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Controlled Synthesis of Dicarboxyl-Terminated Poly(methyl acrylate) Macromonomers Using a New Blocked Carboxyl Functional Metal-Free Carbanionic Initiator†

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Introduction

Macromonomers have emerged as a powerful and versatile method for the synthesis of well-defined graft copolymers.[1-3] In most cases, however, macromonomers have a radically or ionically polymerizable function such as the styryl or (meth)acryl group. There are only a few examples of macromonomers that can be used in polycondensation reactions.[4-10] Of these, the acrylate-based difunctional macromonomers were prepared by radical polymerization in the presence of dihydroxyl[9] or dicarboxyl[10] functional chain transfer agents.

More recently, GTP and anionic polymerization techniques have been used to synthesize macromonomers of poly(methyl methacrylate).[11,12] and poly(*tert*-butyl acrylate).[13] Metal-free carbanionic initiators were recently discussed in the literature for controlled polymerization of alkyl acrylates.[14] In our laboratory, we have extended this concept to functional carbanionic initiators and showed that these can be used for the controlled synthesis of oxazoline-terminated poly(methyl acrylate) macromonomers.[15,16] We now report a novel synthesis of dicarboxyl-terminated poly(methyl acrylate) macromonomers using a new blocked carboxyl functional metal-free carbanionic initiator.

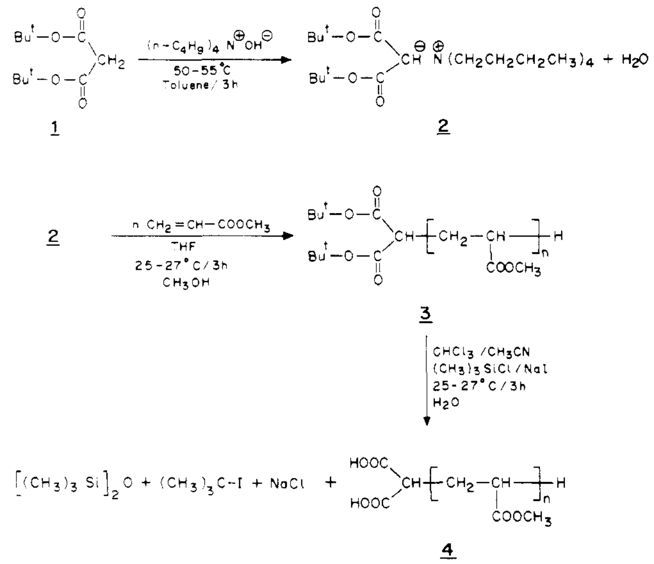
Experimental Section

Materials. Methyl acrylate (MA) (Loba Chemie Industry, Bombay) was passed through a column of neutral alumina and then stirred over calcium hydride and distilled under argon prior to use. Tetrahydrofuran (THF) was freshly distilled under argon atmosphere from purple sodium benzophenone ketyl. Tetrabutylammonium hydroxide (TBAOH), 20% in methanol/toluene, was obtained from Sisco Research Laboratories, Bombay. Sodium iodide was dried at 150 °C for 12 h before use. Trimethylsilyl chloride (TMSCl) was freshly distilled from calcium hydride. Di-*tert*-butyl malonate (1) was prepared according to a procedure reported in the literature.[17]

Synthesis of Tetrabutylammonium Di-*tert*-butyl Malonate (2). In a 100-mL three-neck flask equipped with an argon inlet were placed TBAOH (2 mL, 1.54 mmol) and distilled water (5 mL) and the contents heated to 50–55 °C. (This treatment ensures the hydrolysis of tetrabutylammonium methoxide present, if any, in the TBAOH solution.) Water was removed by azeotropic distillation with toluene under reduced pressure. 1 (0.496 g, 2.0 mmol) was added dropwise, and the water formed during the reaction was removed by azeotropic distillation over a period of 3 h. Excess toluene was removed under reduced pressure. The oily product obtained was washed repeatedly with dry hexane to remove excess 1, dried in vacuum at room temperature, and stored under argon.

Synthesis of Di-*tert*-butyl Ester Terminated Poly(methyl acrylate) (3). The desired quantities of 2 and THF were taken in a dry three-neck flask equipped with a gas inlet tube, a thermowell, and a rubber septum. MA was added dropwise via a hypodermic syringe at 25–27 °C. The polymerization was continued for 3 h and then terminated by addition of methanol. The solvents were removed under reduced pressure. The viscous material obtained was taken up in chloroform and washed repeatedly with distilled water. The chloroform layer was separated, dried over anhydrous sodium sulfate, and filtered. The solvent was evaporated and the residue was dried under vacuum to obtain di-*tert*-butyl ester terminated poly(methyl acrylate) (3).

Scheme I
Synthesis of Dicarboxyl-Terminated Poly(methyl acrylate) Macromonomers



Synthesis of Dicarboxyl-Terminated Poly(methyl acrylate) (4). Into a two-neck flask fitted with a nitrogen inlet tube was taken 3 (1 mmol) and dissolved in 30 mL of an acetonitrile–chloroform (2:1 v/v) mixture. To this solution were added sodium iodide (10 mmol) and TMSCl (10 mmol) in that order, and the mixture was stirred at room temperature for 3 h. The solvents and excess TMSCl were removed under reduced pressure. The residue obtained was dissolved in chloroform (50 mL) and washed successively with 1% aqueous sodium thiosulfate solution (2 × 50 mL) and water (50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated to obtain 4.

Characterization. The ^{13}C NMR spectrum of 2 was recorded on a Bruker MSL 300 (7.05 T) NMR spectrometer operating at 75.48 MHz. ^{1}H NMR spectra were recorded in $CDCl_3$ on a WH 90 FT NMR (Bruker) spectrometer. The number-average molecular weights ($\bar{M}_n$) were determined using a Knauer vapor-phase osmometer in chloroform at room temperature. The molecular weight distribution for the polymers (0.3% w/v in THF) was determined by using Waters gel permeation chromatograph Model GPC/ALC 150 C equipped with a refractive index detector. The measurements were carried out using Waters μ-Styragel columns (2 × 100, 2 × 500, 10^3 Å) at a temperature of 40 °C and THF as eluent at a flow rate of 2 mL/min. Polystyrene standards of known molecular weights were used to calibrate the columns. The acid contents of polymers were determined by dissolving the samples in a toluene–methanol mixture and titrating with standard methanolic tetrabutylammonium hydroxide solution. The functionality values of 4 were calculated using the expression functionality = $\bar{M}_n$ (calcd)/equiv wt, where equivalent weight was obtained from carboxyl group content.

Results and Discussion

Di-*tert*-butyl malonate (1) was converted to the corresponding anion (2) by reaction with TBAOH at 50–55 °C (Scheme I, 1 → 2). The carbanion (2) was characterized[18] by ^{13}C NMR. The carbon atom bearing the negative charge showed a large downfield chemical shift from 44.37 to 77.12 ppm.

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Table I
Synthesis of Di-*tert*-butyl Ester Terminated Poly(methyl acrylate)s 3[a]

entry	M, g	yield, %	$\bar{M}_n$ (calcd)[b]	$\bar{M}_n$ (VPO)	$\overline{DP}_n$ calcd	$\overline{DP}_n$ NMR	$\bar{M}_w/\bar{M}_n$
1	0.778	85	720		5.9	6.2	
2	1.190	98	990		9.0	9.5	
3	1.699	94	1320	1260	12.8	11.7	
4	1.932	97	1470	1580	14.6	13.7	
5	2.749	92	2000	1840	20.8	20.6	1.4
6	5.367	94	3700		40.5	40.1	1.5
7	15.070	95	10000	9500	113.8		1.5

[a] Polymerization reactions were carried out with monomer concentration of 1.8 mol/L in THF at 25–27 °C; $I = 1.54 \times 10^{-3}$ mol. [b] $\bar{M}_n$ = (g of methyl acrylate/mol of initiator) + initiator fragment mol wt (215 g/mol).

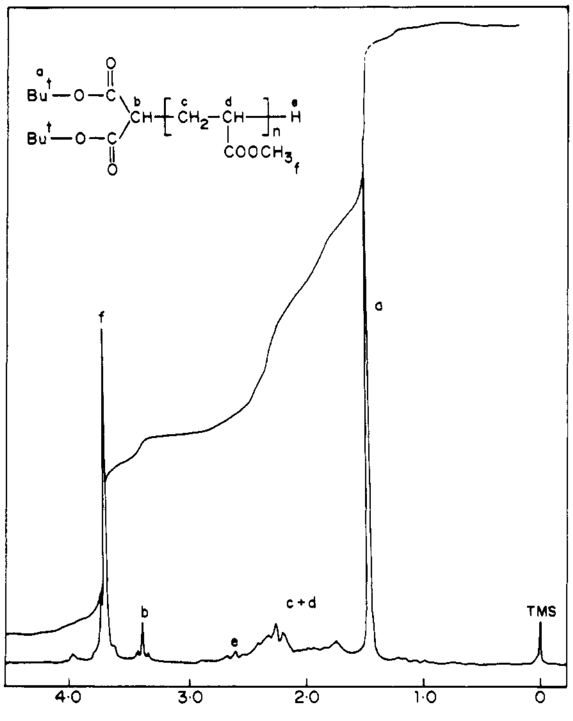

Figure 1. ¹H NMR spectrum of di-*tert*-butyl ester terminated poly(methyl acrylate) 3 (entry 1, Table I).

The carbanion (2) smoothly initiated the polymerization of MA at ambient temperature. The reaction was accompanied by an appreciable exotherm. The results are shown in Table I. Conversions to the polymer were in the range of 85–98%. The average degree of polymerization ($\overline{DP}_n$) of the polymers was routinely calculated (entries 1–6, Table I) from ¹H NMR spectra (Figure 1) by assuming that two *tert*-butyl ester groups are present per poly(methyl acrylate) molecule.[19] The $\overline{DP}_n$ calculated from monomer to initiator ratio agreed well with $\overline{DP}_n$ calculated from ¹H NMR, indicating the absence of any undesirable side reactions during polymerization. For a few samples $\bar{M}_n$ was independently determined by VPO. Results showed satisfactory agreement with $\overline{DP}_n$ calculated from NMR.

Three samples of 3 (entries 5–7, Table I) were evaluated by GPC for polydispersity. The polydispersity index was found to be 1.5. These values are similar to that observed for poly(methyl acrylate) prepared by the GTP technique.[20]

The terminal *tert*-butyl ester groups of 3 could be selectively converted in quantitative yields to the carboxylic acid groups under mild conditions using TMSCl/NaI[21] (Scheme I, 3 → 4). The chemoselectivity of this reagent for ester hydrolysis is documented in the literature.[22]

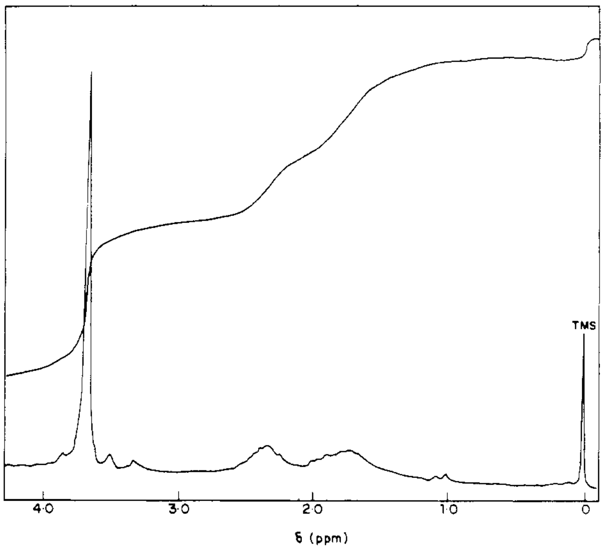

Figure 2. ¹H NMR spectrum of dicarboxyl-terminated poly(methyl acrylate) 4.

Table II
Synthesis of Dicarboxyl-Terminated Poly(methyl acrylate)s 4

entry	$\bar{M}_n$ of 3 (by NMR)	$\bar{M}_n$ of 4 (calcd)[a]	equiv wt[b]	functionality[c] (COOH)
1	750	638	300	2.1
2	1030	918	420	2.2
3	1220	1108	610	1.8
4	1390	1278	650	2.0
5	1990	1878	1050	1.8
6	3660	3548	1850	1.9

[a] Calculated by subtracting 112 (corresponding to the loss of two *tert*-butyl groups) from the molecular weight of parent di-*tert*-butyl ester terminated poly(methyl acrylate). [b] Equivalent weight determined from carboxyl content. [c] Functionality = $\bar{M}_n$ (calcd)/equiv wt.

The completeness of conversion was judged by the total disappearance of the peak at 1.40 ppm in ¹H NMR attributable to the *tert*-butyl group (Figure 2). It was further confirmed by ¹H NMR that the poly(methyl acrylate) backbone was unaffected under these experimental conditions. The ratio of the protons due to the methyl ester groups to the backbone methylene and methine protons was close to unity, indicating no hydrolysis of the methyl ester groups.

The carboxyl functionality values of 4 were estimated by acid–base titration. The functionality was found to be in the range of 1.8–2.2 (Table II).

Thus, using a blocked carboxyl functional metal-free carbanionic initiator, it has been possible to synthesize well-defined dicarboxyl-terminated poly(methyl acrylate) macromonomers. Utilization of these macromonomers for the synthesis of novel graft polycondensates is currently in progress.

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(18) ^{13}C NMR spectrum of **2** in CDCl$_3$: δ 12.77 (CH$_3$, tetrabutyl), 18.90 (CH$_2$), 23.30 (CH$_2$), 27.42 (CH$_3$, *t*-Bu), 58.06 N$^+$CH$_2$) 77.12 (C-H), 77.80 (OC(CH$_3$)$_3$), 169.6 (CO), and 170.0 (CO).

(19) Let *A* represent the intensity of the peak at 3.70 ppm which corresponds to the methyl ester protons of the poly(methyl acrylate) chain and let *B* represent the integrated area over the range 1.30–3.50 ppm which corresponds to the sum of the intergation due to backbone methylene and methine protons and the integration due to protons from the initiator fragment. By subtracting *A* from *B*, one obtains integration corresponding to 20 protons (19 protons from the initiator fragment and 1 proton introduced in the termination step), from which integration corresponding to 1 proton can be found. The ratio of *A* to 3 times the integration due to one proton gives $\overline{\mathrm{DP}}_n$.

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