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Tailoring Carbanion Structures for Controlled Anionic Polymerization of Acrylonitrile[1,2]

Synthesis of vinyl/olefin polymers with well-defined molecular weight and structure 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.[3-5] On the other hand, living polymerization of acrylic and methacrylic monomers has been less successful. Living anionic polymerization of these monomers using organometallic initiators brings about undesired side reaction involving ester functionality and needs very low temperature experimentation.[6] The technique of "group-transfer polymerization" has been successful for polymerization methacrylate monomers at room temperature in a controlled manner, although it is less controllable for acrylates.[7] Using metal-free carbanion initiators, Reetz et al. have recently demonstrated the controlled synthesis of acrylate polymers at room temperature.[8]

In spite of these recent dramatic achievements in the synthesis of acrylic polymer, controlled polymerization of acrylonitrile still remains an elusive goal. Even group-transfer polymerization could not provide any degree of control on acrylonitrile polymerization at −50 °C.[9]

We report for the first time a synthetic strategy for controlled polymerization of acrylonitrile at temperatures as high as 30 °C. Toward this end, we have developed a generalized synthetic methodology for obtaining functional carbanion initiators with varying reactivities. The latter could be achieved by judicious selection of the functional groups α to the carbanion. These carbanions are metal free, with tetrabutylammonium ion serving as countercation in all the cases.

The initiators under discussion are metal-free ammonium methanides possessing different functional groups. They are easily accessible by reacting the corresponding carbon acids with tetrabutylammonium hydroxide (TBAOH). Thus, we have prepared the carbanion salts **1b**–**4b** in quantitative yield from the precursors **1a**–**4a** (Scheme I). These products are either oils (**1b** and **2b**) or solids (**3b** and **4b**). The compounds have been well characterized by infrared and NMR spectroscopy.[10] The proton NMR spectra reveal absence of the methine proton in case of **3b** and a downfield shift of the benzylmethylene carbon resonance of **1b** from 33.4 to 77.0 ppm. They are quite stable, conveniently handled at room temperature, and can be stored for several weeks in the refrigerator, either neat or as solutions in THF.

These carbanion initiators were utilized for polymerization of acrylonitrile. Dropwise addition of acrylonitrile to a THF solution of the initiator under nitrogen/argon atmosphere resulted in polymerization yielding poly(acrylonitrile) (PAN). Although the reaction could be performed at room temperature, cooling the reaction mixture to 0 °C provided a better control on the reaction exothermicity and hence molecular weights. The reaction proceeds almost quantitatively within 1 h. By mere variation of the monomer/initiator ratio, it is possible to control the molecular weight of the polymers to a predictable extent. The results on polymer yield, molecular weight, and reaction conditions for different initiators are summarized in Table I. A perusal of the data clearly reveals a close agreement between the calculated and observed molecular weights, thus manifesting the living nature of polymerization. However, PAN precipitates out of the reaction medium at a threshold value of ~10 000 molecular weight, thus limiting the synthesis of high molecular weight PANs in THF as solvent.

Scheme I
Synthesis of Functional Carbanion Initiators

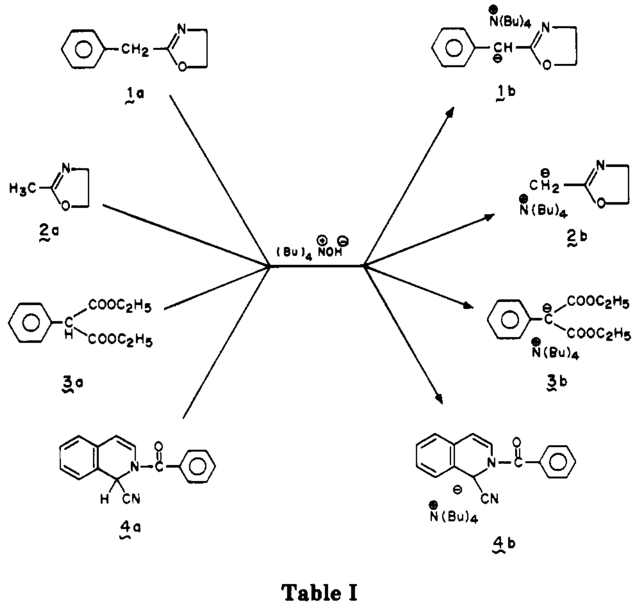

Table I
Polymerization of Acrylonitrile with Functional Carbanion Initiators[a]

entry no.	initiator	temp, °C	$\bar{M}_n$ obsd[b]	$\bar{M}_n$ calcd[c]
1	**1b**	0	1150	1010
2	**1b**	0	1310	1500
3	**1b**	0	1750	2000
4	**1b**	0	3180	2690
5	**2b**	0	1440	1510
6	**2b**	0	480	585
7	**3b**	27	1020	1090
8	**3b**	27	620	530
9	**3b**	27	770	790
10	**3b**	27	1230	1370
11	**3b**	27	1050	1110
12	**3b**	27	1670	1700
13	**3b**	27	1530	1320
14	**4b**	0	1490	1280
15	**4b**	0	1995	2020
16	**4b**	0	2995	2805
17	**4b**	0	3650	3330

[a] Polymerization was carried out by addition of neat acrylonitrile dropwise to a solution of initiator in THF under nitrogen/argon followed by stirring for 1 h. [b] By VPO or single-point viscosity measurement in DMF at 30 °C. [c] Calculated from the ratio of weight of monomer to initiator concentration.

The polymers obtained were subjected to molecular characterization by IR and ^1H and ^{13}C NMR spectral methods. The spectra reveal the presence of all the desired functional groups intact. The polymers were found to exhibit atactic stereochemical structures, as evidenced from ^{13}C NMR spectral data.

A few samples of PANs synthesized in THF using initiators **1b** and **3b** have been characterized by GPC for their polydispersity index. The PANs obtained in THF exhibit a polydispersity of 1.15–1.25 (Figure 1). To the best of our knowledge, PANs of such narrow polydispersities have never been reported in the literature.

The precise mechanism by which carbanions described in this paper lead to controlled polymerization of a very active vinyl monomer such as acrylonitrile is not well understood. It appears that matching the reactivity of the initiating and the propagating anion must be in some

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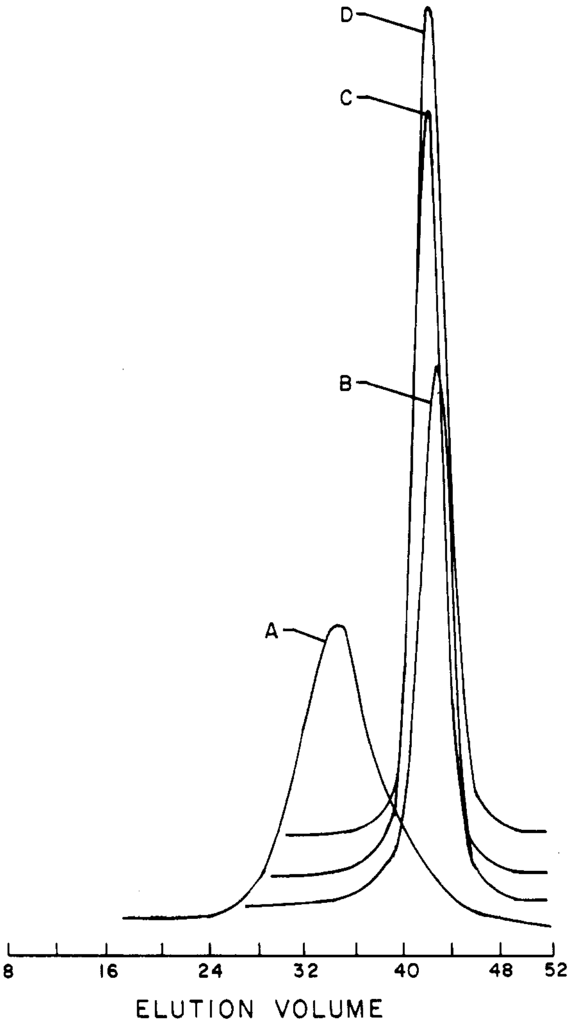

Figure 1. GPC of poly(acrylonitrile) prepared using (A) free-radical initiator, (B and D) $ArCH(CO_2Et)_2$ (**3b**), and (C) ArCHOxz (**1b**).

manner responsible for this observation. A more detailed description of the mechanism must await additional experimentation, which is presently in progress.

The polymerization method described herein offers the advantages associated with living chain ends. Also the reaction can be performed in a controllable manner in the temperature range of 0–30 °C. The functional groups bearing initiators enable incorporation of reactive terminal groups on the polymer chain, which can be further manipulated. These new initiators are also useful for controlled polymerization of acrylic ester monomers.[11]

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(10) The syntheses of carbanion salt **3b** from diethylphenyl malonate (DEPM) and **1b** from 2-benzyl-1,3-oxazoline (BO) are given as follows. Preparation of **3b**: In a three-neck 100-mL flask equipped with an argon inlet, dropping funnel, and a distillation unit was charged 7.7 mmol of TBAOH in 40 mL of dry toluene. DEPM (9.3 mmol) was slowly added at 75 °C, an azeotrope of toluene/water was distilled out slowly over a period of 3 h, and then vacuum 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 vacuo at room temperature and stored under argon. ^{1}H NMR ($CDCl_3$): δ 1.2 (6 H, $-OCH_2\mathit{CH}_3$), 4.15 (4 H, $-O\mathit{CH}_2CH_3$), 7.3 (5 H, aromatic), 1 (12 H, $-\mathit{CH}_3$), 1.1–1.9 (16 H, $-\mathit{CH}_2\mathit{CH}_2-$), 3.2–3.4 (8 H, $N\mathit{CH}_2-$). Preparation of **1b**: In a three-neck 100-mL flask equipped with a nitrogen inlet, rubber septum, and a thermometer was placed 2.5 mmol of BO in 50 mL of dry THF. TBAOH (2.5 mmol) was added dropwise, and reaction mixture was stirred at room temperature for 0.5 h. The temperature was then raised to 50 °C and maintained for 3 h. A deep red solution appeared. The reaction mixture was cooled to room temperature, solvent was evaporated under vacuum, and product was dried at 40 °C in vacuo. ^{13}C NMR ($CDCl_3$): δ 129–126.5 and 134.6 (aromatic), 77.0 ($-\mathit{C}H-$), 165.8 ($-N{=}CO-$), 53.5 ($=N\mathit{C}H_2-$), 67.2 ($-O\mathit{CH}_2-$), 58.4 ($=NCH_2-$), 23.6 ($-CH_2\mathit{C}H_2-$), 19.3 ($-\mathit{C}H_2CH_3$), 13.2 ($-CH_2\mathit{C}H_3$).

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