21).

Notes and references

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5 *Typical procedure*: to resin **1** (165 mg, bromoisobutyrate unit: 0.1 mmol) swelled in THF (1 mL) were added MMA (500 mg, 5 mmol) and DEPA (126 mg, 0.8 mmol) under N_2. The resulting mixture was cooled to −78 °C, and SmI_2 (0.1 mM solution in THF; 2 mL, 0.2 mmol) was added to the mixture which was shaken at the same temperature for 12 h. Then 1 M HCl (5 mL) was added to quench the reaction. The mixture was filtered and the residual resin washed successively with water, THF and then methanol. It was dried *in vacuo* to obtain the resin bearing poly(MMA) (660 mg; quant.).

6 *Typical procedure*: the resin bearing poly(MMA) (660 mg) was swelled in TFA (50% in CH_2Cl_2, 5 mL) and shaken at room temperature for 6 h. The mixture was filtered and the residual resin was washed with CH_2Cl_2. The filtrate was concentrated by rotary evaporation to give poly(MMA) (500 mg; quant.).