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HOMOPOLYMERIZATION OF 1,3-DIOXAN-2-ONE TO HIGH MOLECULAR WEIGHT POLY(TRIMETHYLENE CARBONATE)

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ABSTRACT

1,3-Dioxan-2-one was synthesized from 1,3-propanediol and diethyl carbonate by using either sodium ethoxide or stannous 2-ethylhexanoate as the transesterification catalyst. The latter method gave the monomer in a yield of over 50%. 1,3-Dioxan-2-one was polymerized by ring-opening polymerization to poly(trimethylene carbonate) by using cationic and anionic initiators. The conditions were varied with different solvents and without solvent, and with different reaction temperatures, different reaction times, and different atmospheres. Polymerization in solution gave mixtures of oligomers and polymers with molecular weights less than 50,000. Bulk polymerization, especially at higher temperatures, and preferably using $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as initiator, gave poly(trimethylene carbonate) with a molecular weight in excess of 100,000. Higher reaction temperatures gave a higher molecular weight and a faster polymerization rate, but excessive heating caused thermal degradation of poly(trimethylene carbonate). The new, high molecular weight poly(trimethylene carbonate) has a rubbery character at room temperature with a glass transition temperature of -17°C . It was found that the polymer contained 2.6% ether linkages formed by decarboxylation during polymerization at high temperatures.

INTRODUCTION

Literature reports concerning the homopolymer of the six-membered cyclic carbonate 1,3-dioxan-2-one (1) (Fig. 1) are rather few in number. In the 1930s, Carothers et al. [1, 2] studied 1,3-dioxan-2-one and established that the cyclic monomer (1) polymerized on heating with small amounts of potassium carbonate as initiator. The molecular weight of the polymer obtained by this method was, however, low, about 4000. In a more recent publication by Kricheldorf and Jenssen [3], the cationic polymerization of 1,3-dioxan-2-one was studied by ring-opening polymerization in solution, but the molecular weights were also less than 6000. Kricheldorf et al. proposed a mechanism for the polymerization and for a possible side reaction during the polymerization. Thermal degradation of poly(trimethylene carbonate) (2) was studied by McNeill and Rincon [4]. Compound (2) was prepared by polymerization of (1) in a melt at 150°C with potassium carbonate as initiator in a nitrogen atmosphere to a molecular weight of less than 4000. Degradation products reported were the monomer and low molecular weight oligomers. The authors also proposed mechanisms for the degradation.

There are other ways to prepare poly(trimethylene carbonate) (2). Baba and coworkers [5, 6] used a route in which carbon dioxide was alternating copolymerized with the four-membered cyclic ether oxetane. Organotin compounds were used as initiators for this copolymerization, and only low molecular weight polymers were obtained. One drawback of this alternating copolymerization is that it is difficult to achieve a perfectly alternating copolymer. Poly(oxetane) units are also incorporated in the polymer, giving a copolymer of poly(oxetane) and poly(trimethylene carbonate). These workers also polymerized the cyclic carbonate (1) at 100°C for a 4-h period in a CO₂ atmosphere; Bu₂SnI₂ and Bu₂SnI₂·Bu₃P were used as initiators, giving molecular weights of 2100 and 4250, respectively.

It has been shown that cyclic carbonates can be polymerized with the same type of initiators as lactones [7, 8]. Mechanisms for the polymerization of substituted cyclic carbonates have been studied by Kricheldorf et al. [3, 7] (cationic) and by Höcker et al. [8, 9] (anionic).

We earlier reported our work on the synthesis and characterization of aliphatic polyesters based on the cyclic monomer 1,5-dioxepan-2-one (DXO) [10, 11] and of aliphatic polyanhydrides based on the cyclic anhydride oxepan-2,7-dione [12]. As an additional line of research in the field of biodegradable polymers, we are now focusing our attention on aliphatic polycarbonates as possible systems with which to obtain useful biodegradable polymers for medical applications. The search for new materials with tailor-made properties is still of very great interest [13].

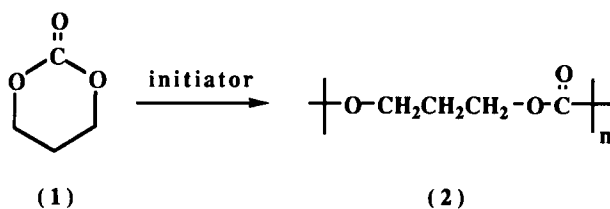


FIG. 1. Ring-opening polymerization of 1,3-dioxan-2-one (1).

The object of this work was to study the ring-opening polymerization of the cyclic carbonate 1,3-dioxan-2-one (Fig. 1) into high molecular weight polymer, and to show how the polymerization results depend on parameters such as temperature and reaction time in the cases of solution and bulk polymerizations using cationic and anionic polymerization mechanisms.

EXPERIMENTAL

Materials

The chemicals used in this work, 1,3-propanediol (p.a.) (Merck-Schuchardt) and diethyl carbonate (GC 99%) (Aldrich Chemie) were used as received.

The initiators used were boron trifluoride etherate ($\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) (p.a.) (Merck-Schuchardt), stannous 2-ethylhexanoate (Sn-oct) (p.a.) (Sigma Chemical comp.), potassium acetate ($\text{CH}_3\text{COO}^-\text{K}^+$) (p.a.) (Fischer Scientific Allied Comp.), 18-crown-6 ether (p.a.) (Merck-Schuchardt), potassium carbonate (K_2CO_3) (p.a.) (Merck, Darmstadt), sodium hydride (NaH) (with 20% paraffin) (Merck-Schuchardt), aluminum trichloride (AlCl_3) (anhydrous, 98%) (Aldrich Chemie), dibutyl tin oxide ($(\text{C}_4\text{H}_9)_2\text{SnO}$) (98%) (Aldrich Chemie), and aluminum isopropoxide (Aldrich Chemie).

The solvents used were ethanol (99.5%) (Kemetyl, Sweden), toluene (p.a.) (May & Baker Ltd.), dichloromethane (CH_2Cl_2) (p.a.) (May & Baker Ltd.), diethylether (p.a.) (Merck, Darmstadt), 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) (anhydrous, +99%) (Aldrich Chemie), and deuterated chloroform (CDCl_3) with 1 wt% TMS (Aldrich Chemie). Dichloromethane was distilled over calcium chloride (CaCl_2), and aluminum isopropoxide (Aldrich Chemie) was distilled under reduced pressure (27°C at 10 mmHg). All other chemicals were used as received.

Measurements

The polymers were characterized by gel permeation chromatography (GPC), viscosity measurements, ^1H nuclear magnetic resonance spectroscopy (^1H NMR), and differential scanning calorimetry (DSC).

The GPC system consists of a Waters 510 pump, five μ -Styragel columns (500, 10^3 , 10^4 , 10^5 , 100 Å) and a Waters Differential Refractometer 410. An automatic injector (WISP 710 B) was used. Tetrahydrofuran was used as eluant with a flow rate of 1 mL/min, and the measurements were performed at 30°C. Polystyrene standards ($M_w/M_n < 1.06$) were used for calibration. Intrinsic viscosities were measured in CHCl_3 at 25°C by using a Ubbelohde viscometer.

The ^1H -NMR spectra were obtained by using a Bruker AC-250 FT-NMR spectrometer. The samples were measured in a solution of deuterated chloroform (CDCl_3) with tetramethylsilane as internal standard ($\delta = 0$ ppm). The percentage of ether linkages in the polymer was calculated from the area of the peaks.

The differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC-7. The spectra were taken at the second scan after a cooling rate of 40°C/min with a heating rate of 10°C/min. Indium was employed as a temperature calibration standard.

Monomer Synthesis

Two different methods were used to synthesize the 1,3-dioxan-2-one monomer.

The first was a slightly modified version of a transesterification reaction earlier described by Carothers and Van Natta [1]. To a carefully dried three-necked round-bottomed flask, 130 g (1.1 mol) diethyl carbonate, 76 g (1.0 mol), 1,3-propanediol, and a solution of 0.5 g sodium dissolved in 8 mL ethanol (99.5%) were added. The mixture was allowed to boil with constant stirring at a temperature below 80°C (oil bath temperature 110–140°C) for 8 h. Ethanol was collected in the receiver. The mixture was allowed to cool to room temperature and an equal amount of toluene was added. The organic phase was washed once with acidified water (1 vol% HCl) and twice with water and dried over magnesium sulfate (MgSO₄). Toluene was removed and the residue was distilled under 0.6 mmHg pressure. After an initial fraction of diethyl carbonate, crude (1) distilled at 94°C which solidified in the receiver. The solid was dissolved in warm toluene (50°C) and precipitated in cold diethyl ether. The resulting white crystals were dried in vacuum at 10 mmHg, room temperature over silica gel. Yield: 38%.

The second method was similar to the first. Diethyl carbonate (118 g) and 1,3-propanediol (76 g) were used in equal molar portions (1.0 mol) and stannous 2-ethylhexanoate (20 g, 5 mol%) was used as the transesterification catalyst. The reactants were allowed to reflux for 8 h and the mixture was allowed to cool after the removal of ethanol. No work-up was needed and the thermal degradation of the prepolymer was performed by vacuum distillation and the crude monomer was recrystallized as before. Yield: 53%.

The crude compound (1) showed the following characteristics: boiling point 94°C at 0.6 mmHg; ¹H-NMR chemical shifts are shown in Table 1; melting point for recrystallized (1): 50°C.

Polymerization

The polymerizations were carried out in dry 25 mL serum bottles containing a magnetic stirring bar. The monomer (1) was added to these vials in an amount of 2 g (19.6 mmol) together with 0.08 mmol of the initiator. The initiators used were BF₃O(C₂H₅)₂ (10 μL), AlCl₃ (11.0 mg), stannous 2-ethylhexanoate (32.4 mg), dibutyl

TABLE 1. ¹H-NMR Shifts for 1,3-Dioxan-2-one, Poly(Trimethylene Carbonate) and Poly(Oxetane) Recorded in CDCl₃

Compound	δ, ppm ^a
1,3-Dioxan-2-one	4.44 (t), ^b 2.15 (quint.)
Poly(trimethylene carbonate)	4.17 (t), ^b 1.98 (quint.)
Poly(oxetane)	3.43 (t), ^b 1.86 (quint.)

^aChemical shift in ppm relative to TMS as internal standard.

^bMethylene protons next to oxygen.

tin oxide (19.5 mg), $\text{CH}_3\text{COO}^- \text{K}^+$ (7.7 mg) with 18-crown-6 ether (20.7 mg), NaH (2.4 mg), aluminum isopropoxide (16.0 mg), and K_2CO_3 (5.4 mg, $[\text{M}]/[\text{I}] = 500$) with 18-crown-6 ether (20.7 mg). The monomer-to-initiator molar ratio ($[\text{M}]/[\text{I}]$) was 250. The bottles were sealed and flushed with nitrogen. Several reaction temperatures (20, 40, 80, 100, and 120°C) and reaction times (4–48 h) were studied. Solution polymerization were performed in CH_2Cl_2 , 1,2-dichloroethane, and toluene, and they were terminated by precipitation in cold methanol. The organic phase residue after precipitation was evaporated to dryness in some cases. This low molecular weight polycarbonate residue was analyzed by GPC to estimate the oligomer content.

The effect of monomer-to-initiator ratio was studied with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as initiator with $[\text{M}]/[\text{I}]$ ratios of 100, 250, 500, 750, and 1000 at a reaction temperature of 100°C for 5 h.

Polymers for the DSC and NMR studies were reprecipitated. $^1\text{H-NMR}$ chemical shifts are shown in Table 1.

RESULTS AND DISCUSSION

Monomer Synthesis

The well-established method described by Carothers and Van Natta [1] with small modifications gave a yield of 38%. The method includes an extraction step to remove the sodium and unreacted reactants. The low yield depends on several factors. First, the conversion to prepolymer is not sufficiently high; the ethanol collected contains some diethyl carbonate, although the distillation temperature never exceeded the boiling point of ethanol (78°C). Second, an extraction always results in a loss of material as in the subsequent dehumidification and filtration.

The other method is a shorter and more simple way to obtain 1,3-dioxan-2-one, and it gave a yield of 53%. After the first distillation, the vacuum distillation can be executed immediately after cooling. Stannous 2-ethylhexanoate, Sn-oct, can probably promote formation of prepolymer, but mechanisms for polymerization by Sn-oct are still not completely understood [14]. It has also been reported that Sn-oct can act as a depolymerization agent [15–17].

Polymerization in Solution

The results of the polymerizations performed in a solution of dichloromethane (CH_2Cl_2) (dielectric constant 9) are summarized in Table 2. No polymerization occurred at 20°C with the initiators tested, as can be seen in entries 1, 4, and 8. When the reaction temperature was raised to 40°C, only low molecular weight polymers were formed when the reaction was initiated with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, AlCl_3 , Sn-oct, or $\text{CH}_3\text{COO}^- \text{K}^+$ ($M_w < 11,000$) (entries 2, 3, 5, 9). Reaction time had no influence on the polymer obtained (entries 6, 8, 10, 11).

Table 3 shows the results of polymerization of (1) in 1,2-dichloroethane (dielectric constant 10.4). With a reaction time of 8 h (24 h for NaH), only AlCl_3 was capable of initiating polymerization of the monomer.

Table 3 also shows the results of polymerization in toluene (dielectric constant 2.4). During the polymerization, the molecular weight increased, and above a cer-

TABLE 2. Polymerization of 1,3-Dioxan-2-one in Solutions of Dichloromethane with Different Initiators and at a Temperature of 40°C for 24 h (molar ratio $[M]/[I] = 250$)

No.	Initiator	M_n^a	M_w^a	M_w/M_n
1	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (20°C)		Oligomers	
2	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	5000	9000	1.64
3	AlCl_3^c	6000	11000	1.71
4	Stannous 2-ethylhexanoate (20°C)		Monomer	
5	Stannous 2-ethylhexanoate	2000	3000	1.36
6	$(\text{C}_4\text{H}_9)_2\text{SnO}$		Oligomers	
7	$(\text{C}_4\text{H}_9)_2\text{SnO}^c$ (48 h)		Monomer	
8	$\text{CH}_3\text{COO}^- \text{K}^{+b}$ (20°C)		Monomer	
9	$\text{CH}_3\text{COO}^- \text{K}^{+b}$	4000	6000	1.44
10	NaH^c		Oligomers	
11	NaH^c (48 h)		Oligomers	
12	No initiator		Monomer	

^aMeasured by GPC in tetrahydrofuran at 30°C.

^bWith 18-crown-6 ether.

^cInert atmosphere.

tain level the solubility of the polymer in the solvent decreased drastically, preventing further polymerization. The solvent phase was retained in the $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ polymerization and, after removal of toluene, the molecular weight of the residue was estimated by gel permeation chromatography (GPC). The GPC trace (Fig. 2) shows that the fraction contained monomer and different oligomers. Toluene was

TABLE 3. Polymerization of 1,3-Dioxan-2-one in Toluene and 1,2-Dichloroethane with Different Initiators at 80°C. Reaction times: 8 and 24 h (molar ratio $[M]/[I] = 250$)

No.	Initiator	t , h	M_n^a	M_w^a	M_w/M_n	Yield, %
<u>1,2,-Dichloroethane</u>						
1	AlCl_3^b	8	7,000	12,000	1.62	
2	$(\text{C}_4\text{H}_9)_2\text{SnO}^b$	8		Monomer		
3	NaH^b	24		Oligomers		
<u>Toluene</u>						
4	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	24	23,000	49,000	2.15	45
5	AlCl_3^b	24	15,000	25,000	1.67	
6	$(\text{C}_4\text{H}_9)_2\text{SnO}^b$	8	37,000	68,000	1.85	
7	NaH^b	24	2,000	2,000	1.12	

^aMeasured by GPC in tetrahydrofuran at 30°C.

^bInert atmosphere.

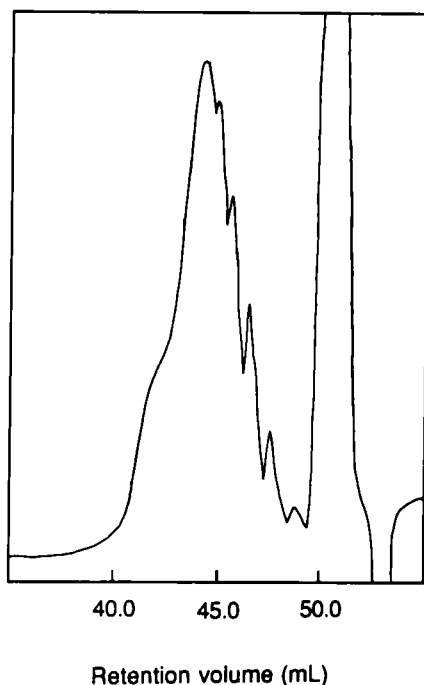


FIG. 2. GPC curve for the evaporated solute phase in the polymerization of 1,3-dioxan-2 one with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as initiator in toluene.

the only one of the tested solvents in which polymerization occurred with all initiators. The molecular weights of the polymers were in most cases much higher than the polymers formed in CH_2Cl_2 or $\text{C}_2\text{H}_4\text{Cl}_2$ solution, but they were still mixed with cyclic oligomers.

As shown in cases of polymerization in CH_2Cl_2 , a high reaction temperature is favorable for the reaction. Previous polymerizations of (1) by Kricheldorf and Jensen [3] to low molecular weight poly(1) were performed at lower temperatures (and with an alkylating initiator).

It is obvious that the polymerization of 1,3-dioxan-2-one in solution gives mixtures of monomer, cyclic oligomers, and linear polymer. At elevated temperature, a nonpolar solvent, the latter with phase separation, forces the equilibrium toward higher molecular weight linear polymers.

Polymerization in the Melt

Several polymerizations have been performed in the melt. The monomer has a melting point of 50°C , which means that the bulk polymerization temperature must be above 50°C . The results are shown in Tables 4 and 5.

Table 4 shows the results for a temperature of 80°C and a reaction time of 24 h (except entries 5 and 6). The molecular weights of poly(trimethylene carbonate) are clearly above those achieved by solution polymerization of (1).

TABLE 4. Melt Polymerization of 1,3-Dioxan-2-one with Different Initiators at a Temperature of 80°C and with a Reaction Time of 24 h (molar ratio [M]/[I] = 250)

No.	Initiator	M_n^d	M_w^d	M_w/M_n	Yield, %
1	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	58,000	99,000	1.72	100
2	Stannous 2-ethylhexanoate	25,000	44,000	1.78	
3	$\text{CH}_3\text{COO}^- \text{K}^{+c}$	24,000	42,000	1.74	
4	No initiator		Monomer		
5	Al-isopropoxide ^b	56,000	101,000	1.80	
6	$\text{K}_2\text{CO}_3^{a,c,e,f}$	51,000	77,000	1.56	

^aPolymerization temperature 100°C.

^bReaction time 4 h.

^cReaction time 5 h.

^dMeasured by GPC in tetrahydrofuran at 30°C.

^eWith 18-crown-6 ether.

^fMonomer to initiator ratio [M]/[I] = 500.

Table 5 shows the results for a temperature of 100°C and a reaction time of 5 h. A comparison of Table 5 with Table 4 therefore shows the effect of higher temperature in combination with a shorter reaction time. In order to be able to compare the influence of atmosphere on the polymerizations, they were carried out both in a normal atmosphere and in a nitrogen atmosphere for each initiator. Flushing the polymerization vessel with nitrogen lowers the moisture content in the

TABLE 5. Melt Polymerization of 1,3-Dioxan-2-one with Different Initiators at a Temperature of 100°C and with a Reaction Time of 5 h (molar ratio [M]/[I] = 250)

No.	System	M_n^a	M_w^a	M_w/M_n
1	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	58,000	98,000	1.69
2	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2^c$	69,000	129,000	1.88
3	AlCl_3	15,000	27,000	1.82
4	AlCl_3^c	16,000	32,000	2.00
5	Stannous 2-ethylhexanoate	30,000	53,000	1.78
6	Stannous 2-ethylhexanoate ^c	45,000	85,000	1.88
7	$(\text{C}_4\text{H}_9)_2\text{SnO}$	38,000	65,000	1.72
8	$(\text{C}_4\text{H}_9)_2\text{SnO}^c$	71,000	115,000	1.62
9	$\text{CH}_3\text{COO}^- \text{K}^{+b}$	39,000	67,000	1.73
10	$\text{CH}_3\text{COO}^- \text{K}^{+b,c}$	40,000	71,000	1.76
11	NaH	11,000	18,000	1.61
12	NaH^c	54,000	102,000	1.90

^aMeasured by GPC in tetrahydrofuran at 30°C.

^bWith 18-crown-6 ether.

^cInert atmosphere.

vessel since the nitrogen contained only trace amounts of water. The results clearly show that an inert atmosphere is to be preferred in all cases.

In order to evaluate the effect of polymerization time at high temperature on the molecular weight, some polymerizations were carried out at 120°C for 0.5, 3, and 24 h. The results are shown in Fig. 3. In all cases, a drop in molecular weight occurs when the reaction is allowed to proceed for a longer time. When evaluating these results, it must be realized that different batches were used for each reaction time and that the molecular weight could therefore vary to some extent. Figure 3 shows that polymerization temperature is extremely important. The polymerization itself is promoted by a higher temperature with respect to the molecular weight (shown in Tables 2 and 3) and to the polymerization rate (shown in Tables 4 and 5). The polymer, however, is depolymerized by heat (used in the monomer synthesis). Polymerization at 120°C for 0.5 h resulted in a slightly yellow poly(1), 3 h gave a yellow product, and after 24 h the polymer was brown. Polymerization at 100°C for 5 h resulted in a colorless and transparent material. The color probably arose because chromophoric groups are formed during degradation.

To confirm that it was the polymer that degraded on heating, a reprecipitated poly(1) sample was exposed to 130°C for 24 h in a sealed tube. The molecular weight dropped from $M_w = 110,000$ to $M_w = 60,000$ with an increase in dispersity from 1.76 to 2.02.

The effect on the degree of polymerization of the monomer-to-initiator ratio ($[M]/[I]$ molar ratio) is shown in Fig. 4. The initiator used was $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ at a reaction temperature of 100°C for 5 h. The molecular weight of the polymer was at an intermediate level when the ratio was 100 and increased up to a ratio of 250. No significant deviation from this molecular weight could be seen at higher ratios.

Character of the Polymers Obtained

Immediately after polymerization, all the polymers were transparent, but on cooling the polymers with low molecular weight became opaque due to crystallization of unreacted monomer. The reprecipitated low molecular weight polymers (M_w

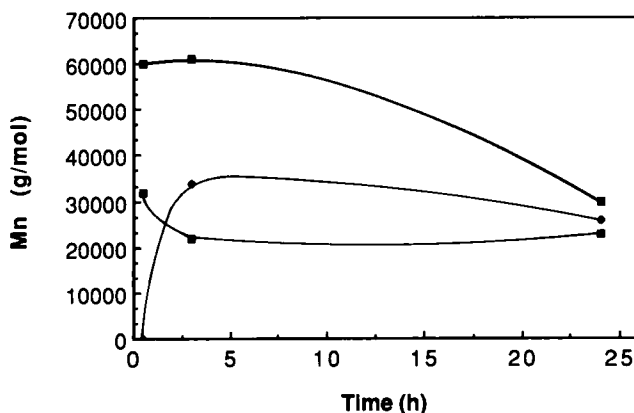


FIG. 3. The effect of polymerization time on the molecular weight at a polymerization temperature of 120°C. Initiators: (□) $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, (◇) Sn-oct, (■) $\text{CH}_3\text{COO}^- \text{K}^+$, $[M]/[I] = 250$.

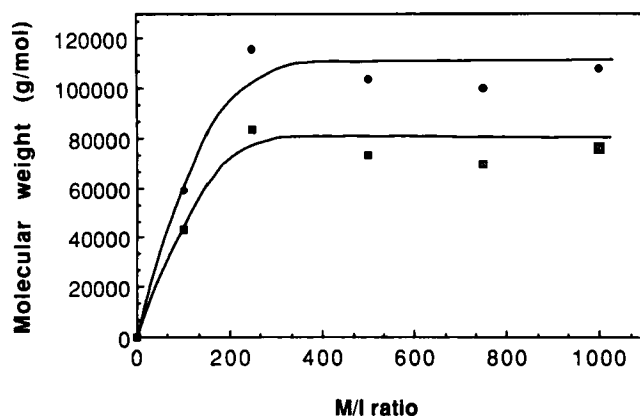


FIG. 4. The effect of the monomer-to-initiator ratio ($[M]/[I]$) on the molecular weight for the polymerization initiated by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ at a reaction temperature of 100°C and a reaction time of 5 h: (◆) M_w , (□) M_n .

< 14,000) became opaque on standing after approximately 1–2 weeks when the polymer became semicrystalline.

The physical appearance of the polymers depends on the molecular weight. Low molecular weight polymers ($M_w < 6000$) are oily, viscous liquids containing mostly oligomers, whereas polymers with molecular weights between 6000 and 50,000 are soft, sticky plastic materials which can be drawn out and do not regain their original shape. Materials over 50,000 in molecular weight have more interesting properties. The surface is not sticky and, when a force is applied, the material shows some elastic characteristics which increase with molecular weight. At higher molecular weights ($M_w \approx 120,000$), the material is harder and becomes even more

TABLE 6. Poly(Trimethylene Carbonate) Obtained by Polymerization with Various Initiators at a Reaction Temperature of 100°C in the Melt. Examined by DSC for T_g and ^1H NMR for Percentage Ether Linkages in the Polymer

No.	Initiator ^a	t	M_n^b	M_w^b	M_w/M_n	$T_g, ^\circ\text{C}^c$	% Ether ^d	$[\eta]^e$
1	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	5 h	47,000	92,000	1.96	-17.0	2.6	0.85
2	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	2 min	46,000	87,000	1.90	-19.6	—	—
3	$(\text{C}_4\text{H}_9)_2\text{SnO}$	5 h	51,000	110,000	2.16	-17.2	0	1.07
4	$(\text{C}_4\text{H}_9)_2\text{SnO}$	70 min	27,000	50,000	1.89	-17.6	—	—
5	NaH	5 h	6,000	14,000	2.19	-35.8	0	0.12
6	NaH	30 min	1,000	3,000	2.15	-37.6	—	—

^a $[M]/[I]$ ratio 250, polymerization at 100°C , 5 h, inert atmosphere.

^bMeasured by GPC in chloroform at 27°C .

^cMeasured by DSC.

^dMeasured by ^1H NMR.

^eIntrinsic viscosity $[\eta]$ measured in chloroform at 25°C .

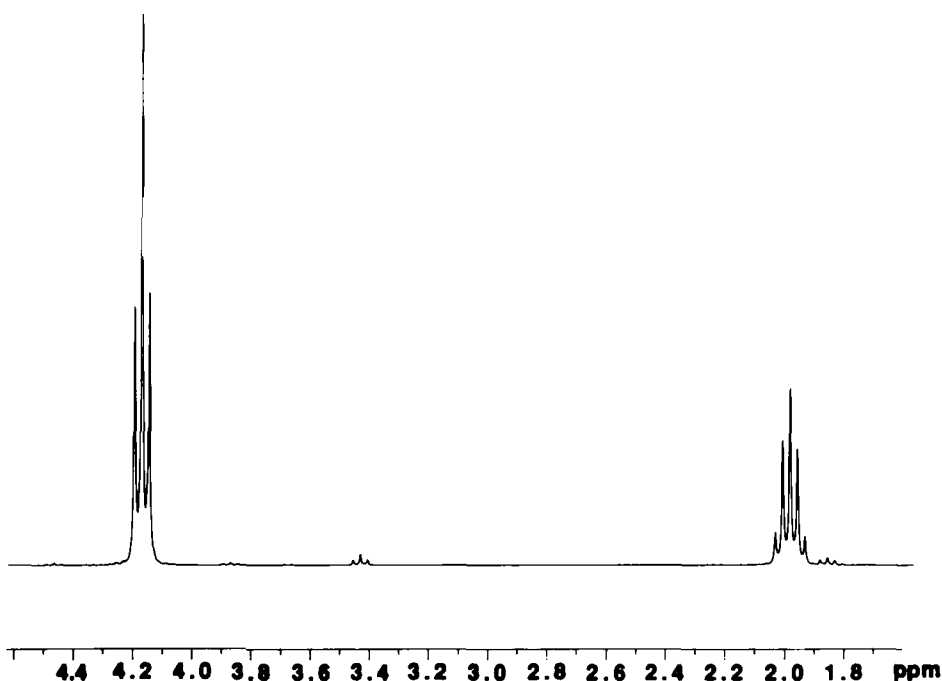


FIG. 5. ^1H -NMR spectrum (250 MHz) of the poly(trimethylene carbonate) containing ether linkages.

elastic. The glass transition temperatures (T_g) for three polymers are shown in Table 6. The results show, as expected, a significant difference in T_g depending on the molecular weight.

Polymerization with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as initiator gave a rubbery material containing small bubbles, probably due to the liberation of small amounts of carbon dioxide, also noted in previous studies [2-4]. The formation of CO_2 from a carbonate linkage should stoichiometrically give a residual ether linkage. The percentage of ether can easily be determined by ^1H -NMR (Fig. 5), with the chemical shifts for polycarbonate-polyether presented in Table 1, and the results are shown in Table 6. The formation of ether linkages during polymerization is not entirely unexpected, as the thermal degradation of the polymer also causes the evolution of carbon dioxide with the formation of ether linkages [4].

CONCLUSIONS

1,3-Dioxan-2-one has been polymerized into rubberlike materials with molecular weights over 100,000 with several initiators. Polymerization in solution gives mostly oligomers or in some cases an equilibrium with a linear polymer with a molecular weight less than 50,000. Less polar solvents, such as toluene, give higher molecular weights with phase separation due to the limited solubility of the poly(trimethylene carbonate). Solution polymerization (dichloromethane, 1,2-dichloroeth-

ane) without separation gives a molecular weight less than 10,000. Polymerization in an inert atmosphere was shown to favor the achievement of a high molecular weight. A higher polymerization temperature lead to an increase in molecular weight and a faster reaction rate. Excessive heating causes thermal degradation. The polymers from cationic melt polymerization contain ether linkages to an extent of 2.6%. Poly(trimethylene carbonate) with a molecular weight of 100,000 has a glass transition temperature of -17°C .

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