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Notes

First Example of Anionic Polymerization with Azo-Containing Radical Initiators: Anionic Ring-Opening Polymerization of Cyclic Carbonate Initiated by Azobis(isobutyronitrile) and Related Azo Initiators

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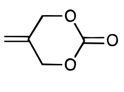
Azobis(isobutyronitrile) (AIBN) is one of the typical radical initiators widely used. Recently, in our continuing studies on radical ring-opening polymerizations,[1,2] we have found that *AIBN and related azo initiators cause anionic polymerization* of a cyclic carbonate under conditions universally applied to radical polymerizations.[3]

When 4-methylene-1,3-dioxan-2-one (**1**)[4] was heated at 80 °C for 4 h in the presence of 3 mol % of AIBN in chlorobenzene ([C] = 5 M) in a sealed tube, ca. 50% of **1** was consumed to give a polymer, which was collected by precipitation into ether, in 43% yield (M_{w}, 24 600; M_{n}, 8900; $M_{\mathrm{w}}/M_{\mathrm{n}}$, 2.76). The polymerization of **1** examined under various conditions [varying temperature (60−80 °C), time, solvent, and concentration] afforded similar results to the above one. Gelled polymer was formed in any bulk polymerization. However, the IR spectrum of this gelled polymer was nearly the same as that of the soluble polymer. The obtained polymer was suggested to mainly consist of a linear polycarbonate by its ^{1}H NMR, ^{13}C NMR, and IR spectra. IR showed both $\nu_{\mathrm{C=O}}$ at 1747 cm^{-1} and $\nu_{\mathrm{C-O}}$ at 1250 cm^{-1}. ^{1}H NMR indicated two major singlets at 5.37 and 4.68 ppm (Figure 1a). The chemical shifts of those signals were similar to those of the two kinds of methylene protons of the linear polycarbonate **2** obtained by the anionic polymerization of **1** with sodium methoxide (1 mol %) at 0 °C (Figure 1b).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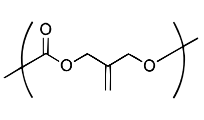
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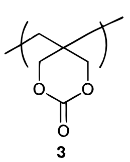
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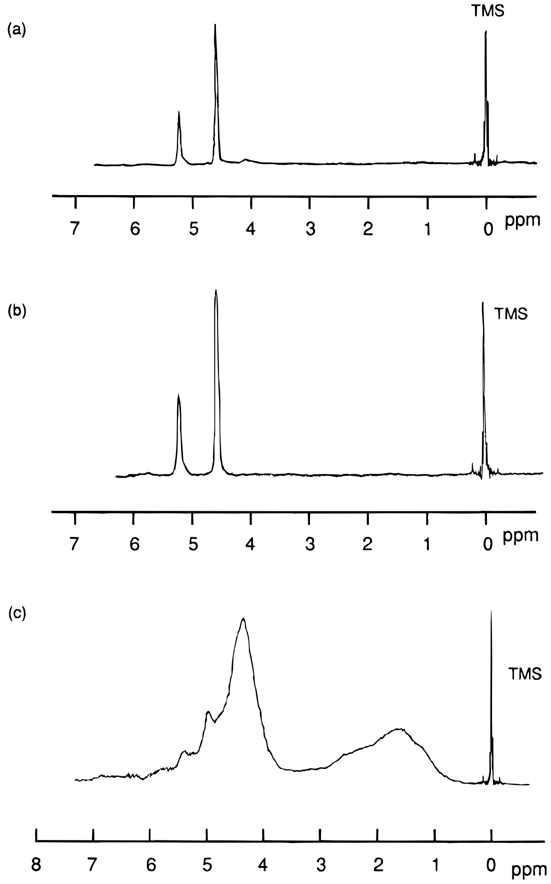

Figure 1. ^{1}H NMR spectra: (a) polymer **7** obtained by polymerization of **1** with AIBN (3 mol %) at 80 °C for 4 h in PhCl ([C] = 5 M), solvent of $CDCl_3$; (b) polymer **2** prepared by anionic polymerization of **1** with sodium methoxide (1 mol %) at 0 °C, solvent of $CDCl_3$; and (c) polymer **3** formed by polymerization of **1** with BPO (3 mol %) at 80 °C for 48 h in PhCl ([C] = 5 M), solvent of DMSO-d_6.

On the other hand, a completely different polymer was obtained in the polymerization of **1** with benzoyl peroxide (3 mol %) as initiator at 80 °C for 48 h in acetonitrile or chlorobenzene ([C] = 5 M). The polymer, precipitated during the polymerization (47% yield), shows $\nu_{\mathrm{C-O}}$ around 1150 cm^{-1} and $\nu_{\mathrm{C=O}}$ at 1751 cm^{-1} in the IR spectrum and two broad signals around 4.36 and 1.65 ppm in the ^{1}H NMR spectrum (Figure 1c). From these spectral data, the obtained polymer was suggested to correspond to a vinyl polymer (**3**). The polymer was not soluble in ordinary solvents such as dichloromethane, chloroform, dimethylformamide, etc. The results suggest that the radical polymerization of **1** affords structure-different polymers depending on the kind of initiator.

Analysis of the ^{1}H NMR (Figure 1) spectrum shows that the polymer formed with AIBN consists of two units, i.e., the ring-opening polymerization unit (X) and the vinyl polymerization unit (Y), in a ratio of 92:8. In order to clarify the polymerization behavior, the time-conversion curve[5] of the polymerization of **1** with AIBN (3 mol %) at 60 °C was measured (Figure 2). Figure 2 indicates an initial slow consumption of the monomer followed by a fast consumption after ca. 24 h. In similar experiments, X−Y ratio of the polymers obtained at low conversion[5] was estimated from the ^{1}H NMR spectra (Table 1 and Figure 3). The X−Y ratio clearly changes from 7:93 to 36:64 as the conversion of **1** increases from

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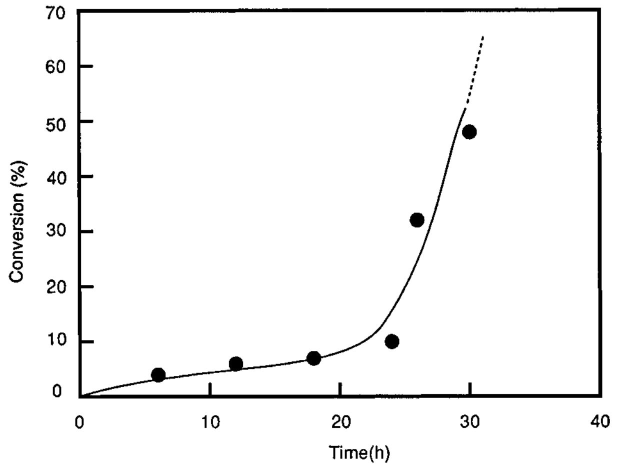


Figure 2. Time conversion curve of the polymerization of **1** with AIBN (3 mol %) at 60 °C in bulk.

Table 1. X−Y Ratio of the Polymer Obtained from the Polymerization of 1 with AIBN (3 mol %) at 60 °C in Bulk

run	time (h)	yield[a] (%)	X unit[b] (%)	Y unit[b] (%)
1	6	4	7	93
2	18	7	16	84
3	24	10	36	64

[a] Ether-insoluble part. [b] Determined by ^{1}H NMR spectra.

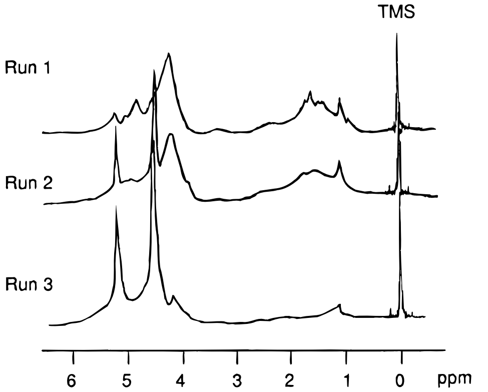
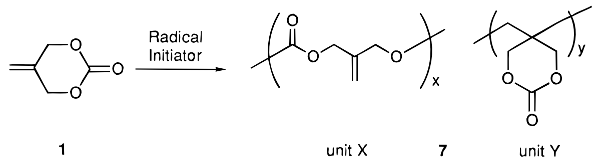
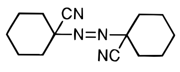


Figure 3. ^{1}H NMR change of the polymer obtained from the polymerization of **1** with AIBN (3 mol %) at 60 °C in bulk.

4% to 10%. These results strongly indicate that the polymerization of **1** involves both slow vinyl polymerization and fast ring-opening polymerization, giving polymer **7** with the two different base units. The vinyl polymerization takes place initially, but the ring-opening polymerization gradually predominates over the vinyl polymerization.



In order to examine the generality of this unique polymerization behavior, various radical initiators were employed. Azo initiators **4** and **5**[6] afforded results similar to that of AIBN, whereas di-*tert*-butyl peroxide (**6**) gave a result similar to that of BPO. Thus, the structure of the polymer from **1** varies depending on the type of radical initiator.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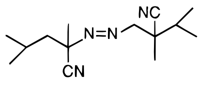
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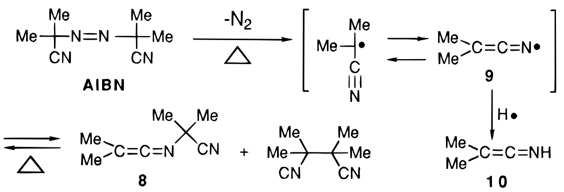
It is impossible to explain the initiator-dependent polymerization modes by assuming only radical ring-opening polymerization varied by initiator because the propagating end should be the same free radical. Meanwhile, **1** is known to undergo cationic and anionic polymerizations.[4,7] Possibility of ionic ring-opening polymerization was verified by experiments of effect of additives. When 2.3 mol % of dicyclohexylamine was added to the polymerization system (AIBN = 3 mol %, 60 °C, 24 h, chlorobenzene [C] = 5 M), the obtained polymer mainly contained the ring-opened unit (X) (yield 29%, unit ratio X:Y = 82:18) like the polymer produced under the conditions without the additive. In contrast, polymer mainly having the vinyl polymerization unit (Y) (yield 9.2%, X:Y = 10:90) was formed in the presence of 1.2 mol % of acetic acid under the same conditions. The results strongly suggests the occurrence of *anionic polymerization* but not a cationic one, in addition to radical polymerization, in this system. When the polymerization was quenched with excess chlorotrimethylsilane, the obtained polymer showed considerable incorporation of trimethylsilyl groups (0.2 ppm in its ^{1}H NMR spectrum). Furthermore, a cyclic carbonate without a vinylic group (5,5-dimethyl-1,3-dioxan-2-one) results in a copolymer with **1**, when it is added into the polymerization system of **1** and AIBN. Conceivable anionic species formed in this system would be ketenimine **8**[8] which is reported by Hammond[9,10] to be isolated as a thermal decomposition product of AIBN.[9] In addition to **8**, the *N*-unsubstituted ketenimine **10** might be a candidate,[11] since **10** has a nucleophilicity stronger than that of **8**. although the detailed mechanism of the polymerization with AIBN is not clear, the anionic polymerization of **1** might be initiated by the nucleophilic attack of **8** or **10** at the carbonyl carbon of **1**.[12]



Thus, this Note reports that *azo initiators such as AIBN are able to initiate anionic polymerization*, when a vinyl monomer capable of polymerizing readily with anionic initiator is used. Although the cationic polymerization with radical initiators in the presence of electron acceptors is reported,[13,14] this Note demonstrates the first example of anionic polymerization with typical radical initiators alone.

References and Notes

(1) (a) Suga, K.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1831. (b) Hiraguri, Y.; Sugizaki, T.; Endo, T. *Macromolecules* **1990**, *23*, 1.
(2) Part of this work has been reported; see: Kanamaru, M.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1991**, *40*, 35.
(3) Endo, T.; Yokozawa, T. Free-Radical Ring-Opening Polymerization. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Publishing Co.: London, 1992; Vol. 29, p 781.
(4) Takata, T.; Igarashi, M.; Endo, T. *Polym. Sci.*, Polym. *Chem. Ed.* **1991**, *29*, 781.

(5) Conversion of **1** was estimated from yield of the polymer because the yield was nearly corresponding to the conversion, namely, no low molecular weight polymer, other than monomer **1**, was detected in ether-soluble fraction by precipitation into ether.

(6) Both **4** and **5** are commercially available.

(7) Nemoto, H.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1990**, *39*, 284.

(8) In fact, **8** prepared by the reported method[9] served as polymerization initiator for **1** to give polymer **7** having the two different base units.

(9) Hammond, G. S.; Trapp, O. D.; Keys, R. T.; Neff, D. L. *J. Am. Chem. Soc.* **1959**, *81*, 4878.

(10) Hammond, G. S.; Wu, C. S.; Trapp, O. D.; Warkentin, J.; Keys, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 5394.

(11) **10** may be incipiently generated by hydrogen abstraction of **9**.

(12) ^{13}C NMR of the obtained polymer showed small carbonyl carbon signals at 172.1 and 176.3 ppm besides a carbonate carbonyl signal around 155 ppm. These two signals could be attributable to the initiation end which might consist of *N*-acylcarbamate structure formed by attack of a ketenimine at **1** followed by hydrolysis during workup. However, it is not clear which ketenimine (**8** or **10**) is more likely to be formed as the initiation species at the present time.

(13) Takakura, K.; Hayashi, K.; Okamura, S. *J. Polym. Sci., Part A-1* **1966**, *4*, 1731.

(14) Suga, S.; Nakajima, T.; Ishihara, T. *Nippon Kagaku Kaishi* **1972**, 477.

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