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STRATEGIES FOR CONTROLLED POLYMERIZATION OF ACRYLIC/METHACRYLIC MONOMERS AND SYNTHESIS OF NOVEL GRAFT POLYMERS

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INTRODUCTION

Controlled synthesis of acrylic and methacrylic ester polymers is of both fundamental and practical interest. Some excellent initiators for the polymerization of methyl methacrylate (MMA) with controlled molecular weight and narrow polydispersity have been reported. These are ketene silylacetal based GTP initiators[1], t-BuMgBr coupled with $MgBr_2$[2] or R_3Al[3], metalloporphyrins of aluminum[4], 1,1-diphenylhexyllithium/LiCl[5], organolanthanum[6] and cationic zirconocene[7] compounds, lithium aluminum alkyls[8] and diphenyl sodium complexed with crown ethers[9]. Very recently, a stabilized radical promoted polymerization of MMA with narrow polydispersities (1.2-1.3) has been reported[10]. On the contrary, less success has been achieved with acrylic monomers, presumably because of labile α-hydrogen atom. Use of hindered anionic initiators such as t-butyl-α-lithio isobutyrate/t-butoxy lithium[11] or α-methylstyryl lithium/LiCl[12] have proven useful at low temperatures (-60 to -78°C) Reetz and coworkers have reported that stabilized carbanions derived from malonic esters in association with tetrabutylammonium cation are useful initiators for room temperature polymerization of n-butyl acrylate[13].

In our laboratory, we have studied the anionic polymerization of acrylic monomers using stabilized carbanions-tetra-n-butylammonium cations[14]. Besides exploring synthetic utility[15] we have been intrigued by the ubiquitous role of large ("soft") cations involving enolate ester intermediates, in both anionic and group transfer polymerizations[16].

Thus, we undertook a detailed structural study of stabilized carbanions with tetra-n-butylammonium cation by NMR and X-ray crystallography[17]. We also studied the initiating ability of tetra-n-butyl ammonium salt of di-t-butylmalonate and diethylphenyl malonate with acrylic monomers ($C=C-CO_2R$, R = Me, n-Bu and t-butyl) and tetra-n-butylammonium fluorenide with methyl methacrylate[18]. We exploited this chemistry for controlled grafting of acrylic polymers using polymer bound metal free carbanions as initiators[19].

EXPERIMENTAL

Manipulations involving air sensitive compounds were done under a positive pressure of high purity argon, using standard bench top inert atmosphere/vacuum techniques.

Materials

Tetra-n-butylammonium hydroxide (TBAOH) was obtained as 20% solution in toluene/methanol (SISCO, India), or as a 40% aqueous solution (Aldrich), methyl methacrylate (MMA), methyl acrylate (MA), n-butyl acrylate (BA), t-butylacrylate (t-BA) obtained from Aldrich, USA were purified according to reported procedures[20]. Diethylphenyl malonate (DEPM, Aldrich) was used as received. Di-t-butyl malonate was prepared from malonic acid chloride and t-butanol.

Preparation of initiators

(a) Tetra-n-butylammonium diethylphenyl malonate (1) : To 10 mL (7.7 mmol) of TBAOH in 45 mL of toluene 1.6 mL (7.7 mmol) of DEPM was added and three azeotropic distillations were performed of 20mL distillate. The initiator thus generated was washed with dry n-hexane to remove excess DEPM. Pale yellow crystals of the initiator separated out. The initiator was dissolved in THF and used directly..

(b) Tetra-n-butylammonium di-t-butyl malonate (2) : To 0.2 g (0.93 mmol) of di-t-butylmalonate in 10 mL of toluene 0.42 mL (0.6 mmol) of TBAOH was added (40% solution in water). Water was azeotropically distilled out using toluene as entrainer. Excess di-t-butyl malonate was removed by washing with n-hexane thrice and the solvent removed in vacuo. The carbanion was obtained as a white solid.

(c) Tetra-n-butylammonium fluorenide (3) : To 1.4 g (8.4 mmol) of fluorene in 40 mL toluene 10 mL (7.7 mmol) of TBAOH (20% solution in toluene/methanol) was added. Water was azeotropically distilled out by adding toluene four times in increments of 15 mL each. Excess fluorene was removed by washing with n-hexane. Upon removal of solvent in vacuo, the carbanion separated as deep orange crystals.

Polymerization

(a) Polymerization of acrylic monomers by initiators 1/2 : t-BA (4.4 g) was introduced into a solution of 1 (0.25 g, 0.52 mmol) in 45 mL THF under nitrogen. A strong exotherm developed. Polymerization was terminated by addition of acidified methanol and solvent removed under vacuum. The polymer yield was 4.2 g (96%).

(b) Polymerization of MMA by initiator 3 : MMA (4 mL, 37.4 mmol) was introduced into a solution of 3 (6 ml, 0.49 mmol) in 30 mL THF under nitrogen. Polymerization was terminated after 30 min by addition of acidified methanol. The polymer yield was 3.7 g (100%).

(c) Graft polymerization using polymer bound benzyl oxazoline carbanion : A linear copolymer of styrene and 4-vinylbenzylchloride (in a 6:4 molar ratio) was converted to a copolymer of styrene and 4-vinylbenzylnitrile by treating with KCN under phase transfer conditions[21]. The latter was converted to a benzyl oxazoline containing copolymer (4) by reacting with ethanol amine at 70°C for 8 h. Polymer 4 (0.14 g) was treated with 20 mL of THF and 0.3 mmol of TBAOH under argon atmosphere and warmed to 60°C for 6 h. Solvent was removed and the polymer repeatedly washed with dry hexane. The polymeric carbanion (5) was dried in vacuo. Stock solutions of 5 in THF were stable for several weeks at room temperature. Anionic graft polymerization acrylic monomers using 5 was brought about by addition of an excess of monomer (0.6 mmol) in THF at 25°C. Initiator was evidenced by an exotherm and disappearance of the red color of initiator solution.

Analysis

^1H and ^{13}C NMR analyses were performed using a Bruker AC 200 or MSL 300 Spectrometer. FT-IR measurements were performed using a Perkin Elmer PC-16 FT-IR Spectrometer. Crystallographic studies were done on well formed crystals using Enraf-Nonium CAD 4 Diffractometer. Detailed measurement parameters have been reported elsewhere[17]. Molecular weights and their distribution were determined using Waters 150C GPC using μ-styragel columns in THF at 30°C (0.2 % w/v polymer, flow rate 1 mL/min). Monodisperse polystyrene and poly(MMA) standards were used for molecular weight calibrations.

RESULTS AND DISCUSSION

Structural characterization of initiators 1-3 : The initiator carbanions (1-3) were prepared in quantitative yields using an original procedure first developed in our laboratory[15b]. These carbanions were unequivocally characterized by ^{13}C NMR spectroscopy (Table 1). The carbanions show a range of charge delocalization behaviour. For example, in **1**, the negative charge is extensively delocalized in the aromatic ring as shown by the large upfield chemical shift of the ortho and para carbon atoms. Carbanion **1** could be isolated as pale yellow crystals and was subjected to single crystal X-ray diffraction studies. While our studies were in progress Reetz and coworkers published the crystal structure of tetra-n-butylammonium diethyl-2-ethyl malonate[22]. Although both the carbanions form hydrogen bonded aggregates with short O---H-C interactions with adjacent cations, carbanion **1** did not possess a U-shaped geometry as reported by Reetz. Based on crystallographic evidence, it was concluded that on account of both steric and electronic reasons the tendency to form O---H-C bridges was reduced in case of **1** and the carbonyl groups assumed a more stable transoid configuration.

Polymerization of acrylic and methacrylic monomers by initiators 1-3 : Using both initiators **1** and **2**, MA, n-BA and t-BA were polymerized in THF at 27°C. The objective was to explore the effect of increasing steric demand on both the initiator and monomer on polymerization. It was found that under similar conditions ([I] = 11.6 mmol L^{-1} [M] = 0.76 mol L^{-1}) quantitative conversions to polymer were obtained with initiator **1**. However, MWD of the polymer progressively decreased from a value of (3.7) in case of MA to (3.4) for BA and (1.6) for t-BA. This indicates that increasing steric demand around the ester carbonyl minimizes unwanted side reactions. We have, therefore, explored the use of initiator **2**, for polymerization of the above monomers. Conditions have been established for obtaining greater than 90% conversion to polymer. The ability of initiator **2** to produce controlled molecular weight poly(MA) with a MWD of 1.4-1.5 has been demonstrated[15b]. We have also found that **3** is capable of initiating polymerization of MMA in THF at 27°C with > 99% conversion. Using $[M] = 1.23$ mol L^{-1}, $[I] = 16.1$ mmol L^{-1}, a polymer with Mn (SEC) = 6870 (theory 7600) was obtained with a MWD of 1.47. Quirk and Bidinger had earlier reported that with tetra-n-butyl ammonium-9-methfluorenide, poly(MMA) was obtained in 14% yield with poor control on Mn and MWD (= 2)[23]. Reasons for this difference is not clear. However, our experience with both initiators **2** and **3** appear to indicate that the additional acidic hydrogen does not interfere in polymerization[24].

Controlled grafting of acrylic polymers : We had earlier reported that a carbanion derived from benzyl oxazoline associated with tetra-n-butylammonium cation enables controlled polymerization of acrylic monomers[14]. We therefore generated a polymeric carbanion (**5**, Scheme 1) and used it as an initiator for graft copolymerization with n-butyl methacrylate, t-butyl methacrylate and acrylonitrile at 27°C. Evidence of grafting was obtained by FT-IR and ^{13}C NMR spectroscopy. GPC indicated increase in molecular weight after grafting, with no change in MWD. The grafting efficiency ranged from 13-55% whereas, grafting varied from 70-94%.

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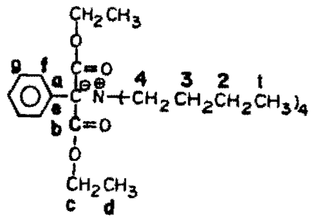
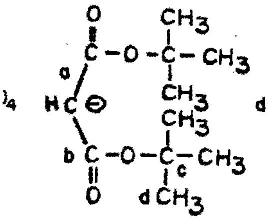
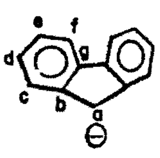
Table 1 : ^{13}C NMR of **2** in DMSO-d_6 and **1** and **3** in THF



1

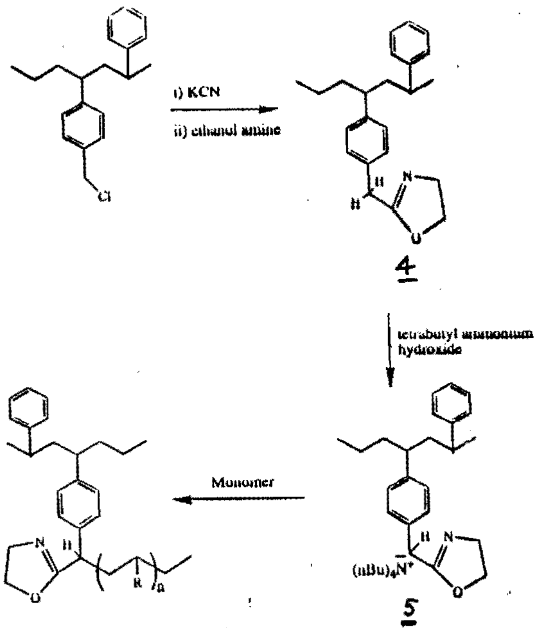


2



3

C No.	**1**	**2** (ppm)	**3** (ppm)
1	14.6	15.0	13.8
2.	20.9	21.2	19.6
3.	25.2	25.0	23.5
4.	59.1	57.8	57.9
a	79	85.0	77.9
b	170	123.0	167.5, 170
c	56.9	120.0	72.2
d	16.4	110.0	28.33
e	146.7	117.5	
f	126.7	120.5	
g	132.4		
h	120.2		



R = COOMe, COOtBu, COOnBu or CN

Scheme 1