Notes

A Study of the Mechanism of the Free-Radical Ring-Opening Polymerization of 2-Methylene-1,3-dioxepane

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Introduction

Chain polymerizations, especially the free-radical polymerizations, of cyclic ketene acetals have recently evoked a lot of interest.[1−6] Bailey and co-workers studied the free-radical ring-opening polymerizations of different cyclic monomers, including the cyclic ketene acetal 2-methylene-1,3-dioxepane. The latter, in the presence of radical initiators, is reported to have undergone quantitative free-radical ring-opening polymerization to form poly(ϵ-caprolactone).[1] This is an important material whose biodegradability and medical applications have been widely studied and applied.[7]

The free-radical polymerization of cyclic ketene acetals can occur by two possible routes, leading to two different structures.[1] One is ring opening producing a polyester, and the other is ring retention producing a polyacetal (Scheme 1).[1] The extent of ring opening depends on the ring size and also the substituents on the ring. The free-radical polymerization of the monomer 2-methylene-1,3-dioxepane (MDO) was reported to proceed with 100% ring opening to form poly(ϵ-caprolactone).[1] The free radicals proposed in both the initiating and propagating steps were primary alkyl radicals (Scheme 2). Primary radicals are very reactive and are likely to undergo intramolecular hydrogen transfer (backbiting) to form more stable radicals.[8] Whether backbiting occurred during the free-radical polymerization of MDO has not been reported previously.

In this study, the mechanism of free-radical ring-opening polymerization of 2-methylene-1,3-dioxepane was examined by ^{1}H and ^{13}C NMR spectroscopy. The observed chemical shifts of H and C provided information on the chemical structure of the polymer. The analysis of the structure indicated intramolecular hydrogen transfers during propagation.

Experimental Section

The monomer 2-methylene-1,3-dioxepane (MDO) was synthesized as reported by Bailey et al.[1] The purity of the monomer was checked by GC−MS and found to be 99.99% pure. The polymerization was carried out neat in a 25 mL pressure tube at a temperature of 50 °C for 72 h using AIBN (2 mol %) as the initiator. After polymerization, chloroform was added to the tube to dissolve the polymer. The polymer was first precipitated by adding the chloroform solution into hexane and then filtered and dried under vacuum at 40 °C overnight. Commercial poly(ϵ-caprolactone) (PCL; MW = 100 000−200 000) was obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AF-500 NMR spectrometer. FT-IR spectra were obtained on a Nicolet 60SX FTIR spectrometer. Differential scanning calorimetry (DSC) of the polymers was performed using a TA Instrument, DSC 2929, in N_2 at a heating rate of 20 °C/min. GPC analysis was conducted in THF with a Waters 150-C ALC/GPC equipped

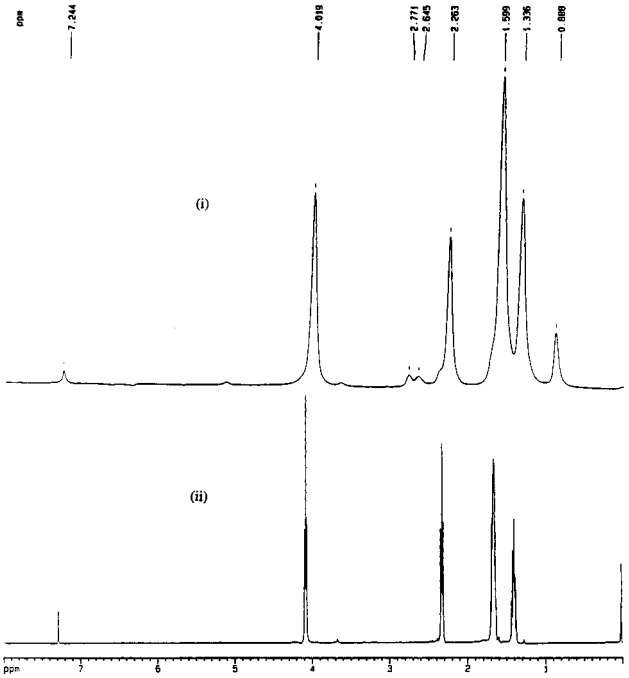
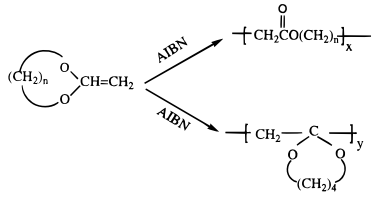


Figure 1. ^{1}H NMR spectra of polymers in $CDCl_3$: (i) P(MDO) and (ii) PCL.

Scheme 1. Free-Radical Polymerization of a Cyclic ketene Acetal



Scheme 2. Branch Formation in the Free-Radical Polymerization of 2-Methylene-1,3-dioxepane

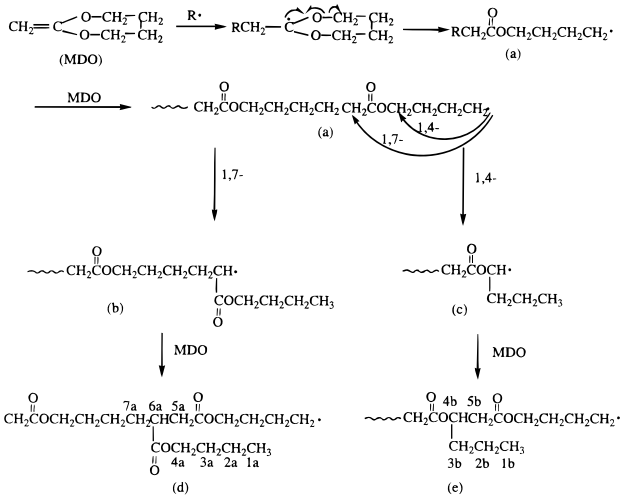


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Table 1. Chemical Shifts of Carbons in Branches of P(MDO)

	carbon atom position											
	1a	2a	3a	4a	5a	6a	7a	1b	2b	3b	4b	5b
chemical shifts (ppm)												
calcd	13.4	22.2	31.2	64.4	29.9	41.1	24.1	13.6	19.6	35.6	69.6	35.5
obsd	13.8	23.6	31.6	64.6	30.8	41.2	23.6	13.8	19.3	36.1	69.9	36.1

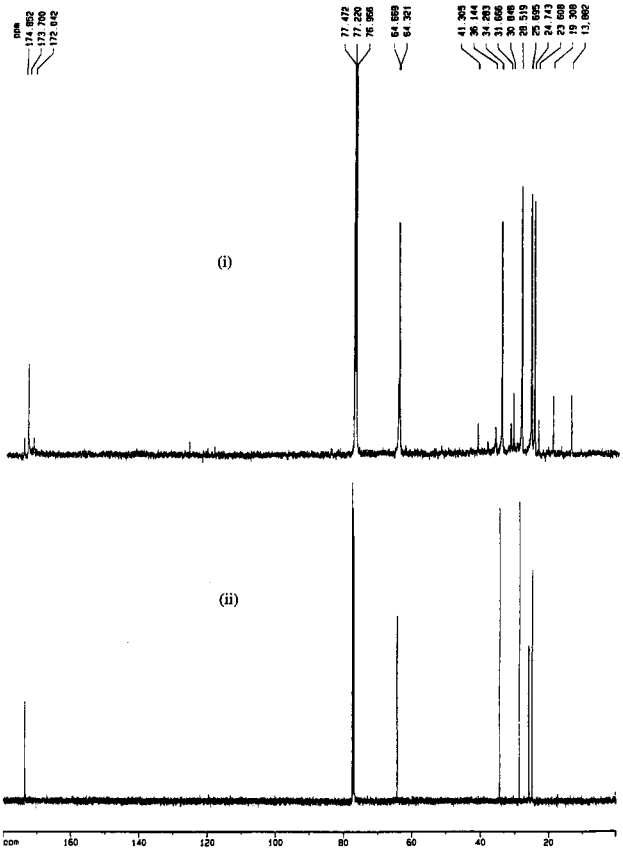

Figure 2. ^{13}C NMR spectra of polymers in $CDCl_3$: (i) P(MDO) and (ii) PCL.

with μ-styrene HT columns of 10^5, 10^5, 10^3, and 10^3 Å pore size at 35 °C and a flow rate of 1 mL/min. Narrow molecular weight polystyrene standards were used for calibration.

Results and Discussion

The chemical structure of P(MDO) was examined by IR and ^1H and ^{13}C NMR spectroscopy. The IR spectra of both polymers showed an ester peak at 1734 cm^{-1}. Figures 1 and 2 are the ^1H NMR and ^{13}C NMR spectra of the synthesized polymer P(MDO) and the commercial PCL, respectively. The major peaks of these two polymers are the same. However, the ^1H NMR of P(MDO) (Figure 1(i)) showed a peak at 0.89 ppm and two small peaks at 2.64 and 2.77 ppm. Also in the ^{13}C NMR spectrum of P(MDO) (Figure 2(i)), there is a peak as low as 13.8 ppm and several other small peaks. Commercial PCL has neither a peak at 0.89 ppm in the ^1H NMR spectrum nor a peak at 13.8 ppm in the ^{13}C NMR spectrum (Figures 1(ii) and 2(ii), respectively). Furthermore, the commercial polymer does not contain several of the other small peaks in ^{13}C NMR (Figure 2(ii)). The detailed NMR spectra of P(MDO) were exactly the same as the NMR spectra of poly(ϵ-caprolactone) synthesized in the same way by Bailey et al.,[1] indicating that the small peaks were not caused by any impurity. Also the chemical structure of the polymer synthesized by the free-radical ring-opening polymerization of MDO was reproducible. A chemical structure

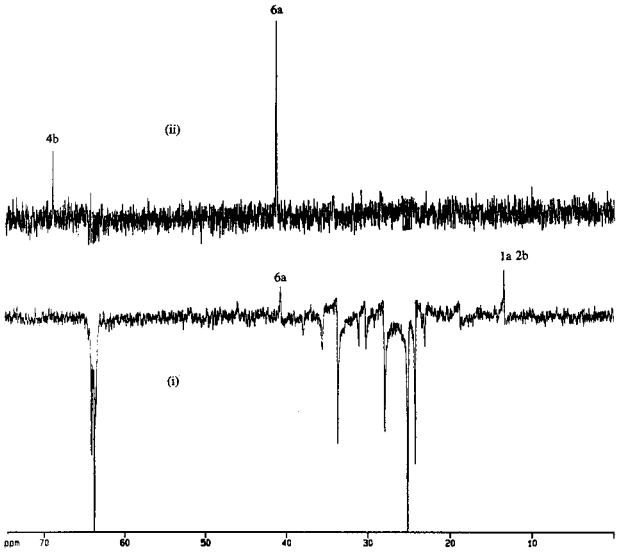

Figure 3. DEPT ^{13}C NMR spectra of P(MDO) in $CDCl_3$: (i) DEPT 135 and (ii) DEPT 90.

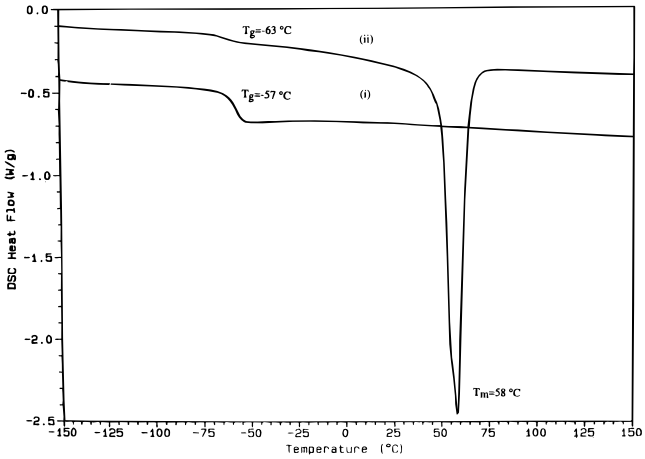

Figure 4. DSC thermograms for polymers: (i) P(MDO) and (ii) PCL.

for P(MDO) is proposed to elucidate the difference between the NMR spectra of the polymer P(MDO) and commercial PCL.

The structure of P(MDO) will depend on the polymerization mechanism of MDO, which is followed as depicted in Scheme 2. A primary alkyl radical (a) is produced in the initiation step and propagates, as outlined in Scheme 2. Primary alkyl radicals are very reactive and are likely to undergo intramolecular hydrogen transfers. Intramolecular hydrogen transfers are commonly observed in the radical polymerizations of some vinyl monomers such as ethylene. Only branched polyethylene can be obtained by free-radical polymerization reactions.[8] The predominant hydrogen transfer is a 1,5-shift which results from a stable six-membered transition state. 1,6-, 1,7-, and 1,8-H-transfers can also occur easily due to the relatively close activation energies and the transition state strains with respect to the 1,5-H-transfer.[9] A 1,4-H-transfer has an activation energy comparable to the 1,5-H-transfer.[9]

Other H-transfers have very little possibility due to unfavorable transition states. These calculations have not considered the stabilization of radicals by resonance.[8]

The free radical (a) in Scheme 2 will not undergo 1,5- or 1,6-H-transfer because of the presence of O and C=O in the skeleton. A 1,7-H-transfer will give a radical (b) (Scheme 2), which is stabilized by its neighboring carbonyl group.[8] The propagation of radical (b) will give radical (d) with a branched ester in the polymer structure. As listed in Table 1, the calculated chemical shifts[10] of all the carbons in the new ester unit (d) fit the observed chemical shifts in the ^{13}C NMR spectrum very well. This was further proved by the DEPT 135 and DEPT 90 ^{13}C NMR spectra (Figure 3). In DEPT 135, all CH_2 signals face downward and CH or CH_3 signals face upward. In DEPT 90, only CH signals can be recorded.[11] Methane carbons CH (6a) and CH_3 (1a) were distinguished from methylene CH_2 by DEPT 135 and DEPT 90 spectra, respectively. As shown in Scheme 2, more branches can be formed by further 1,7-H-shifts. A 1,4-H-transfer will give a free radical (c), which is not stabilized by resonance as radical (b), but the formation of radical (c) is possible. The activation energy of a 1,4-H-transfer is comparable to that of a 1,5-H-transfer, and the angle strain of the five-membered ring as the transition state is small.[9] The propagation of radical (c) gives radical (e) with a propyl branch. The calculated chemical shifts of the carbons in (e) also fit the observed chemical shifts in the ^{13}C NMR spectrum very well (Table 1). The carbon in CH (4b) was detected by DEPT 90, although it was not observed in DEPT 135 due to the small signal.

The molecular weight of P(MDO) was determined by GPC. The M_w and M_n of the polymer are 72 000 and 42 000, respectively. The branching density can be calculated from the ^1H NMR of P(MDO) using the integrals of CH_3 (0.89 ppm, from branch) and CH_2 (2.26 ppm, from linear polyester). The calculated branch density is 20%. The high branch density effects the crystallinity of the polymer. Unlike commercial PCL which has a very pronounced melting peak at 58 °C, the DSC profile of P(MDO) showed no T_m (Figure 4). Branching causes a disorder of the polymer structure and thus decreases the crystallinity.[12]

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