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Metal-Free Carbanion Salts for the Living Anionic Polymerization of Alkyl (Methyl) Acrylates

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In recent years considerable efforts have been made toward the polymerization of alkyl (methyl) acrylates with well-defined molecular weights and low polydispersities. Webster et al.[1] performed the first living polymerization of methyl methacrylate (MMA) using *O*-silyl ketene ketals as initiators in the presence of nucleophilic catalysts. This method, known as group-transfer polymerization (GTP), enables living polymerizations of alkyl (methyl) acrylates at room temperature.[2,3] Other groups have reported the living synthesis of low-polydispersity alkyl (methyl) acrylates using metal-containing initiators such as the lithium salt of diphenylmethane.[4,5] In this case, attack of the (methyl) acrylate carbonyl group by the metal ion is sterically inhibited. However, these syntheses must still be performed at very low temperatures (−78 °C) to avoid the terminating side reaction.[6]

An alternate approach to the living synthesis of alkyl (methyl) acrylates which has recently gained attention exploits metal-free salts as initatiors,[7−14] which are less reactive and hence have a lower propensity for undesirable side reactions. Reetz et al.[3,10] reported the room-temperature polymerization of low-molecular-weight poly(*n*-butyl acrylate), using tetrabutyl thiolates and malonates as initiators, with molecular weight distributions (MWD) ~ 1.14. Sivaram et al.[11] reported the preparation of dicarbonyl-terminated low-molecular-weight poly(methyl methacrylate) (PMMA) with broad molecular-weight distribution using tetrabutylammonium di-*tert*-butyl malonate at room temperature. Bidinger and Quirk[12] used the Bu_4N^+ salt of 9-methylfluorene as an initiator for the polymerization of MMA in tetrahydrofuran (THF) at ambient temperature. The reported product had a low yield and high MWD (2.16). Seebach et al.[13] reported the polymerization of MMA using the P4-phosphazine base as part of a metal-free initiator with high molecular weight and MWD < 1.3. Recently, Zagala and Hogen-Esch[14] described the synthesis of PMMA with narrow molecular-weight distribution (<1.2) and high yield at ambient temperature, initiated by tetraphenylphosphonium triphenyl methanide in THF. The success of this most recent approach prompted us to further explore the utility of triphenyl methanide-based organic initiators for the living synthesis of alkyl (methyl) acrylates and their block copolymers, as part of a broader study to develop acrylate-based block copolymers for application in lithium polymer batteries.[15] Here, we report preliminary results of the room temperature polymerization of PMMA, poly(butyl acrylate) and block copolymers of MMA with lauryl methacrylate (LMA) or butyl acrylate (BA) using initiators consisting of a triphenyl methane carbanion and tetraoctylphosphonium or tetrahexylammonium cation. These initators are generally shown to produce materials with well-controlled molecular weights and polydispersities.

Table 1. MMA Polymerization Initiated by Ph_3C^- Oct_4P^+ in THF

entry	temp. (°C)	$M_{n,SEC}$	MWD	% yield	f^a	mm^e	mr^e	rr^e
1	0	17 000	1.06	>95	0.16	0.07	0.37	0.56
2	0	20 300	1.10	>95	0.17			
3	0	20 900	1.12	>91	0.17	0.09	0.36	0.55
4	25	18 700	1.07	>95	0.16			
5	25	20 200	1.06	>96	0.17	0.07	0.37	0.54
6	25	19 100	1.03	>89	0.17	0.09	0.41	0.50
7	25	30 600	1.14	>96	0.18	0.08	0.39	0.53
8[b]	25	93 100	1.28	>90	0.16			
9[c]	25	15 000	1.13	>88	0.17			
10[d]	25	23 000	1.06	>85	0.16			

[a] Initiator efficiency (f) = $M_{n,cal}/M_{n,SEC}$. [b] P(MMA-*b*-LMA) block copolymer. [c] Monomer was butyl acrylate. [d] P(MMA-*b*-BA) block copolymer. [e] By ^1H NMR integration of α-methyl resonances.

Triphenylmethane was dried under vacuum for 2 days at 40 °C. $Ph_3C^-K^+$ was prepared by reacting potassium metal and triphenylmethane in dry THF under argon at room temperature. Tetraoctylphosphonium bromide ($Oct_4P^+Br^-$) or tetrahexylammonium bromide ($Hex_4N^+Br^-$) was dried under vacuum for 1 day at room temperature and added to THF. The salt initiator was prepared by titrating the colorless THF solution of tetraoctylphosphonium or tetrahexylammonium cation with the red solution of potassium triphenylmethanide at −78 °C (eq 1), until an orange-red color persisted, at roughly stoichiometric additions of $Ph_3C^-K^+$. Upon equilibrating to room temperature, the phosphonium initiator solution remained colored, indicating that this initiator is quite stable. By contrast, the tetrahexylammonium triphenyl methanide initiator is stable at 0 °C, but at 25 °C the red color of the initiator persists for only a few minutes.

$$\mathrm{Ph_3C^-K^+ + Oct_4P^+Br^-\ (or\ Hex_4N^+Br^-) \rightarrow Ph_3C^-\ {}^+POct_4\ (or\ {}^+NHex_4) + KBr} \quad (1)$$

To prepare a PMMA homopolymer, a MMA monomer in solution (10% v/v MMA in THF) was added dropwise to a phosphonium initiator solution of concentration ~3×10^4 M. The reaction proceeded rapidly after the addition of MMA, as evidenced by an immediate loss of color. After several minutes the polymerization was terminated by the addition of methanol. The PMMA was precipitated in methanol, dried under vacuum at 60 °C for 1 day, and subsequently weighed to determine yield. A similar protocol was followed for the preparation of a poly(butyl acrylate) (PBA) homopolymer, the block copolymers P(MMA-*b*-LMA) and P(MMA-*b*-BA), and syntheses employing the tetrahexylammonium triphenyl methanide initiator. For the block copolymers, MMA was first polymerized followed by the addition of LMA or BA after 15 min.

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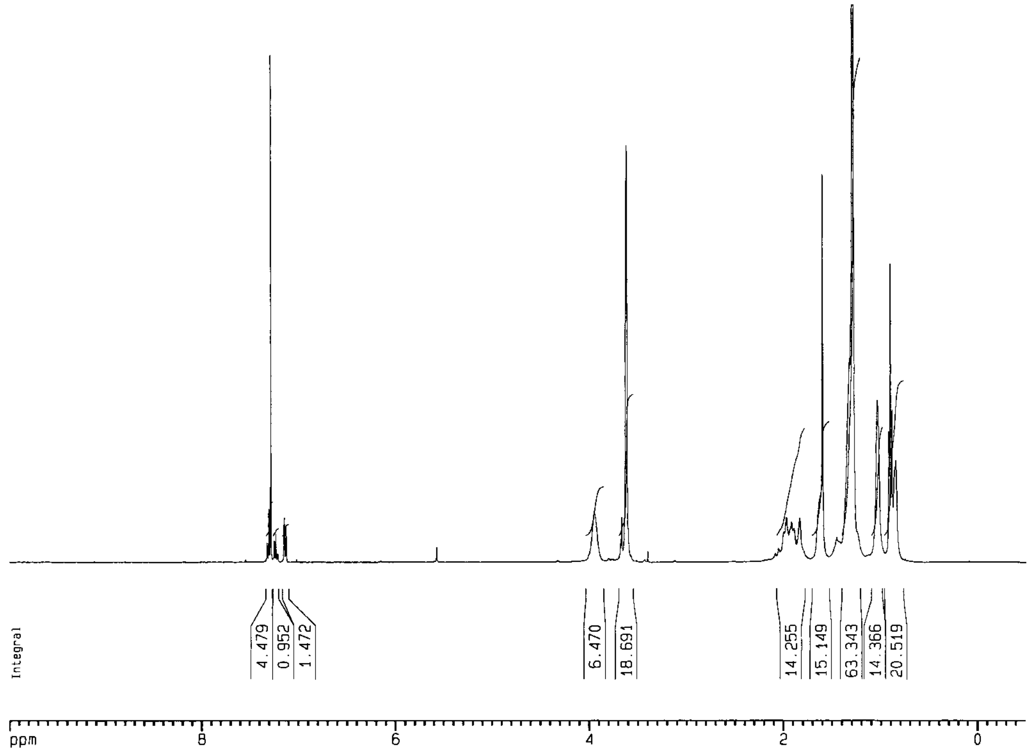

Figure 1. Proton NMR spectrum of P(MMA-*b*-LMA) prepared by tetraoctylphosphonium triphenyl methanide.

Table 2. MMA Polymerization Initiated by $Ph_3C^- \ {}^+NHex_4$ in THF

entry	temp. (°C)	$M_{n,SEC}$	MWD	% yield	f^a	mm^d	mr^d	rr^d
1	0	42 300	1.21	>96	>1%	0.07	0.42	0.51
2	0	42 000	1.19	>97	<1%	0.09	0.36	0.55
3	25	43 400	1.28	>97	>1%			
4^b	25	92 600	1.33	>88	>1%			
5^c	25	42 500	1.27	>72	>1.5%			

[a] Initiator efficiency (f) = $M_{n,cal}/M_{n,SEC}$. [b] P(MMA-*b*-LMA) block copolymer. [c] Initiator was tetrabutylammonium tetraphenyl borate. [d] By ^1H NMR integration of α-methyl resonances.

Table 1 summarizes the results obtained for the polymerization of MMA at 0 and 25 °C using the phosphonium initiator solution. The polymers produced have a narrow MWD (1.06−1.15) and are obtained almost in quantitative yield, confirming that the intramolecular Claisen-type termination reaction, which is common in the case of anionic polymerization of MMA at a higher temperature using alkali-metal cation initiators,[3] is practically eliminated. The number-average molecular weight of the products was determined by size-exclusion chromatography (SEC) using polystyrene standards. The SEC results indicate low initiator efficiency ($M_{n,cal}/M_{n,exp}$) on the basis of the molar quantity of tetraoctylphosphonium bromide utilized. The low efficiency (~16%) is probably due to the presence of moisture and small amounts of hydrobromic acid in the phosphonium bromide salt, which cause decomposition of the initiator.

Table 2 summarizes the results of polymerizations performed using the tetrahexylammonium triphenyl methanide initiator at a concentration of $\sim 2 \times 10^{-3}$ M. After addition of MMA at 0 °C, the initiator slowly turns yellow and then colorless. At 25 °C the red color of the solution is immediately lost upon addition of MMA. In our study, the yield of the polymerizations was uniformly high (>85%), though most previous reports using ammonium salt initiators gave lower yields[12] and a broad (>1.2) MWD. A disadvantage of this initiator is the very low efficiencies observed. An attempt was made to use another ammonium salt initiator, the salt of tetrabutylammonium tetraphenyl borate and potassium triphenyl methanide. Though PMMA was obtained at high yield with low MWD, the efficiency was still lower in that case (~1%).

The stereochemistry of PMMA prepared using both types of initiator (~ 50% *rr*, Tables 1 and 2) is similar to the PMMA obtained by GTP or other anionic polymerization schemes at comparable temperatures.[16,17]

To confirm the living nature of PMMA prepared by both types of initiators, block copolymers were synthesized. From the ^1H NMR spectra (Figures 1 and 2), it was confirmed that in both cases the theoretical monomer feed composition is almost equal to the polymer composition. Figure 1 shows the spectrum obtained from the block copolymer prepared using tetraoctylphosphonium triphenyl methanide. The observed weight ratio of 52/48 (MMA/LMA) was in agreement with the calculated value from the monomer feed ratio. For the block copolymer of methyl methacrylate and lauryl methacrylate prepared using tetrahexylammonium triphenyl methanide, the observed ratio, 56/44 (MMA/LMA), was again close to the calculated value (52/48) from the monomer feed ratio. The weight compositions of P(MMA-*b*-LMA) in both cases were calculated particularly from the characteristic resonances: 3.62 ppm for $-OCH_3$ and 3.94 ppm for $-OCH_2-$. Figure 2 shows the spectrum from the block copolymer of methyl methacrylate and butyl acrylate prepared using tetraoctylphosphonium triphenyl methanide. Resonances at 3.66 ppm for $-OCH_3$ and 0.91 ppm for the methyl group of BA gave an observed ratio of 56/44 (MMA/BA), somewhat higher than the calculated value (50/50) from the monomer feed ratio. Figure 3 shows the SEC results of (a) P(MMA-*b*-BA) prepared by tetraoctylphosphonium triphenyl

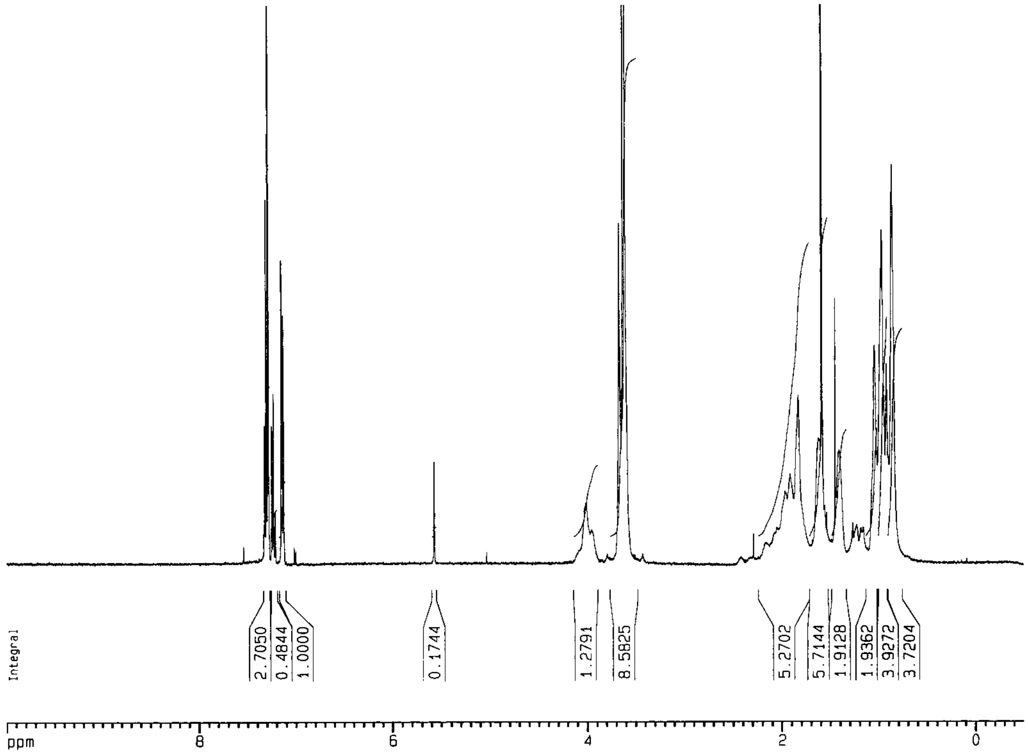

Figure 2. Proton NMR spectrum of P(MMA-*b*-BA) prepared by tetraoctylphosphonium triphenyl methanide.

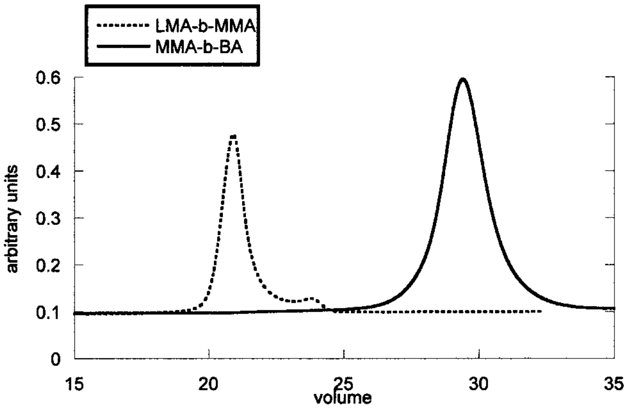

Figure 3. Size-exclusion chromatogram of (a) P(MMA-*b*-BA) (Table 1, entry 10) and (b) P(MMA-*b*-LMA) (Table 2, entry 4).

methanide and (b) P(MMA-*b*-LMA) prepared by tetrahexylammonium triphenyl methanide. A low-molecular-weight shoulder (4−7%) is evident in Figure 3b, which we attribute to the PMMA homopolymer generated by impurities in the LMA monomer upon its addition to the reactor.

In conclusion, the living anionic polymerization of alkyl (methyl) acrylates and their block copolymers has been carried out using initiators consisting of a triphenylmethane carbanion and tetraoctylphosphonium or tetrahexylammonium cation. These metal-free initiators enable the synthesis of controlled molecular weight, low-polydispersity acrylates at ambient temperature with good yields, though they have low efficiencies. Preliminary results indicate that these systems are also suitable initiators for polymerizing methoxy poly(ethylene glycol) methacrylate macromonomers at room temperature, and thus may be good initiators for large-scale syntheses of lithium ion conducting block copolymers.[15]

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