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Free Radical Ring-Opening Polymerization of 4,7-Dimethyl-2-methylene-1,3-dioxepane and 5,6-Benzo-2-methylene-1,3-dioxepane[1]

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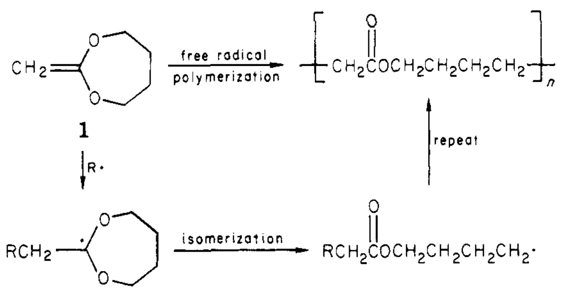
ABSTRACT: In order to extend the study of free radical ring-opening polymerization to include diverse structures and to determine the scope of the reactions, two cyclic ketene acetals, *cis-* and *trans*-4,7-dimethyl-2-methylene-1,3-dioxepane (**3**) and 5,6-benzo-2-methylene-1,3-dioxepane (**5**), were prepared by dehydrohalogenation. Free radical polymerizations of both monomers **3** and **5** were shown to proceed at 120 °C with essentially quantitative ring opening to produce the corresponding polyesters. Similarly, both monomers **3** and **5** were shown to copolymerize readily with styrene and methyl methacrylate to produce a copolymer containing ester linkages in the backbone of the addition polymer representing nearly quantitative ring opening. Both the increased stability of the ring-opened radical and the increase in steric hindrance to direct non-ring-opened polymerization are believed to promote the extent of free radical ring opening during polymerization.

Introduction

Although there are many examples of ionic ring-opening polymerization of cyclic monomers, ethylene oxide, tetrahydrofuran, caprolactam and caprolactone, and the Ziegler–Natta catalytic ring-opening polymerization of cyclic olefins, examples of free radical ring-opening polymerization are quite rare and have been limited to the dimer of *o*-xylylene,[3] vinylcyclopropane derivatives,[4] and the bicyclobutane monomers.[5] Recent work in these laboratories, however, has shown that a variety of heterocyclic monomers will undergo free radical ring-opening polymerization to put a functional group into the backbone of an addition polymer.[6–9]

In the course of searching for monomers that would undergo ring opening in free radical polymerization, a very interesting and promising result was observed.[10] Although the five-membered cyclic ethylene ketene acetal at 60 °C underwent polymerization by a free radical mechanism to give a polymer in which 50% of the monomer units had undergone ring opening,[8] the seven-membered cyclic ketene acetal 2-methylene-1,3-dioxepane (**1**), when polymerized with free radical initiator, underwent nearly complete ring opening and gave essentially pure poly(ϵ-caprolactone) (Scheme I).[10] In addition, while the ethylene ketene acetal was extremely sensitive to traces of acids,[8] the seven-membered cyclic monomer **1** was comparatively easy to handle and was convenient to polymerize with only normal precautions to avoid acid-catalyzed polymerization.[10] Acid-catalyzed polymerization of either ethylene ketene acetal or monomer **1** proceeds without ring opening. Also in the copolymerizations with several vinyl monomers, ester linkages representing quantitative ring opening were found in the backbone of the addition copolymers. These results clearly indicate the seven-membered cyclic ketene acetal polymerizes with almost quantitative ring opening by a free radical mechanism in both homo- and copolymerizations.

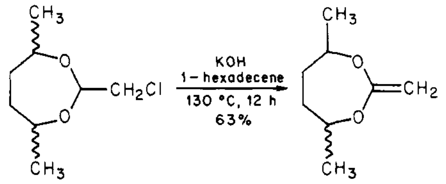
Scheme I



In the extension of this method to make polymers of diverse structures and to determine the scope of the ring-opening polymerization, two substituted seven-membered cyclic ketene acetals, 4,7-dimethyl-2-methylene-1,3-dioxepane (**3**) and 5,6-benzo-2-methylene-1,3-dioxepane (**5**), were synthesized and their free radical polymerizations were studied.

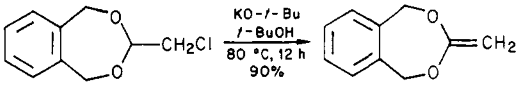
Monomer Preparation

Monomer **3** was synthesized by acetal exchange reaction of chloroacetaldehyde dimethyl acetal with 2,5-hexanediol, followed by base elimination to form a mixture of *cis-* and *trans*-4,7-dimethyl-2-methylene-1,3-dioxepane (**3**). A similar procedure was applied to the synthesis of monomer **5**. Chloroacetaldehyde dimethyl acetal was allowed to react with 1,2-benzenedimethanol to give **4**, which in turn was dehydrochlorinated to yield the corresponding 5,6-benzo-2-methylene-1,3-dioxepane (**5**) in good yield.



(1)

2 **3**



(2)

4 **5**

Results and Discussion

It was expected that both monomers **3** and **5** would undergo free radical polymerization with even a greater extent of ring opening than that of the parent monomer **1**. The extent of ring opening during polymerization is determined by the ratio of the rate of ring opening to the rate of addition of the unopened-ring radical to the monomer (Scheme II).[11] Although the seven-membered ring containing two oxygen atoms does not have a large strain, the relief of this strain will favor ring opening. The formation of the relatively stable ester group is a strong driving force for the ring opening and the relative stability of the resulting ring-opened radical is also a factor. Since the benzyl radical formed from monomer **5** and the secondary alkyl radical formed from monomer **3** are both more stable than the primary radical formed from monomer **1**, ring opening in both of the substituted monomers

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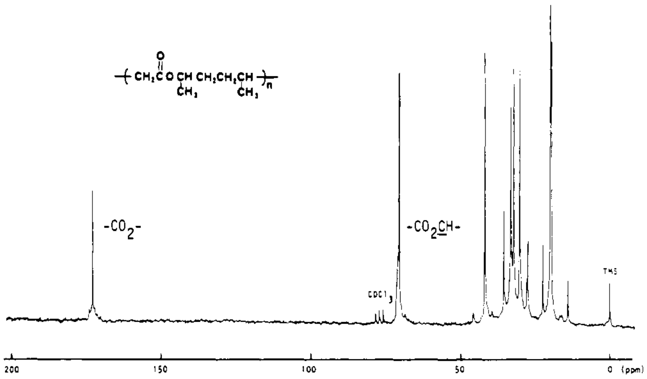


Figure 1. ^{13}C NMR spectrum of poly[ε-(β,ε-dimethyl)caprolactone].

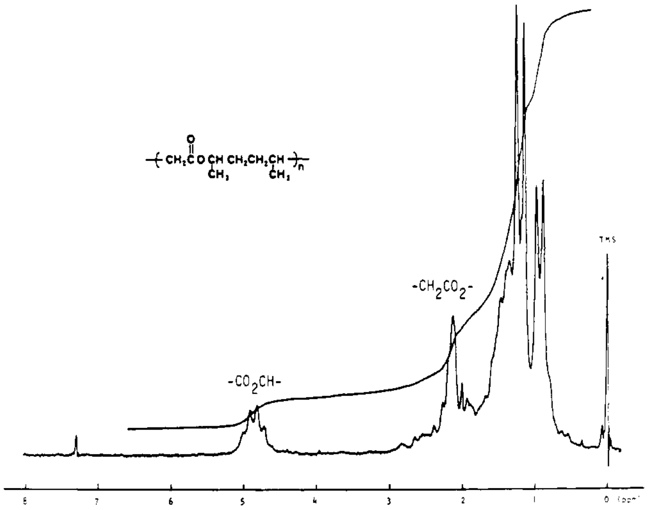
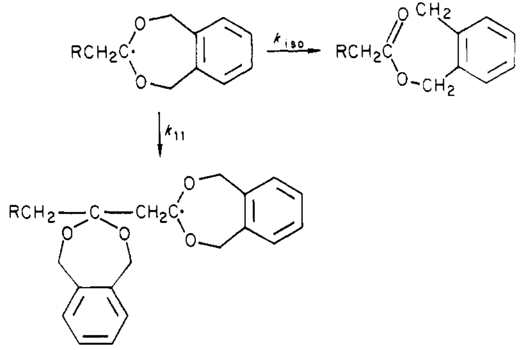


Figure 2. ^{1}H NMR spectrum of poly[ε-(β,ε-dimethyl)caprolactone].

Scheme II



would be even more favored. On the other hand, the seven-membered dioxepane ring produces more steric hindrance to the direct polymerization of monomers **1**, **3**, and **5** than in ethylene ketene acetal. The substituents in the non-ring-opened polymer from monomer **3**, even though they are not adjacent to the main polymer chain, contribute more steric hindrance than is present in the non-ring-opened polymer from monomer **1**, to favor the extent of ring opening during polymerization by slowing down the rate of the direct polymerization.

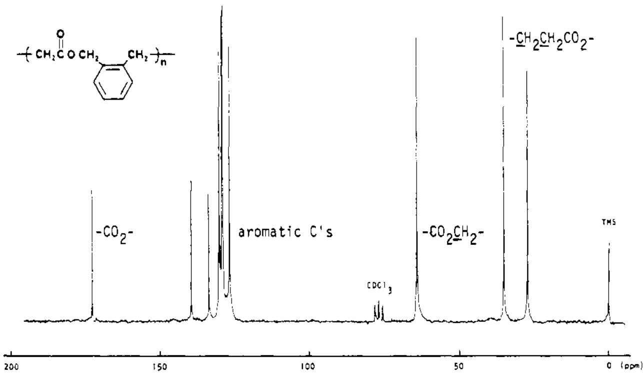


Figure 3. ^{13}C NMR spectrum of poly[ε-(γ,δ-benzo)caprolactone].

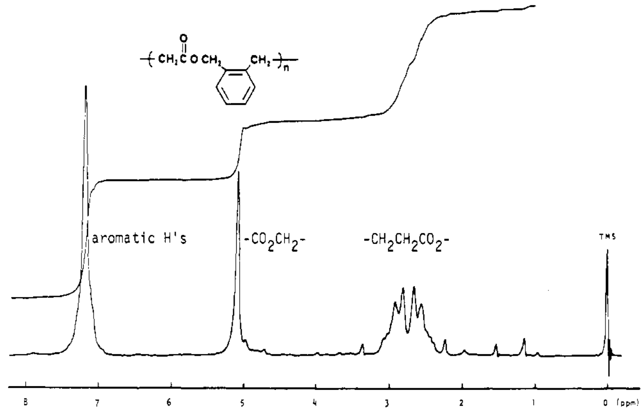
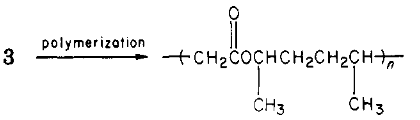
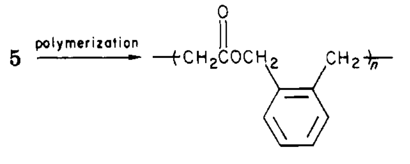


Figure 4. ^{1}H NMR spectrum of poly[ε-(γ,δ-benzo)caprolactone].

Monomer **3** was polymerized at 120 °C for 72 h in bulk with 2 mol % of di-*tert*-butyl peroxide (DTBP) as the free radical initiator. After purification, an 86% yield of a viscous liquid polymer was isolated. The presence of a signal in the ^{13}C NMR spectrum at δ 172.29 corresponding to the ester carbon and the absence of a peak around δ 100–110 corresponding to a ketal carbon (Figures 1 and 2) indicated that **3** had undergone almost quantitative ring opening to form the polyester. It was reasoned that the formation of the more stable secondary free radical intermediate during ring opening of **3** might make it even more prone to ring open than **1** during polymerization. Similarly, when **5** was polymerized with 2.5 mol % of DTBP at 120 °C for 15 h, a white solid polymer was isolated after purification. The presence of a peak in the ^{13}C NMR spectrum at δ 172.01 and the absence of a signal around δ 100–110 (Figures 3 and 4) showed that **5** also had undergone essentially quantitative ring opening.



$$\mathbf{3} \xrightarrow{\text{polymerization}} \left[CH_2\overset{\overset{O}{\|}}{C}O\underset{\underset{CH_3}{|}}{CH}CH_2CH_2\underset{\underset{CH_3}{|}}{CH}\right]_n \qquad (3)$$



(4)

Several vinyl monomers were chosen for copolymerization with monomer **3** and monomer **5**. The results are shown in Tables I and II. These results indicate that both of these monomers also had undergone quantitative ring opening during the copolymerization with various vinyl monomers.

Thus, it has been demonstrated that 2-methylene-1,3-dioxepane (**1**) and its derivatives **3** and **5** are very useful monomers that can be homo- or copolymerized with quantitative ring opening by a free radical mechanism to introduce the ester linkage into the backbone of an addition polymer. The incorporation of the ester group can be expected to change both the chemical and physical

Table I
Homopolymerization and Copolymerization of 3

comonomer[a]	polymerization conditions[b]	% polymer yield	mol % of 3 in copolymer[c]	% ring opening[d]	[η],[e] dL/g
none	2.0 mol % of DTBP, 120, 72	86		100	0.20
50 mol % of styrene	3.0 mol % of DTBP, 120, 72	62	27.2	100	0.21
50 mol % of methyl methacrylate	2.5 mol % of AIBN, 50, 48	40	24.1	100	0.72

[a] Comonomer in feed. [b] Initiator, temperature (°C), polymerization time (h). [c] From elemental analysis and ^{1}H NMR study. [d] From ^{1}H and ^{13}C NMR studies. [e] Measured at 30 °C with benzene as the solvent.

Table II
Homopolymerization and Copolymerization of 5

comonomer[a]	polymerization conditions[b]	% polymer yield	mol % of 5 in copolymer[c]	% ring opening[d]	[η],[e] dL/g
none	2.5 mol % of DTBP, 120, 15	43		100	0.10
52 mol % of styrene	2.5 mol % of DTBP, 120, 42	69	31.1	100	0.14
50 mol % of 4-vinylanisole	3.4 mol % of DTBP, 120, 42	72	32.6	100	0.14
49 mol % of methyl methacrylate	1.0 mol % of AIBN, 50, 45	46	13.2	100	0.25

[a] Comonomer in feed. [b] Initiator, temperature (°C), polymerization time (h). [c] From elemental analysis and ^{1}H NMR study. [d] From ^{1}H and ^{13}C NMR studies. [e] Measured at 30 °C with benzene as the solvent.

properties of the copolymers.

Experimental Section

2-(Chloromethyl)-4,7-dimethyl-1,3-dioxepane (2). A mixture of 50 g (0.4 mol) of chloroacetaldehyde dimethyl acetal and 47.3 g (0.4 mol) of 2,5-hexanediol was heated at 120 °C with 0.5 g of Dowex 50 (H^+) resin in a 200-mL flask equipped with a 10-cm Vigreux column. After about the calculated amount of methanol had been collected by distillation, the resin was removed by filtration. The crude product was then fractionally distilled through a 10-cm Vigreux column to afford 53 g (74%) of a mixture of *cis*- and *trans*-**2**: bp 79–80 °C (4 mm); IR (neat) 2960, 2930, 2830, 1125, 1065, 760 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.17, 1.27 (2 s, 6 H, 2 CH_3), 1.60–1.86 (m, 4 H, CH_2CH_2), 3.45 (d, 2 H, J = 5.0 Hz, CH_2Cl), 3.70–4.25 (broad, 2 H, 2 OCH), 4.64–5.03 (m, 1 H, OCHO). Anal. Calcd for $C_8H_{15}ClO_2$: C, 53.76; H, 8.47; Cl, 20.03. Found: C, 53.85; H, 8.75; Cl, 20.03.

***cis*- and *trans*-4,7-Dimethyl-2-methylene-1,3-dioxepane (3).** A mixture of 9 g (0.05 mol) of *cis*- and *trans*-2-(chloromethyl)-4,7-dimethyl-1,3-dioxepane (**2**) and 20 g of KOH in 20 mL of 1-hexadecene was heated at 130 °C for 12 h. After product was separated from the mixture by distillation under partial vacuum, it was further purified by distillation from metallic sodium to afford 4.5 g (63%) of a mixture of *cis*- and *trans*-**3**: bp 49–50 °C (4 mm); IR (neat) 3140, 2975, 2930, 1660 (s), 1260, 1050 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.20, 1.32 (2 s, 6 H, 2 CH_3) (cis and trans isomers, about 1:1 ratio), 1.46–1.86 (m, 4 H, CH_2CH_2), 3.42 (s, 2 H, $CH_2{=}C$), 3.65–4.33 (broad, 2 H, 2 OCH); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 22.26, 35.50, 76.87 (6 C,$\mathit{C}H_2\mathit{C}H(\mathit{C}H_3)O$), 67.07 ($\mathit{C}H_2{=}C$), 162.84 ($CH_2{=}\mathit{C}$). Anal. Calcd for $C_8H_{14}O_2$: C, 67.55; H, 9.93. Found: C, 67.75; H, 10.20.

2-(Chloromethyl)-5,6-benzo-1,3-dioxepane (4). A mixture of 50 g (0.4 mol) of chloroacetaldehyde dimethyl acetal and 55 g (0.4 mol) of 1,2-benzenedimethanol in 100 mL of 2-methoxyethyl ether was heated at 120 °C with 0.5 g of Dowex 50 (H^+) resin in a 250-mL flask equipped with a 30-cm Vigreux column. The methanol was collected slowly over a period of 24 h. After removal of the resin by filtration while the solution was hot, most of the solvent was removed by distillation under partial vacuum. The residue was then recrystallized from benzene to yield 38 g (48%) of colorless needles of **4**: mp 92.5–93.5 °C; IR (KBr) 3080, 3040, 2960, 2870, 1130, 1035, 765, 730 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.67 (d, 2 H, J = 5.0 Hz, CH_2Cl), 4.93 (s, 4 H, 2 OCH_2), 5.07 (t, 1 H, OCHO), 7.23 (s, 4 H, aromatic H's). Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.44; H, 5.59; Cl, 17.86. Found: C, 60.70; H, 5.65; Cl, 17.96.

5,6-Benzo-2-methylene-1,3-dioxepane (5). In a 250-mL flask 9.8 g (0.05 mol) of 2-(chloromethyl)-5,6-benzo-1,3-dioxepane (**4**) in 100 mL of *t*-BuOH was allowed to react with 6.2 g (0.055 mol) of *t*-BuOK at 80 °C overnight under a nitrogen atmosphere. After the addition of 200 mL of ether, the precipitate was removed by filtration and the solvents were removed by distillation under reduced pressure. The residue was vacuum distilled from metallic sodium to give 7.2 g (90%) of **5**, which solidified on standing: mp 43–44 °C; bp 51 °C (0.1 mm); IR (neat) 3060, 3030, 2980, 2930, 2870, 1680 (s), 1265, 1070, 1030, 740 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.70 (s, 2 H, $CH_2{=}C$), 5.05 (s, 4 H, 2 OCH_2), 6.90–7.40 (m, 4 H, aromatic H's); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 69.36 ($\mathit{C}H_2{=}C$), 71.77 (OCH_2), 125.92, 127.1, 135.62 (aromatic C's), 164.01 ($CH_2{=}\mathit{C}$). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: 73.81; H, 6.32.

Homopolymerization of *cis*- and *trans*-4,7-Dimethyl-2-methylene-1,3-dioxepane (3). In a 10-mL sealed polymerization tube 1.2 g of **3** was heated at 120 °C for 72 h with 2 mol % of di-*tert*-butyl peroxide (DTBP) as the initiator. After the reaction mixture was dissolved in CH_2Cl_2, the solution was added dropwise into a vigorously stirred hexane solution to give a viscous liquid precipitate. After the liquid was dried in vacuo at 100 °C overnight, 1.03 g (86%) of a viscous liquid polymer was obtained: [η] = 0.20 dL/g at 30 °C in benzene; IR (neat) 2955, 2930, 1725 (s), 1175 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.73–1.75 (broad, 11 H, $CO_2CH(CH_3)CH_2CH_2CH(CH_3)$), 1.80–2.73 (broad, 2 H, CH_2CO_2), 4.60–5.20 (m, 1 H, CO_2CH); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 19.56, 19.90, 30.23, 32.26, 33.18, 41.95 ($\mathit{C}H_2CO_2CH(\mathit{C}H_3)\mathit{C}H_2\mathit{C}H_2\mathit{C}H(\mathit{C}H_3)$), 70.69 ($CO_2\mathit{C}H$), 172.29 ($CO_2$). Anal. Calcd for $(C_8H_{14}O_2)_x$: C, 67.55; H, 9.93. Found: C, 67.99; H, 10.20.

Homopolymerization of 5,6-Benzo-2-methylene-1,3-dioxepane (5). In a 10-mL sealed polymerization tube 1.15 g of **5** was heated with 2.5 mol % of di-*tert*-butyl peroxide at 120 °C for 15 h. After the tube was cooled and opened, the mixture was dissolved in CH_2Cl_2. This solution was then added to hexane to precipitate the polymer, which was dried in vacuo at 70 °C overnight to give 0.5 g (43%) of a white powdery polymer: [η] = 0.10 dL/g at 30 °C in benzene; IR (film) 3060, 3020, 2960, 1730 (s), 1150, 750 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.30–3.15 (broad, 4 H, $CH_2CH_2CO_2$), 5.07 (s, 2 H, CO_2CH_2), 7.17 (s, 4 H, aromatic H's); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 27.24, 35.22 ($\mathit{C}H_2\mathit{C}H_2CO_2$), 64.20 ($CO_2\mathit{C}H_2$), 126.42, 128.65, 128.91, 129.82, 133.35, 139.18 (aromatic C's), 172.01 (CO_2). Anal. Calcd for $(C_{10}H_{10}O_2)_x$: C, 74.05; H, 6.22. Found: C, 73.83; H, 6.40.

Copolymerization of 5,6-Benzo-2-methylene-1,3-dioxepane (5) with Methyl Methacrylate. In a 10-mL sealed polymerization tube, a mixture of 1.0 g (6.17 mmol) of **5**, 0.605 g (6.05 mmol) of methyl methacrylate, and 1.0 mol % of azobis(isobutyronitrile) (AIBN) was heated at 50 °C for 45 h. After the tube was opened, the mixture was dissolved in $CHCl_3$. After this solution was added to hexane to precipitate the copolymer, the collected solid was dried in vacuo at 70 °C overnight to give 0.74 g (46%) of a white solid copolymer: IR (KBr) 3020, 2980, 2940, 1735 (shoulder), 1720 (s), 1140, 745 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.60–1.40 (broad, $CH_2C(CH_3)$), 1.40–2.20 (broad, $CH_2C(CH_3)$), 2.20–2.90 (broad, CH_2CO_2 and $C_6H_4CH_2$), 3.70 (CO_2CH_3), 5.05 (CO_2CH_2), 7.20 (aromatic H's); ^{13}C NMR (25.2 MHz, $CDCl_3$)[12] δ 16.56, 18.80, 21.49 (CH_3), 26.86 (CH_2CO_2), 34.79, 40.42 ($C_6H_4CH_2$), 44.52 (CCO_2CH_3), 51.69 (CO_2CH_3), 54.33 ($CH_2C(CH_3)$), 63.85 (CO_2CH_2), 126.22, 128.63, 129.30, 129.67, 132.94, 140.24 (aromatic C's), 169.81 (CH_2CO_2), 177.55 (CO_2CH_3). Anal. Calcd for $(C_{10}H_{10}O_2)_{0.132}$-$(C_5H_8O_2)_{0.868}$: C, 62.76; H, 7.69. Found: C, 62.77; H, 7.63.

Similar procedures were applied to the syntheses of other copolymers and the identification of their structures.

References and Notes

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Absolute Rate Constants for the Free Radical Polymerization of Ethylene in the Supercritical Phase

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ABSTRACT: The absolute rate constants for propagation, k_p, and for termination, k_t, were determined for the free radical polymerization of ethylene in supercritical solutions at 130 °C and about 1800 kg/cm^2 using the rotating sector method. Under these conditions, k_t was found to equal 2.0×10^8 L (mol s)$^{-1}$ and k_p to equal 5.4×10^3 L (mol s)$^{-1}$. The magnitude of $k_p k_t^{-1/2}$ calculated from these values is in reasonable agreement with literature values based on isothermal polymerization rates. The value of k_t found in this study, 2×10^8 L (mol s)$^{-1}$, is well within an order of magnitude of values reported for the polymerization of ethylene as saturated liquid and in benzene solution at low pressure. This result cannot be readily accounted for if the termination rate is controlled by segmental diffusion of the polymer chain at a rate controlled by the solvent viscosity.

I. Introduction

Recent compilations[1] of the individual rate constants for propagation, k_p, and for termination, k_t, in vinyl polymerizations contain entries for some monomers other than those listed in earlier summaries.[2] The only published results pertaining to these constants for ethylene appear to be in the publications by Rabel and Ueberreiter,[3] who studied the polymerization of saturated liquid ethylene at about −20 °C, and by Laita and Machacek,[4] who studied the polymerization of ethylene in benzene at 83 °C as a two-phase gas–liquid mixture at pressures well below those required to form a homogeneous solution of the reactants. It seemed desirable to study the polymerization of ethylene in the homogeneous supercritical phase, i.e., at a temperature above about 115 °C and at pressures above about 1500–1900 kg/cm^2, to ensure the miscibility of monomer and polymer at all conversions[5] and so to avoid kinetic complications associated with heterogeneous polymerization. Choice of these conditions also made it possible to perform our experiments within, or very close to, the operating range of most high-pressure reactors producing low-density polyethylene.

At the temperature chosen for these experiments, 130 °C, the rate of polymerization of ethylene initiated thermally is negligible[6] and initiation by oxygen can be avoided if the oxygen content of the ethylene can be kept below several ppm.[5] In principle, therefore, the rotating sector method of intermittent illumination[7] with a photoinitiator should be applicable.

It will be recalled[2,7] that the rotating sector method involves the independent determination of radical lifetimes, τ, polymerization rates under steady illumination, $(R_p)_s$, and initiation rates, R_i. Measurement of the first of these parameters, τ, posed the main difficulty, inasmuch as the reactor chosen was a constant-volume reaction cell in which the reaction rate was monitored by the rate of pressure drop, $\Delta p/\Delta t$. This required use of a leak-free reaction cell and the minimization, or correction, of factors causing pressure changes other than that brought about by the isothermal polymerization induced by the photodecomposition of the initiator. Beyond the correction for deviations from isothermal conditions, this implied use of

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