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CATIONIC POLYMERIZATION OF 1,5-DIOXEPAN-2-ONE WITH LEWIS ACIDS IN BULK AND SOLUTION

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ABSTRACT

1,5-Dioxepane-2-one (DXO) was coordinatively ring-opening polymerized with different Lewis acids in bulk and solution. The reactivities of a series of initiators ($SnCl_4$, $FeCl_3$, $AlCl_3$, BCl_3, and BF_3OEt_2) at different temperatures and reaction times were analyzed. Polymerization of DXO in bulk with $SnCl_4$, $FeCl_3$, $AlCl_3$, and BCl_3 gave only oligomers or low molecular weight polymers irrespective of temperature and/or reaction time. Polymerization of DXO with BF_3OEt_2 at 70°C gave yields of nearly 100% and molecular weights up to $M_w = 10,000$. The polymerization temperature was increased to 100°C and the reaction time prolonged, which resulted in nearly equal molecular weights as at 70°C but with lower yields, higher polydispersity, and generally not full conversion. In addition, side reactions, such as backbiting, transesterification and thermal degradation, occurred to a larger extent at higher reaction temperatures. Solution polymerization using the same initiators and THF, dioxane, or nitrobenzene as the solvent gave polymers of low molecular weights and of low yields, except with $FeCl_3$ and BF_3OEt_2. The rates of polymerization were significantly higher in nitrobenzene than in dioxane and THF due to polarity and coordination of these solvents to the growing chain. Comparison of the initiators BF_3OEt_2 and $SnCl_4$ in solution polymerization showed equal reactivity in nitrobenzene for both of them. The BF_3OEt_2-initiated systems give polymers with lower molecular weights than $SnCl_4$-initiated systems, but with narrower polydispersity.

INTRODUCTION

Aliphatic polyesters [1] are the most widely used biodegradable materials for implants, sutures, and drug delivery systems. They hydrolyze in the body, giving metabolizable low molecular weight products. Aliphatic polyesters are frequently made by ring-opening polymerization of lactones with a variety of initiating systems based on ionic initiators. Few fundamental studies on this subject have been reported, although there is a substantial number of examples of polymerizations of lactones using cationic initiators, especially acids [2, 3]. Most of the earlier studies of lactone homopolymerization only described the preparation of low molecular weight polyesters with acid catalysts [4, 5]. Some of the polyesters, such as polyglycolide, polylactide, and copolymers of these polymers, are produced commercially by cationic polymerization. These polymers are used, for example, as synthetic biodegradable surgical sutures (Dexon by American Cyanamide or Vitcar by Ethicon). The mechanical and biological properties of polyester sutures are described in several reviews [6–8].

Poly(ε-caprolactone) (PCL) is formed by the ionic polymerization of cyclic ester ε-caprolactone [9], and it forms interesting degradable blends with other polymers [10–12]. PCL blends are used as adhesives for polymer films of various compositions, as the "low-profile" additive in a matrix for glass-fiber reinforced polyesters, and as pigment dispersants. PCL and copolyesters of ε-caprolactone and D,L-lactide have been investigated especially in regard to their biodegradability and use in drug delivery systems [13, 14]. Poly(1,5-dioxepane-2-one) (PDXO) has attracted a considerable amount of attention because of its potential as a polymer for biomedical applications. Unlike crystalline PCL, PDXO is amorphous, but both PDXO and PCL have good flexibility and are soluble in most organic solvents. PDXO was used as a comonomer with other lactones to give random copolymers which are more elastic than the respective homopolymers [15–19]. PDXO and PCL degrade by a similar degradation mechanism, and the degradation seems to follow an autocatalytic hydrolysis mechanism [20]. In particular, PDXO gives a less pronounced foreign body reaction in comparison to other semicrystalline aliphatic polyesters. We have studied and described different routes of polymerizing DXO [21, 22], including coordination polymerization with initiator systems such as zinc chloride and stannous octoate [22]. We have already shown that when DXO is polymerized, it approaches living coordination anionic polymerization conditions [22]. This polymerization gives block copolymers with controllable molecular weights and a narrow molecular weight distribution.

The objective of the present work was to study the reactivity of a series of initiators for polymerizing DXO in bulk and solution. The obtained molecular weights of PDXO as functions of initiator type, polymerization temperature, and reaction temepature are discussed.

EXPERIMENTAL

Materials

Boron trifluoride etherate (BF_3OEt_2) was obtained from the Aldrich Chemical Co. $AlCl_3$, $FeCl_3$, BCl_3, and $SnCl_4$ were purchased from Merck & Co. and were used from freshly opened bottles without further purification. Tetrahydrofuran (THF)

(J.T. Baker) was heated to reflux from CaH_2 and distilled. Nitrobenzene and dioxane (Merck & Co) were refluxed from phosphorus pentoxide (P_4O_{10}) and distilled.

Preparation

Synthesis of 1,5-Dioxepan-2-one

Tetrahydro-4*H*-pyran-4-one, 55 g (0.55 mol), was added to a slurry of 160 g (0.75 mol) of 82% 3-chloroperbenzoic acid and 82 g (1 mol) sodium bicarbonate in 800 mL dry methylene chloride. The slurry was kept under constant stirring at 0°C while tetrahydro-4*H*-pyran-4-one was added dropwise over a period of 1 hour through a dropping funnel. The slurry was then maintained at 20°C for 16 hours. After filtration, the methylene chloride phase was washed with sodium bisulfite and sodium bicarbonate to eliminate any remaining peracid.

The methylene chloride phase was evaporated to give a slightly yellow oil. Distillation under reduction pressure (68°C, 1 mbar) gave 83% yield of DXO. Before polymerization, DXO was recrystallized twice in anhydrous diethyl ether and dried in vacuum over P_2O_5, mp 37°C.

Polymerization of 1,5-Dioxepan-2-one

Bulk Polymerization. Monomer and initiator were added to a dry N_2 purged 20 mL serum bottle equipped with a magnetic stir bar and a rubber septum cap. The polymerization was carried out at 20, 50, 70, and 100°C in a thermostated oil bath. After the polymerization was completed, the polymer was dissolved in chloroform and precipitated by pouring the solution into cold petroleum ether to remove the monomer residue. The polymer was isolated by filtration and dried at reduced pressure at room temperature.

Solution Polymerization. Freshly recrystallized DXO and catalyst were dissolved in the solvent and the solutions were transferred into a serum bottle under a stream of dry nitrogen. The polymerizations were carried out in the same manner as the one described under "bulk polymerization".

Characterization

A Waters size exclusion chromatography (SEC) system, which was run with THF (1 mL/min) in all measurements, consisted of a solvent delivery system (model 510), an automated injector (Wisp 710B), and a differential refractometer (model 410). Five μ-Styragel columns (500, 10^3, 10^4, 10^5, 100 Å) were calibrated with narrow molecular weight distribution polystyrene standards and maintained at 30°C. For data recording and calculations of the data obtained, a Copam PC-501 Turbo Unit was used.

^{1}H-NMR analysis was made by a Bruker AC-250 FT-NMR spectrometer. All spectra were obtained in $CDCl_3$ solutions in 3 mm diameter sample tubes. The percent conversion was calculated from the ratio of the peak representing the methylene protons in the ring next to the ester bond (triplet, 2 H, $d = 4.32$) to the peak representing the protons in the linear polyester (ring-opened) structure (triplet, 2 H, $d = 4.22$).

RESULTS AND DISCUSSION

The cationic polymerization of DXO using Lewis acid initiators was investigated in order to find means to obtain degradable polymers with controllable molecular weight and a narrow molecular weight distribution. This work is also part of our research exploring new knowledge about the ring-opening polymerization of DXO. ^{1}H- and ^{13}C-NMR analysis earlier showed that aliphatic PDXO contains both ester and ether functionalities in a regular alternating structure [21]. We recently presented a study of the homopolymerization of DXO which gave high molecular weight polymers ($M_w = 10^5$) through bulk ring-opening polymerization initiated by stanneous 2-ethylhexylhexoctanate [22].

Glycolide and lactide have been polymerized in the melt using Lewis acids (SbF_3, $ZnCl_2$, $SnCl_2$, $SnCl_4$) or other metal salt initiating systems while cationic initiators (e.g., tritylium, atropylium, triethyloxonium salts) did not initiate the polymerization [23-26]. Among the cationic initiators first utilized for these types of polymerizations were trifluoroacetic acid, acetyl perchlorate, and trifluoroacetic anhydride/aluminum trichloride [4].

Bulk Polymerization

The influence of reaction conditions on yields, molecular weights, and conversion rates were elucidated by systematically varying the following experimental parameters: initiator, temperature, reaction time, and monomer/initiator ratio. The subsequent polymerizations were all conducted at 25°C or above, as a polymerization temperature of 0°C was found to be too low for the reaction to proceed.

Table 1 presents the results of the cationic polymerization in bulk using $SnCl_4$, $FeCl_3$, $AlCl_3$, BCl_3, and BF_3OEt_2 as initiators. At room temperature the polymerizations proceed slowly and the molecular weights reached after 24 hours are merely 1000 and the yields are generally low, which shows that the reaction rate is too slow for satisfactory polymerization. The low reactivity of DXO in bulk polymerization at room temperature is comparable with the reaction of ε-caprolactone in bulk, where it was shown that in particular the propagating step is slow at lower temperatures [13, 14]. A polymerization temperature of 50°C resulted in a moderate increase in the molecular weights for the $SnCl_4$, $FeCl_3$, and $AlCl_3$ initiated systems. The $SnCl_4$-initiated polymerization gave a yield of 60% and a molecular weight of 2100 while the BCl_3 initiator was totally inactive. The yield was higher (80%) and the molecular weight reached 9200 (M_w) for the $FeCl_3$ system. The $FeCl_3$ initiator is thus more reactive than the other Lewis acids, which parallels the result reported by Kricheldorf and coworkers [32]. BF_3OEt_2 gives generally higher molecular weights for polymerization temperatures from 50 to 100°C, and the optimal duration of polymerization was found to be 24 hours. BF_3OEt_2 has been described to be a good initiator for the cationic homopolymerization of lactones of glycolide, β-propiolactone, or ε-caprolactone [27-29]. This initiator seems, however, to give low reproducibility, as can be seen in Table 1. For polymerization at 70°C and a 24-hour

TABLE 1. Bulk Polymerization of 1,5-Dioxepan-3-one with $SnCl_4$, $FeCl_3$, $AlCl_3$, BCl_3, and BF_3OEt_2 as Initiator

Initiator	M_0/I_0	Temperature, °C	Time, hours	Yield, %	M_n	M_w
$SnCl_4$	500	RTP	24	38	600	900
	500	50	24	58	1,100	2,100
	500	100	2	2	600	800
$FeCl_3$	500	RTP	24	58	1,400	4,200
	500	50	24	78	6,100	9,200
$AlCl_3$	500	RTP	24	17	Oligo	–
	500	50	24	36	700	1,100
BCl_3	500	RTP	24	–	–	–
	500	50	24	22	Oligo	–
BF_3OEt_2	500	RTP	2	58	800	1,100
	500	RTP	24	15	700	1,000
	500	50	2	42	700	1,100
	1,000	50	2	48	900	2,000
	1,000	50	2	56	500	700
	1,000	50	24	47	1,500	6,200
	1,000	50	24	18	900	1,900
	1,000	50	72	39	6,300	7,600
	500	50	144	88	1,000	2,000
	1,000	50	144	44	1,200	1,800
	500	70	2	98	Gelation	–
	500	70	12	95	6,470	8,400
	500	70	24	97	8,300	10,960
	500	70	24	99	2,400	4,500
	500	100	2	9	1,300	2,700
	500	100	24	24	4,100	8,500
	500	100	72	65	3,800	11,300

reaction time, the span in obtained molecular weights ranged from 4,500 to 11,000. This has probably to do with the age of the BF_3OEt_2 initiator when it was delivered and also the length of time before use in the polymerization studies. At 100°C we never obained 100% conversion and high yields even in the initial phases, because the faster degradation at high temperatures counterbalances the chain growth, parallel to the case of PCL [30]. Gelation occurs after 1 hour at 100°C and in some, but not in all, experiments. This probably due to impurities and side reactions. At higher temperatures the initiator becomes too reactive at the same time as the amount of side reaction increases. The same reasons should also have an impact on the conversion and the resultant yield at 100°C.

Figure 1 shows the reactivity of the $SnCl_4$ initiator in polymerization at 50°C. Although high molecular weights were reached quickly, this fast polymerization was immediately followed by degradation of the initially formed polyester. The molecular weight reached $M_w = 5400$ after 24 hours, but further exposure of the reaction

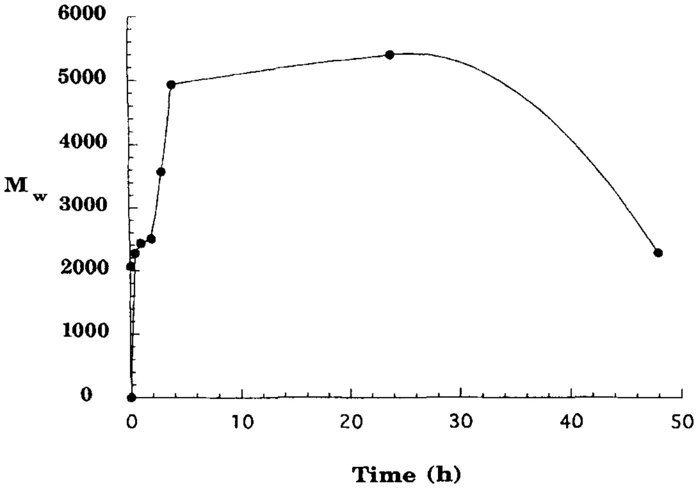

FIG. 1. Molecular weight dependence on time for the bulk polymerization of 1,5-dioxepane-2-one with $SnCl_4$ as initiator. $[M_0]/[I_0] = 500$.

mixtures resulted in a decrease to $M_w = 2000$ after 48 hours due to degradation reactions. Similar results were observed at 100 °C and also with the $FeCl_3$ initiator.

Figure 2 presents data from the conversion study of DXO with BF_3OEt_2 for polymerization times up to 24 hours at three different temperatures (50, 70, and 100 °C). After 5 hours the increase in conversion begins to level off, corresponding

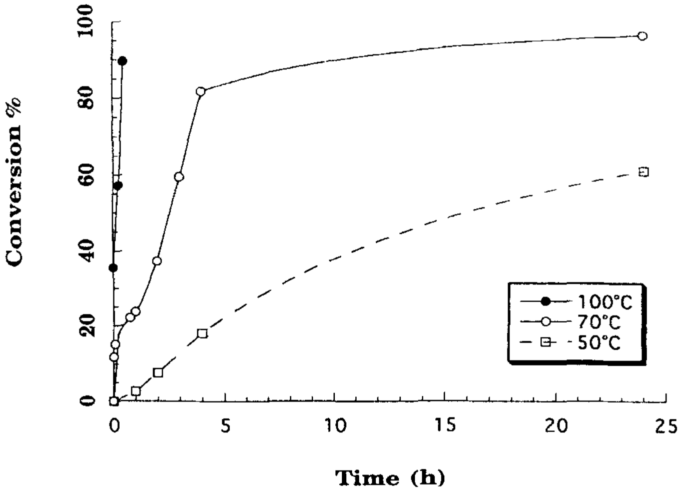

FIG. 2. Conversion vs time for the bulk polymerization of 1,5-dioxepane-2-one with BF_3OEt_2 as initiator at 50, 70, and 100 °C. The conversion was determined by ^1H-NMR. $[M_0]/[I_0] = 500$.

to 80% conversion. Thereafter a slow continuous increase was observed with a maximum conversion of 90% obtained after 24 hours. The slow increase in conversion between 5 to 24 hours of reaction is due to low reactivity for cationic initiators toward lactones when the concentration of monomer becomes low toward the end of the polymerization. The initiation period of the polymerization is as significant at 50°C as it is at 70°C. The increase in conversion versus time is slow and quite uniform and reaches 60% after 1 day (Fig. 2). Reaction times of the order of 3-7 days were required to obtain yields around 80% (Table 1). Even when the most reactive initiators were used, reaction times of the order of 1-2 days were required at 50°C to obtain yields around 90% for other lactones [31]. The molecular weights increased to $M_w = 6000$ after 24 hours, and after 72 hours the molecular weight reached $M_w = 8000$. After 144 hours the molecular weights decreased to around $M_w = 2000$, probably due to backbiting and degradation reactions. A dependence on the monomer/initiator ratio was also seen. The resulting yields and molecular weights were lower when the ratio of monomer/initiator was increased.

Figure 3 shows the molecular weights obtained at the three different polymerization temperatures. At 70°C and a yield of nearly 100% (98-99%), a molecular weight of 11,000 was obtained. Higher temperature increases the polymerization rate and shortens the reaction time. A fast increase in molecular weights was obtained during the first hour; the molecular weight reached 5200 after one hour (Fig. 3). If the polymerization was allowed to proceed for a couple of days (72 hours), the molecular weight slowly increased up to $M_w = 11{,}000$ due to transesterification reactions which are favored at high temperatures.

At higher polymerization temperatures the polymerization rate is generally slow compared with depolymerization or polymer degradation. For polymerization

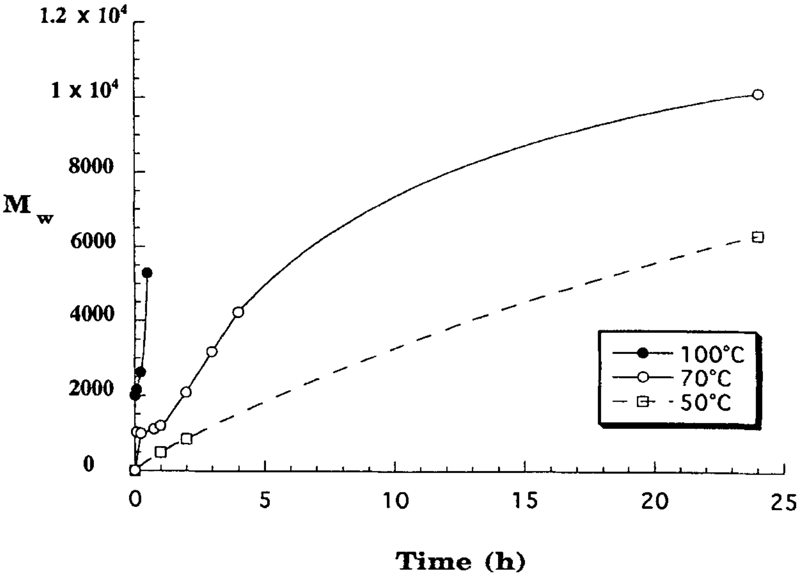

FIG. 3. Molecular weight vs time for the bulk polymerization of 1,5-dioxepane-2-one with BF_3OEt_2 as initiator at 50, 70, and 100°C. $[M_0]/[I_0] = 500$.

at 70°C, the chain growth is judged to be much faster than depolymerization because both the molecular weight and the yield increased continuously. We found that the reaction conditions favoring high overall rates of polymerization also favor degradation of the initially formed polyester and increase the side reactions. However, a reaction temperature of 70°C provides optimal conditions for cationic polymerization with BF_3OEt_2, and the influence of depolymerization and side reactions are kept at a low level.

Solution Polymerization Studies

Tables 2 and 3 present results on solution polymerization studies comparing THF, dioxane, and nitrobenzene. The solvents were chosen because they have very different dielectric constants, and because the solvents allow reaction temperatures up to 67°C (THF) and above 100°C (dioxane and nitrobenzene). Solvents with high boiling points were thought to be desirable because lactones have low reactivities for the initiation reaction toward cationic initiators at low temperatures.

THF has a low dielectric constant and was the first of the solvents to be tested. There is, however, an inherent danger that this solvent may also act as a comonomer and undergo copolymerizations with lactone monomers. $SnCl_4$ gave a higher yield than $FeCl_3$-, $AlCl_3$-, or BCl_3-initiated solvent polymerizations. THF probably coordinated to the initiator ($FeCl_3$, $AlCl_3$, or BCl_3) or to the cation which slows down the initiation of DXO. BCl_3 gave oligomers, and $FeCl_3$ and $AlCl_3$ gave low molecular weight polymers (M_w = 1000) at low yields. Dioxane has a lower dielectric constant than THF, but a degree of dissociation similar to that of THF. The boiling temperature of dioxane is higher (102°C), which allows higher reaction temperatures. For $FeCl_3$ at 50°C, higher yields and molecular weights were obtained in dioxane than in THF. The polydispersity of the polymer obtained in dioxane is lower than the corresponding one in THF, which suggests fewer side reactions. Furthermore, with

TABLE 2. Solution Polymerization of 1,5-Dioxepan-2-one with $SnCl_4$, $FeCl_3$, $AlCl_3$, BCl_3, and BF_3OEt_2 in THF and Dioxane at Different Temperatures and Polymerization Times

Initiator	Solution	Temperature, °C	Time, hours	Yield, %	M_n	M_w
$SnCl_4$	THF	50	72	97	1,600	2,800
	Dioxane	50	72	78	1,700	3,100
$FeCl_3$	Dioxane	50	72	67	2,000	3,000
	THF	50	72	32	499	1,100
	Dioxane	100	2	56	2,000	3,500
	Dioxane	100	24	65	6,200	9,000
	Dioxane	100	72	89	8,100	10,500
$AlCl_3$	THF	50	72	38	700	900
	Dioxane	100	24	45	4,800	6,400
	Dioxane	100	72	56	Gelation	–
BCl_3	THF	50	72	–	Oligo	–

TABLE 3. Solution Polymerization of 1,5-Dioxepan-2-one in Nitrobenzene with $SnCl_4$ and BF_3OEt_2 as Initiators at 50°C. $[M_0]/[I_0] = 500$

Initiator	Time	M_n	M_w	M_w/M_n
$SnCl_4$	1 minute	1405	1518	1.08
	5 minutes	1423	1637	1.15
	15 minutes	1721	2242	1.30
	30 minutes	1772	2307	1.30
	1 hour	1729	2334	1.35
	2 hours	2053	3019	1.47
	3 hours	2307	3508	1.52
	4 hours	2483	4048	1.63
	24 hours	4734	8048	1.70
BF_3OEt_2	1 minute	1008	1144	1.13
	5 minutes	1046	1161	1.11
	15 minutes	1088	1201	1.10
	30 minutes	1104	1295	1.17
	1 hour	1149	1368	1.19
	2 hours	1258	1510	1.20
	3 hours	1378	1729	1.25
	4 hours	1455	1879	1.29
	24 hours	2682	4146	1.54

$FeCl_3$ as initiator at 100°C, the molecular weight increased with time up to M_w = 10,500 after 72 hours and the yield reached 90%. At the same time, the polydispersity was quite low (1.3), which indicated that few side reactions had occurred.

Figure 4 and Table 3 present data concerning the solution polymerization of DXO in nitrobenzene initiated by $SnCl_4$ and BF_3OEt_2. At a reaction temperature of 50°C, PDXO samples reached a molecular weight of about 1500 for $SnCl_4$ and 1000 for BF_3OEt_2 after a polymerization time of 1 minute. The molecular weight of PDXO was 8000 after 24 hours with $SnCl_4$ initiation, and it was 4000 for the corresponding BF_3OEt_2 initiated system. The higher polymerization rates and molecular weights for $SnCl_4$ than for BF_3OEt_2 are probably due to the more coordinative character of the stanneous initiator [25, 30, 33].

Literature reports indicate that cationic copolymerizations of lactones with "purely" cationic initiators form random copolyesters [34]. Examination of the relationship between the basicity of the ether oxygen of the lactones and the ring size indicated the following order of basicity: $6 > 7 > 5 > 4$. It is significant that this is the order of reaction rates observed in previous polymerization studies, with the exception of the five-membered ring [22]. We have therefore concluded that there is at least a qualitative relationship between the basicity of the lactone oxygens and their tendency toward cationic polymerization. Even though potentially facile intra- and intermolecular transesterification reactions can occur in these polyesters under both basic and acidic conditions, this does not seem to play any role during

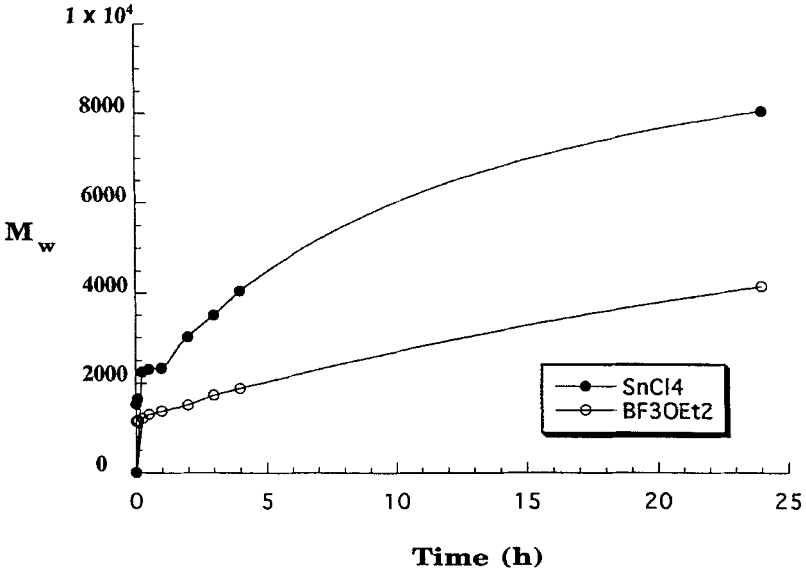

FIG. 4. Molecular weight dependence of time for the solution polymerization in nitrobenzene of 1,5-dioxepane-2-one with BF_3OEt_2 and $SnCl_4$ as initiators at 50°C. $[M_0]/[I_0] = 500$.

polymerization. The monomer is much more basic than the linear ester unit, and the monomer is consumed before transesterification of the polymer chains can start.

CONCLUSION

BF_3OEt_2 was found to be a good initiator for both bulk and solution ring-opening polymerization of DXO, giving an increase in conversion dependent on the reaction time and the temperature. The molecular weights of the resulting PDXO increase with increasing temperature up to 70°C, but further increases in temperature decrease the molecular weights due to a backbiting reaction. We demonstrated that the resulting yields and molecular weights of the PDXO correlate well with the M_0/I_0 ratio and the reaction time. Decreasing the concentration of the initiator (higher M_0/I_0 ratios at constant monomer concentration) results in lower rates of polymerization. This suggests that the initiator is a part of the active chain end. Furthermore, yields and molecular weights increase with time at constant M_0/I_0. Polymerizations with $SnCl_4$, $FeCl_3$, $AlCl_3$, and BCl_3 initiators at room temperature gave only oligomers. When the temperature was increased to 50°C, the results improved somewhat. $SnCl_4$ was shown to be a very reactive initiator, but increasing the polymerization temperature up to 100°C gave very rapid degradation of the initially formed polyester. Solution polymerization gave polymers of lower yields and molecular weights than did bulk polymerization. However, the rates of polymerization in nitrobenzene were significantly higher than in dioxane and THF with equal amounts of the initiator being tested, i.e., molecular weights of 4000–8000 were obtained with BF_3OEt_2 and $SnCl_4$, respectively.

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REFERENCES

[1] D. L. Wise, T. D. Fellmann, J. E. Sanderson, and R. L. Wentworth, in *Drug Carriers in Biology and Medicine*, 1st ed. (G. Gregoriadis, Ed.), Academic Press, New York, 1979, p. 237.
[2] T. Saegusa, S. Matsumoto, and Y. Hashimoto, *Polym. J., 1*, 31 (1970).
[3] R. D. Lundberg and E. F. Cox, in "Lactones," in *Ring Opening Polymerization* (K. C. Frisch, and S. L. Reegan, Eds.), Dekker, New York, 1969, Chapter 6.
[4] H. Cherdon, H. Ohse, and F. Korte, *Makromol. Chem., 56*, 179 (1962).
[5] H. Cherdon, H. Ohse, and F. Korte, *Ibid., 56*, 187 (1962).
[6] E. J. Frazza, in Encyclopedia of Polymer Science and Technology, Vol. Suppl. 1, Wiley, New York, 1976, p. 587.
[7] E. J. Frazza and E. E. Schmitt, *J. Biomed. Mat. Res. Symp., 1*, 43 (1971).
[8] J. J. Cann, *Am. J. Surg., 128*, 19 (1978).
[9] H. K. Hall Jr. and A. K. Schneider, *J. Am. Chem. Soc., 80*, 6409 (1958).
[10] H. C. Brown, *J. Chem. Soc., 60*, 1248 (1956).
[11] J. V. Koelske and R. D. Lundberg, *J. Polym. Sci., Part A-2, 7*, 795 (1969).
[12] D. S. Hubbel and S. L. Cooper, *J. Appl. Polym. Sci., 21*, 3035 (1977).
[13] J. E. Potts, R. A. Clendinning, W. B. Ackait, and W. D. Niegisch, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 13*, 629 (1972).
[14] A. Schindler, R. Jeffcoat, G. L. Kimmel, C. G. Pitt, M. E. Wall, and E. Zweidinger, *Contemp. Top. Polym. Sci., 2*, 251 (1979).
[15] M. Gruvegård and A-C. Albertsson, *Polymer, 36*, 1009 (1995).
[16] A. Löfgren and A-C. Albertsson, *J. Macromol. Sci.—Pure Appl. Chem., A32*, 41 (1995).
[17] S. W. Shalaby, US Patent 4,190,720 (1980), To Ethicon Inc.; *Chem. Abstr., 93*, 73692s (1980).
[18] S. W. Shalaby and A. Kafraway, *J. Polym. Sci., Polym. Chem. Ed., 27*, 4423 (1989).
[19] A. Kafraway and S. W. Shalaby, *J. Bioact. Compat. Polym., 1*, 431 (1986).
[20] A. Löfgren and A-C. Albertsson, *J. Appl. Polym. Sci., 52*, 1327 (1994).
[21] T. Mathisen, K. Masus, and A-C. Albertsson, *Macromolecules, 22*, 3842 (1989).
[22] A-C. Albertsson and R. Palmgren, *J. Macromol. Sci.—Pure Appl. Chem., A30*, 919 (1993).
[23] K. Chup, *Makromol. Chem., 100*, 262 (1967).

[24] G. S. Sania, E. B. Lyudvig, and E. S. Petrov, *Vysokomol. Soedin., B19*, 121 (1977).

[25] C. E. Lowe, US Patent 2,668,162 (1954).

[26] R. C. Shultz, *Int. Symp. Macromol. Chem., 186*, 955 (1985).

[27] H. R. Kricheldorf and R. Dunsing, *Makromol. Chem., 187*, 1611 (1986).

[28] Y. Yamashita, T. Tsuda, M. Okada, and S. Iwatsuki, *J. Polym. Sci., Part A-1, 4*, 2121 (1966).

[29] H. R. Kricheldorf and I. Kreiser, *Makromol. Chem., 188*, 1861 (1987).

[30] E. B. Ludvig and B. G. Belenkaya, *J. Macromol. Sci.—Chem., A8*, 819 (1974).

[31] H. R. Kricheldorf, R. Dunsing, and J. M. Monté, *Ibid., A23*, 495 (1986).

[32] H. R. Kricheldorf, T. Mang, and J. M. Monté, *Macromolecules, 17*, 2173 (1984).

[33] H. R. Kricheldorf and M-V. Sumbél, *Makromol. Chem., 189*, 317 (1988).

[34] H. R. Kricheldorf, T. Mang, and J. M. Monté, *Ibid., 186*, 955 (1985).

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