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# Approaches to controlled polymerization of methyl acrylate through functional anionic initiators*

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## SUMMARY

Controlled 'living ' polymerization of methyl acrylate has been achieved at room temperature using functional carbanionic initiators in THF solvent. Methyl acrylate oligomers with reactive chain ends have been synthesized.

## INTRODUCTION

Synthesis of vinyl/olefin polymers with well defined molecular weights and structures continues to be an important goal in contemporary polymer research. Living anionic, cationic and ring opening metathesis polymerization methods have been successfully utilized to synthesize such polymers based on hydrocarbon (olefinic) monomers(1–3). On the other hand living polymerization of acrylic and methacrylic monomers has been less successful. Living anionic polymerization of these monomers using organometallic initiators require very low temperatures to minimize undesired side reactions involving ester functionality(4). The technique of group transfer polymerization has been successful for polymerizing methacrylate monomers at room temperature in a controlled manner although it is less controllable for acrylates(5). This is due to the higher reactivity of acrylate esters and the presence of $\alpha$ –hydrogen in these monomers. Increase of steric bulk around the carbonyl group(t–bulyl acrylic esters) leads to better control in poymerization as it minimizes the possibilities of undesirable side reactions at the ester carbonyl(1,4 vs 1,2 addition)(6). More recently,resonance stabilized tertiary carbanions with tetrabutyl ammonium ion as countercations have been employed for controlled synthesis of n–butyl acrylates (7). The absence of metal countercation as well as the steric bulk of the anion could be responsible for providing this control. Although the method was claimed as being generally applicable to all acrylic esters, experimental results were demonstrated only with n–butyl acrylate.

We report herein the synthesis and characterization of resonance stabilized carbanions with tetrabutylammonium counter cations which afford controlled polymerization of methyl acrylate at room temperature. These carbanions can be distinguished from those reported previously in the literature by the following features: a) they tolerate $\alpha$ –hydrogens b)the precursor carbon acids span a much wider range of carbon acidity and c) the carbanions carry a functional group capable of being synthetically manipulated.

## EXPERIMENTAL

Materials:

Methyl acrylate(MA)(Loba–Chemie Industry,Bombay)was stirred over $CaH_2$, distilled and stored under $N_2$. Tetrahydrofuran(THF) was freshly distilled under $N_2$ from purple sodium/ benzo-phenone ketyl prior to use. Tetra–n–butyl ammonium hydroxide (TBAOH) (Sisco Research Laboratories, Bombay), 20% in methanol / toluene was used as received. Di-

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**To whom offprint requests should be sent ethyl phenyl malonate (DEPM) (Aldrich) was used as received. 2-Benzyl-1,3-oxazoline(BO) was synthesized by reported procedure(11) and freshly distilled prior to use (100°C/5mm Hg).

## Preparation of Initiators

a) TBAOH,7.7 mmoles in 40 mL of dry toluene was heated to 75°C in a three necked 100 mL flask equipped with an argon inlet, dropping funnel and a distillation unit. DEPM (9.3 mmoles) was slowly added and an azeotrope of toluene-water was distilled out slowly over a period of 3 hrs and then vaccum was applied to remove toluene. Upon cooling , a solid product separated out which was repeatedly washed with dry hexane. The solid product was dried in vaccum at room temperature and stored under $N_2$ or argon.

b) In a three neck 100 mL flask equipped with a nitrogen inlet, rubber septum and a thermometer, was placed 2.5 mmoles of BO in 50 mL dry THF. TBAOH (2.5 mmoles) was added dropwise and reaction stirred at room temperature for 0.5 hr. The temperature was then raised to 50°C and maintained for 3 hr. A deep red colored solution appeared. The reaction mixture was cooled to room temperature, solvent evaporated under vaccum and product dried at 40°C in vaccum.

## Polymerization Procedure

Desired quantity of initiator and THF were charged to a dry three neck flask equipped with a nitrogen inlet, thermowell and a rubber septum. Neat MA was added dropwise by a hypodermic syringe at the desired temperature. A spontaneous exotherm was observed within 3 min. The reaction mixture was stirred futher for 1-2 hr. The polymerization was terminated by acidic water. The reaction mixture was extracted in chloroform , the organic layer evaporated in vaccum and dried.

## Characterization

$^1$H and $^{13}$C-NMR of polymers were recorded in $CDCl_3$ using a WH 90 FT NMR (Bruker) spectrophotometer. $\overline{M}n$ was estimated using a VPO (Knauer, W.Germany) in toluene. Molecular weights were also estimated by $^1$H NMR from the comparison of signal intensities of the aromatic or $-O-CH_2$ protons with the $-O-CH_3$ protons of the monomer unit. The molecular weight calculated from $^1$H NMR were in close agreement with the values obtained by VPO.

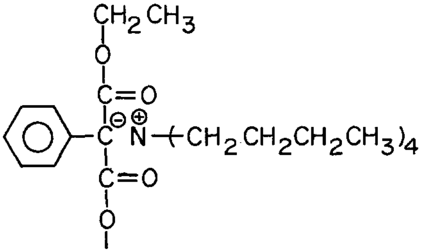
## RESULTS AND DISCUSSION

The initiatior I and II were characterized by their $^1$H and $^{13}$C NMR spectra (Table 1 and Fig.1). The $^1$H NMR of I confirmed the absence of methine hydrogen at 4.4 ppm.

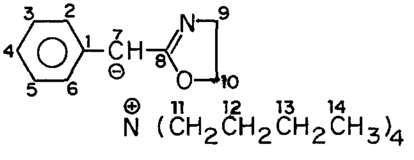
In the $^{13}$C NMR of II the carbon atom bearing the negative charge shows a large down field chemical shift from 33 ppm to 77.0 ppm. The carbanions possessed unusual stability and could be stored indefinitely even at room temperature under $N_2$ or argon.

Both I and II initiated polymerization of MA at room temperature without any induction period. The initiation was accompanied by appreciable exotherms. The results are summarized in Table 2 which clearly indicate that polymer molecular weight is controlled only by initiator concentration. The $^1$H NMR sectra of poly(methyl acrylate) initiated by I is shown in Fig.2. $\overline{M}n$ could be conveniently calculated from the NMR spectrum. This confirms the living nature of polymerization. To the best of our knowledge such control on the polymerization of methyl acrylate has never been achieved before using anionic initiators.

The significant feature of our work is the ability to synthesize carbanions with functional groups (aryl, oxazoline etc.) which in turn lead to functional oligomers. Furthermore, we have discovered that even carbanions bearing two hydrogen atoms can initiate controlled polymerization of acrylate esters(8) and an initiator such as I can be tailored to generate a



I



II

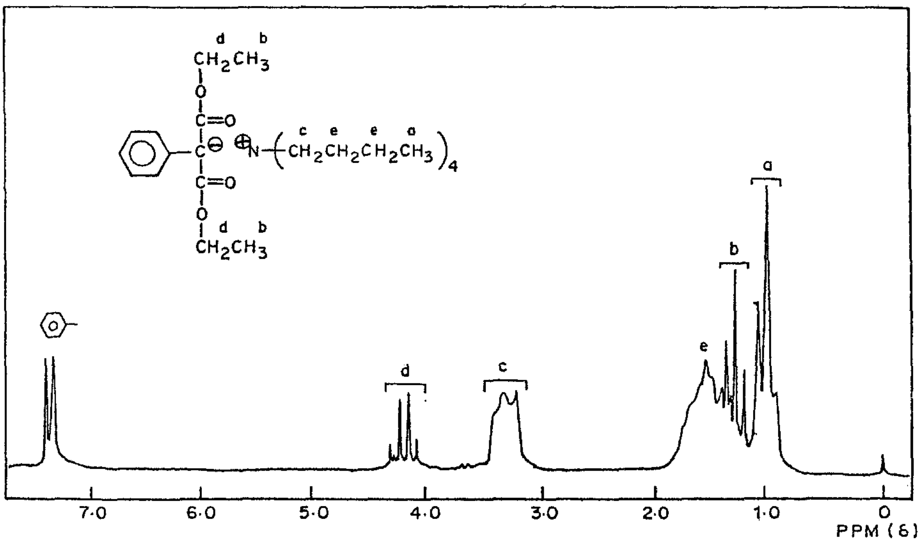


Figure 1: $^1$H NMR of Carbanion I in $CDCl_3$

range of carbanion reactivities by appropriate substitution on the aryl group.

Table 1: $^{13}$C NMR Resonance for II in $CDCl_3$

| carbon–Nos | ppm |
|---|---|
| 1 | 134.6 |
| 2–6 | 126.5–129.0 |
| 7 | 77.0 |
| 8 | 165.8 |
| 9 | 53.5 |
| 10 | 67.2 |
| 11 | 58.4 |
| 12 | 23.6 |
| 13 | 19.3 |
| 14 | 13.2 |

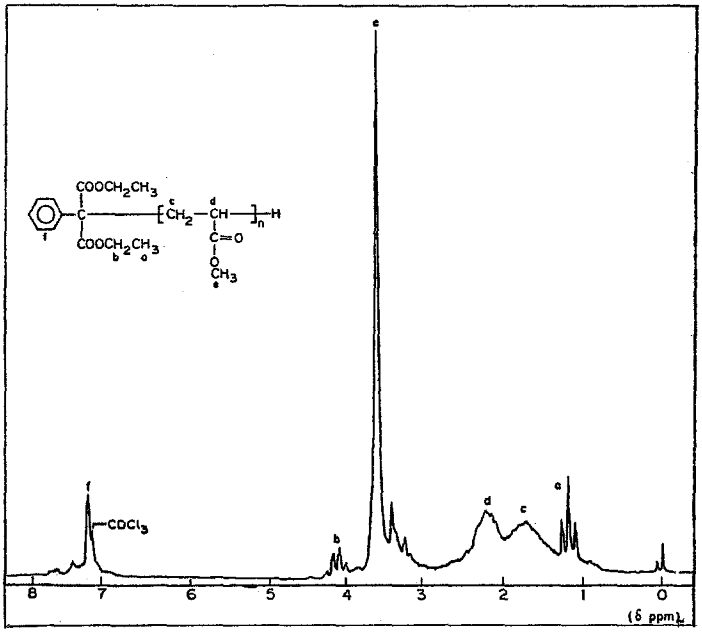


Figure 2: $^1$H NMR of Poly(methyl acrylate) initiated by I

Table 2: Polymerization of methyl acrylate initiated[a] by carbanion I and II

| Entry | Initiator | [I] | [M] | $\overline{Mn}^b$ Observed | $\overline{Mn}^b$ Calculated |
|---|---|---|---|---|---|
| 1 | I | 0.025 | 0.55 | 2300 | 2140 |
| 2 | I | 0.064 | 0.55 | 945 | 970 |
| 3 | I | 0.034 | 0.55 | 1485 | 1620 |
| 4 | I | 0.050 | 0.55 | 1220 | 1200 |
| 5 | I | 0.122 | 1.10 | 965 | 1010 |
| 6 | I | 0.114 | 1.10 | 1380 | 1240 |
| 7 | II | 0.027 | 0.60 | 1790 | 2070 |
| 8 | II | 0.032 | 1.60 | 3960 | 4450 |
| 9 | II | 0.027 | 1.60 | 4800 | 5250 |

a) in THF at 26°C

b) Initiator fragment molecular weight (235 g/m in case of I and 160 g/m in case of II) has been taken into account.

The precise mechanism by which carbanions described herein lead to controlled polymerizaion of acrylic ester monomers is not clearly understood. It appears that matching the reactivity of the initiating and the propagating carbanion must in some manner be responsible for this observation.

The preliminary results reported in this paper provide very exciting prospects for the macromolecular engineering of acrylate esters, i.e. predictable molecular weights, absence of internal claisen reaction of the ester enolate, narrow polydispersity and quantitative control of the nature of end groups. These initiators also promote 'living' polymerization of acrylonitrile to monodisperse poly(acrylonitrile)(9) and to well defined block copolymers(10).

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10. Block copolymers of acrylonitrile with acrylic esters have been synthesized and are under characterization. Details will be published elsewhere.

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