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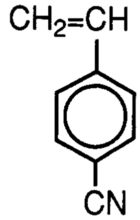
Anionic Polymerization of Monomers Containing Functional Groups. 2.[1] Anionic Living Polymerization of 4-Cyanostyrene

In recent years living polymerizations of a variety of monomers have been developed to give the polymers with controlled primary structures.[2] We have synthesized several functional polymers with predictable molecular weights and narrow molecular weight distributions through the anionic living polymerizations of protected monomers and deprotection of the resulting polymers.[2a] During our research, we have recently found an interesting fact that a series of styrene derivatives para-substituted with electron-withdrawing moieties, such as *N*-alkylimine,[3] oxazoline,[4] *N*,*N*-dialkylamide,[5] and ester,[6] afford anionic living polymers. Although these substituents on monomers and the polymer chains may be susceptible to nucleophilic attack, the anionic initiators and propagating chain ends did not react with these functional groups at all during the course of polymerization. For the explanation why the functional groups could coexist with carbanions of propagating terminals, we consider that the carbanions were stabilized by the electron-withdrawing effects of the substituents to produce the living polymer, avoiding the undesirable side reaction. From the crossover reactions of the living ends and various monomers, the lowered reactivities of propagating carbanions were in fact clarified.[4–6] Since a cyano group is a strongly electron-withdrawing moiety, 4-cyanostyrene might also have the possibility of living polymerization similar to the other styrenes. However, there have been no reports on the anionic polymerization of the monomer, whereas poly(4-cyanostyrene) was prepared with radical initiators.[7] In the present paper, we describe the results of anionic polymerization of 4-cyanostyrene (1)[8] and substantiate the formation of the living polymer.



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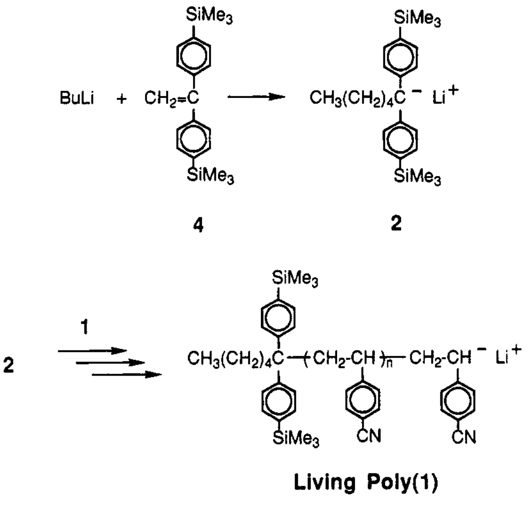
As anionic initiators, 1,1-bis[4′-(trimethylsilyl)phenyl]hexyllithium (2; Scheme I) and 1,1,4,4-tetrakis[4′-(trimethylsilyl)phenyl]butane dipotassium (3) are synthesized by the reactions of butyllithium with 1,1-bis[4′-(trimethylsilyl)phenyl]ethylene (4)[9] in THF/pentane and of potassium naphthalenide with 4 in THF, respectively, at −78 °C.[10] When the monomer 1 in THF was added to a rose red solution of the initiator at −78 °C, the color of the reaction mixture turned to dark red, which was maintained during the course of polymerization (2–12 h). After quenching with methanol, the polymer was isolated and purified by repeating reprecipitation into methanol to obtain white powder, which was soluble in DMF, DMSO, and acetone. The yields of the polymers were almost quantitative.

In IR spectrum of the polymer was observed the C≡N stretching absorption at 2230 cm^{-1}, which was observed in the same region as in the case of the monomer. The resonances due to vinyl group in ^{1}H and ^{13}C NMR spectra of the polymer completely disappeared, and the other signals corresponding to the repeating unit of poly(1) were observed.[11] The spectroscopic results indicate that the vinyl polymerization of 1 proceeds without side reactions.

Scheme I



For the accurate determination of the number-average molecular weights of the end-labeled poly(methyl methacrylate)s, ^{1}H NMR spectroscopy is proposed as a very useful method.[12] Accordingly, molecular weights of the poly(1)s were estimated from the relative NMR signal intensities of aromatic protons[13] on the main chain to trimethylsilyl ones, which were attached to the end and center of the polymer chains produced with mono- (2) and difunctional (3) initiators, respectively.[14] The observed $\bar{M}_n$s of poly(1), 33 000 ($\bar{M}_w/\bar{M}_n$ = 1.04) for no. 1 and 13 000 ($\bar{M}_w/\bar{M}_n$ = 1.07) for no. 2, agree well with the calculated ones, 30 000 and 12 000, based on the molar ratio of monomer to initiator in feed.[15] With use of several samples of the polymer, a calibration curve of gel-permeation chromatography for poly(1) in DMF was obtained. The produced polymers had unimodal and very narrow molecular weight distributions, where the polydispersity indices were in the range of 1.04–1.07.

To confirm persistency of propagating activity at the chain end, postpolymerization was carried out as follows: 1 was polymerized with cumylpotassium capped by 1,1-diphenylethylene in THF at −78 °C for 2 h to complete the reaction. For determination of $\bar{M}_n$ of the prepolymer, an aliquot was withdrawn from the reaction mixture, to which was again added 1 to continue further propagation and which was kept at −78 °C for 2 h. Both pre- and postpolymers were quantitatively isolated. Very good agreements were obtained between the observed molecular weights of the pre- and postpolymers, 9100 ($\bar{M}_w/\bar{M}_n$ = 1.09) and 16 000 ($\bar{M}_w/\bar{M}_n$ = 1.09), and the calculated ones, 8000 and 17 000. As shown in Figure 1, the GPC curve of the prepolymer clearly shifted toward that of the postpolymer in a higher molecular weight region without a shoulder at the elution count of the prepolymer. This indicates that the propagating chain end of poly(1) is stable and able to initiate further polymerization with quantitative efficiency.

The results obtained in this study, quantitative polymer yield, agreement of the measured and calculated $\bar{M}_n$s, narrow molecular weight distribution, and quantitative initiation efficiency in postpolymerization, substantiate that a stable living polymer of 4-cyanostyrene forms at −78 °C in THF without attacking the cyano group. In this way, 4-cyanostyrene is found to be a member of the styrenes

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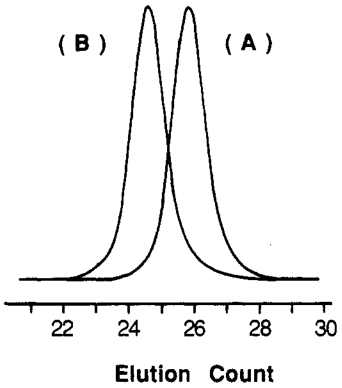

Figure 1. GPC curves of poly(1)s obtained at −78 °C: first polymerization (A), $\bar{M}_n$(obsd) = 9100, $\bar{M}_w/\bar{M}_n = 1.09$; second polymerization (B), $\bar{M}_n$(obsd) = 16 000, $\bar{M}_w/\bar{M}_n = 1.09$ (the second monomer was added 2 h after the first addition).

bearing electron-withdrawing groups, which afford the living polymers with stabilized active chain ends.

References and Notes

(1) The main title of the series of studies was decided to this one. Part 1: ref 5.

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(8) 4-Cyanostyrene was prepared by the one-pot reaction of 4-vinylbenzaldehyde with the hydroxylammonium chloride/pyridine/toluene system followed by azeotropic separation of water in 69% yield according to the literature method, see: Saednya, A. *Synthesis* **1982**, 190.

(9) 1,1-Bis[4′-(trimethylsilyl)phenyl]ethylene (**4**) was prepared by the reaction of [4-(trimethylsilyl)phenyl]magnesium chloride and ethyl acetate and the subsequent dehydration of the resulting alcohol in 66% yield according to the literature method. See: Allen, C. F. H.; Converse, S. *Organic Synthesis*; Wiley: New York, 1941; Collect. Vol. 1, pp 226. **4**: mp 112–113 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.23 (s, 18 H, $-SiCH_3$), 5.48 (s, 2 H, $CH_2{=}$), 7.26–7.55 (m, 8 H, aromatic).

(10) The 18 (initiator **2**) or 36 (initiator **3**) trimethylsilyl protons of these initiator residues in the polymers provide valuable probes for determining number-average molecular weights by ^{1}H NMR analyses.

(11) Poly(4-cyanostyrene): ^{1}H NMR (90 MHz, DMF-d_7) δ 1.4–2.5 (m, 3 H, $-CH_2CH-$), 6.7–7.7 (m, 4 H, aromatic); ^{13}C NMR (DMF-d_7) 40–44 ($-CH_2CH-$), 109.8 (Ar, Cl), 119.2 (−CN), 129.2 (Ar, C3), 132.6 (Ar, C2), 150.5 (Ar, C4). 4-Cyanostyrene: ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.45 and 5.87 (2d, 2 H, J = 11 and 18 Hz, $CH_2{=}$), 6.75 (dd, 1 H, $-CH{=}$), 7.43–7.68 (m, 4 H, aromatic); ^{13}C NMR (23 MHz, $CDCl_3$) δ 110.9 (Ar, C4), 117.6 (vinyl, $CH_2{=}$), 118.7 (−CN), 126.6 (Ar, C2), 132.2 (Ar, C3), 135.2 (vinyl, $-CH{=}$), 141.8 (Ar, Cl).

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(13) Nearly identical values of $\bar{M}_n$ also were obtained by using the relative intensity of methylene and methine protons on the polymer chain to trimethylsilyl ones within ±5%.

(14) Further addition reactions of **2** and **3** to remaining **4** in excess were not observed. Moreover, the propagating end of poly(**1**) caused no crossover reaction with **4** due to the low nucleophilicity, which indicated that the polymer contained no 1,1-bis[4′-(trimethylsilyl)phenyl]ethylene unit other than the initiator residue.

(15) In a typical procedure, to the rose red solutions of initiators (0.045 mmol of **2** in pentane/THF for no. 1, 0.059 mmol of **3** in THF for no. 2) were added THF solutions of **1** (10.3 mmol for no. 1, 5.36 mmol for no. 2) at −78 °C in all-glass apparatus equipped with break-seals under high-vacuum condition. The quantitative yields of poly(**1**)s were obtained after quenching.

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