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MELT POLYMERIZATION OF ADIPIC ANHYDRIDE (OXEPANE-2,7-DIONE)

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ABSTRACT

Oxepane-2,7-dione (1) was prepared by the reaction of adipic acid and acetic anhydride followed by catalytic depolymerization under vacuum. The ring-opening polymerization of (1) was investigated in the melt, and was studied as a function of polymerization temperature, time and concentration of catalyst (stannous 2-ethylhexanoate). From ^1H-NMR and IR spectra it can be deduced that stannous 2-ethylhexanoate coordinates with the anhydride bond of the ring, and that the resulting species reacts with the monomer by ring-opening of the acyl-oxygen bond. These observations indicate a nonionic insertion polymerization mechanism at the beginning of the reaction, but after 2 h at 80°C, anhydride exchange appears to be the dominating reaction. Ring-opening melt polymerization of (1) resulted in low molecular weight poly(adipic anhydride).

INTRODUCTION

The behavior of diacids toward anhydride formation was studied by Hill and Carothers in three papers published in the 1930s [1–3]. They investigated a large number of diacids $HOOC{-}(CH_2){-}COOH$ where *n* is 4,5,6,7,8,9,10,11,12, and 16. The anhydrides were all linear polymers and were found to undergo transformations as in Fig. 1.

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A linear polyanhydride with low molecular weight is first formed from the diacid (prepared by the action of acetic anhydride or acetyl chloride on the dibasic acid). When this polyanhydride (called α-anhydride) is subjected to molecular distillation, a cyclic dimer or monomer (β-anhydride) distills off and ω-polyanhydride residue with a much higher molecular weight remains. The β-anhydride is converted to γ-anhydride on standing. The latter is practically identical with the α-anhydride, and is thought to contain very large ring structures whereas the α-form is linear.

The β-anhydrides are rings of 7, 8, 18 (dimeric), 10, 22 (dimeric), 12, 26 (dimeric), 14, 15, and 19 atoms. In order to distinguish the monomeric form from polymer and dimer, Hill and Carothers used the reaction with aniline. Monomeric anhydride, which has a symmetrical structure, can react with aniline to give only one product, the acid monoanilide. The reaction of polymeric anhydride with aniline may lead to three products: the dibasic acid, the acid monoanilide, and the dibasic acid dianilide [1].

The dimers are crystalline solids which polymerize instantly when heated above their melting points. The monomers are liquids or low melting solids which polymerize at lower temperatures than the dimers. The monomers of 8, 10, and 12 atoms are very unstable and polymerize even below room temperature. The seven-membered ring is a more stable anhydride than the 8, 10, and 12 atom monomers [3], but it polymerizes on being heated at 100°C for a few hours [1].

Cyclic anhydrides like succinic and glutaric anhydride have been used in the so-called spontaneous copolymerization, or no catalyst copolymerization, together with cyclic imino ethers, like 2-oxazoline and 5,6-dihydro-4*H*-1,3-oxazine [4]. These polymerizations took place spontaneously between room temperature and 100°C to produce 2:1 sequence-regulated copolymers. In this copolymerization, one monomer having nucleophilic reactivity M_N reacts with the other M_E to generate a zwitterion $+M_N{-}M_E-$, which is the key species of copolymerization [5]. Cyclic acid anhydrides can also react with epoxides and are known to copolymerize alternately in these reactions to give a polyester [5].

Domb and Langer [6] report the synthesis of high molecular weight poly(anhydrides) by an improved melt polycondensation method and the novel use of a catalyst in the polyanhydride synthesis.

They prepared poly(anhydrides) from diacids such as sebacic acid, bis(*p*-carboxyphenoxy)propane, bis(*p*-carboxyphenoxy)hexane, isophthalic acid, 1,4-phenylene dipropionic acid, and dodecanedioic acid. Their report also included the polymerization of the mixed anhydride from adipic acid and a discussion of ring formation in poly(anhydride) synthesis.

We have recently reported the polymerization of poly(adipic anhydride) using ketene gas [7]. That study included the ring-opening polymerization of adipic anhydride in the presence of $ZnCl_2$ as a catalyst. In view of our efforts to prepare aliphatic backbone-degradable materials based on polyanhydrides for hard crystalline materials in thermoplastic elastomers, it seemed essential to use a reaction route to polyanhydrides that does not involve long reaction cycles and elevated temperatures, which is common practice in the condensation of mixed anhydrides to polyanhydrides [7].

For this reason the bulk polymerization of adipic anhydride was studied in more detail to determine the effects of temperature, time, and catalyst concentration on the molecular weight of poly(adipic anhydride) and on the molecular weight distribution. Organo-tin compounds are known to be effective initiators of the polymerization of lactones [8, 9]. Although some patents deal with copolymerization of aliphatic cycloanhydrides [5], detailed studies on the homopolymerization of cyclic anhydrides are rather scarce, but it may be expected that organo-tin compounds, for example, stannous 2-ethylhexanoate (sn-oct) or dibutyl tin oxide, could also work as initiators or catalysts for the opening of cyclic anhydrides. In order to confirm this idea, the ring-opening polymerization of adipic anhydride has now been studied in more detail.

EXPERIMENTAL

Materials

Adipic acid (p.a.) was recrystallized from ethanol. Acetic anhydride (p.a.), chloroform (p.a.), diethyl ether (p.a.), petroleum ether (p.a.), and stannous 2-ethylhexanoate were used as received. Succinic anhydride (p.a.) was recrystallized from chloroform, and glutaric anhydride (p.a.) from a chloroform–diethyl ether mixed solvent. All chemicals were purchased from Aldrich except stannous 2-ethylhexanoate which was purchased from Sigma Chemical Corp., U.S.A.

Monomer Synthesis

A solution of 15 g (0.1026 mol) adipic acid in 150 mL acetic anhydride in a dry reaction vessel equipped with a magnetic stirrer and reflux condenser was heated under reflux for 4 h while nitrogen was continuously bubbled through the solution. The acetic acid formed in the reaction and the excess acetic anhydride were removed by vacuum distillation.

The residue was transferred to a Claisen flask, the depolymerization catalyst was added (zinc acetate·$2H_2O$), and heating was started to raise the temperature under vacuum (0.9 mbar). After removal of the residual acetic anhydride at 0.9 mbar, no further distillation took place up to a bath temperature of 220°C. Above that temperature, the distillate consisted of a liquid (adipic anhydride) containing

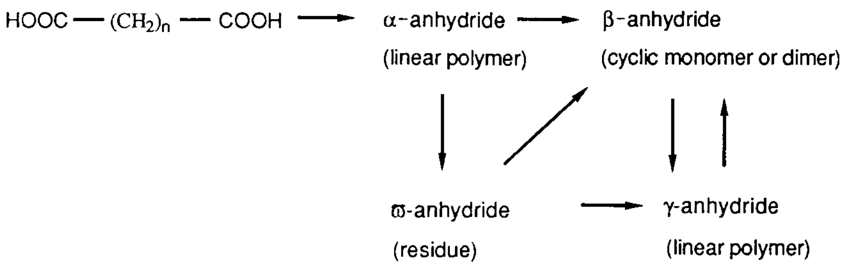


FIG. 1. Poly(anhydride) formation

a small amount of crystalline material (adipic acid) [1], which was separated from the liquid portion by filtration after the distillate had been cooled to room temperature. The monomer was dried over $MgSO_4$ and stored in a refrigerator.

Polymerization

The melt polymerization of monomer (1) was carried out in the following manner. To a previously dried 20 mL serum bottle, containing a magnetic stirrer, 16.0 mmol of monomer (1) and 0.06 mmol of stannous 2-ethylhexanoate, were added (M/I = 250) under nitrogen. The mixture was heated in the sealed tube at 80°C for 5 h, after which time the polymer was too viscous to stir. The polymer was then dissolved in dry chloroform and analyzed by GPC measurement. The percentage conversion of adipic anhydride to poly(adipic anhydride) was calculated from peak integration of the ^{1}H-NMR spectra.

Measurements

The resulting polymers were characterized by GPC, DSC, IR, and ^{1}H-NMR. A Waters 6000 A pump with four SHODEX columns (GPC AC-80 M/S) connected to a differential refractometer was used for GPC with chloroform as the solvent. The flow rate was 1 mL/min. The apparatus was run at 28°C with a solvent pressure of 45.5 MPa (650 psi). PS standards were used for calibration. The apparatus used for DSC was a Perkin-Elmer DSC-2 with a heating rate of 10°C/min and a cooling rate of 20°C/min, giving the samples the same thermal history. The FTIR used was a Perkin-Elmer 1710. Spectra were taken on polymer films cast from chloroform solution on NaCl cells. The NMR used was a JEOL JNM-PMX 60 SI. Samples were dissolved in deuterochloroform.

RESULTS AND DISCUSSION

Results of Syntheses

Following the depolymerization procedure described by Megna and Koroscil [10] for the preparation of ε-caprolactone, an improved synthesis of oxepane-2,7-dione was developed. As in the case of poly-ε-caprolactone, which was used in their work to give high yields of lactones by depolymerization, we used polyadipic anhydride (as described by Hill [1]) to give the 7-membered anhydride ring analogue. The diacid was converted to the mixed anhydride with acetic anhydride and then further converted to polyanhydride, followed by vacuum depolymerization in the presence of zinc acetate. This method resulted in higher yields of the ring (70%) than with depolymerization without catalyst (50%). The product, oxepane-2,7-dione, was characterized by elemental analysis.

Analysis. Calculated for $C_6H_8O_3$: C, 56.25; H, 6.25; O, 37.5%. Found: C, 55.4; H, 6.23; O, 36.7%.

This is in agreement with data previously reported by Hill: C, 55.89; H, 6.51 [1]. The ^{1}H-NMR spectrum in $CDCl_3$ showed a triplet at 2.8 ppm and a multiplet at 2.0 ppm in the ratio 1:1 which is in agreement with the structure outlined in Fig.2. The infrared spectrum showed a doublet at 1801 and 1757 cm^{-1} which is characteristic of the anhydride bound in the cyclic form.

The initiator chosen for this work was stannous 2-ethylhexanoate (sn-oct). The ratio of monomer to sn-oct was varied from 100 up to 1000. The polymerization reaction was studied at 80, 100, and 120°C. These temperatures were chosen because crystallization of polymer from the melt takes place at 75°C and because at temperatures above 120°C only dark brown liquids were obtained. Experimental results of the polymerization of adipic anhydride are summarized in Table 1. The data are valid for the mole ratio (M)/(I) = 250 and polymerization temperatures of 80 and 100°C.

Figure 3 shows that the consumption of oxepane-2,7-dione at the beginning of the ring-opening reaction is very fast in the presence of stannous 2-ethylhexanoate (filled squares) in comparison with the reaction without initiator (open squares). The conversion to polymer was calculated by integration of $-CH_2-CO-O-CO-CH_2-$ protons in the ring and open forms.

After this first period, the increase in molecular weight is moderate. The number-average molecular weight is almost constant after 2 h of reaction, but the weight-average molecular weight increases. The molecular weight is shown in Fig. 4 as a function of time for the melt polymerization of adipic anhydride initiated by stannous 2-ethylhexanoate at 80°C. Open squares represent the number-average molecular weight and filled squares the weight-average molecular

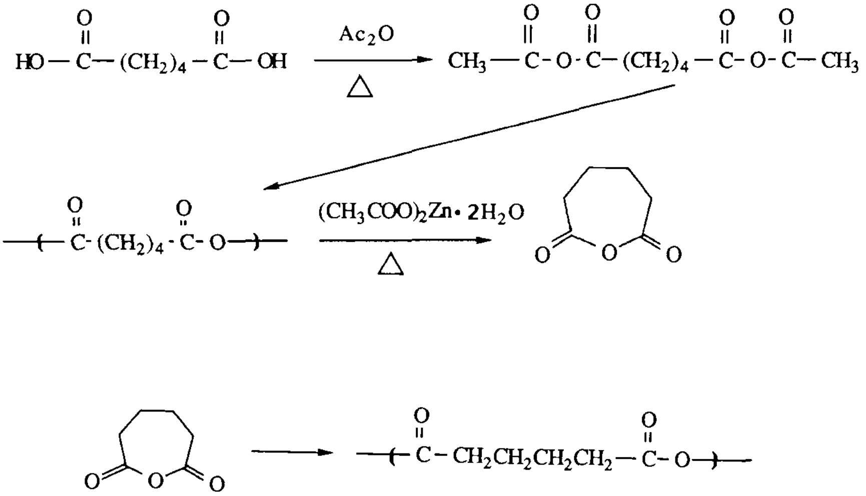


FIG. 2. Monomer synthesis and ring opening of adipic anhydride to polyanhydride.

TABLE 1. Conditions and Results of Melt Polymerization of Adipic Anhydride (1) with Stannous 2-Ethylhexanoate as Initiator. Mole ratio (M)/(I) = 250

Experiment	Initiator	T,°C	Time, h	Yield, %	M_w[a]
1	sn-oct	80	0.5	80	1500
2	sn-oct	80	1.0	78	1500
3	sn-oct	80	2.0	80	1700
4	sn-oct	80	3.0	77	2000
5	sn-oct	80	5.0	75	2700
6	sn-oct	100	0.5	79	2200
7	sn-oct	100	1.0	82	2100
8	sn-oct	100	2.0	84	1400
9	sn-oct	100	3.0	79	1300
10	sn-oct	100	5.0	77	1300
11[b]	sn-oct	80	12.0	0	—
12[c]	sn-oct	80	12.0	0	—
13	sn-oct	80	12.0	75	5000

[a] Measured by GPC in chloroform.

[b] Succinic anhydride.

[c] Glutaric anhydride.

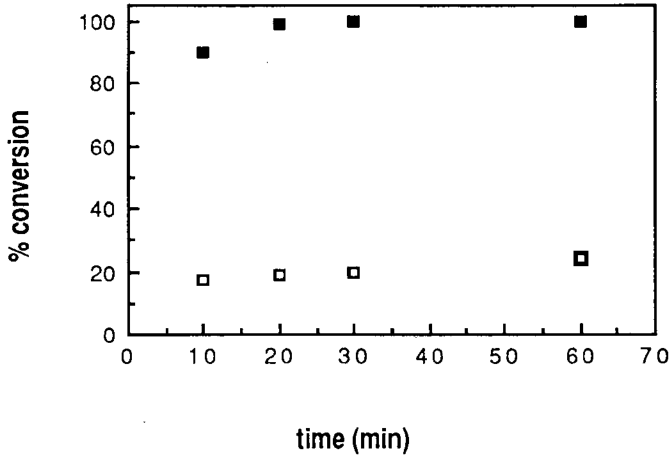


FIG. 3. Conversion curves as a function of time for the melt polymerization of oxepane-2,7-dione without catalyst at 80°C (open squares) and initiated by stannous 2-ethylhexanoate at 80°C (filled squares).

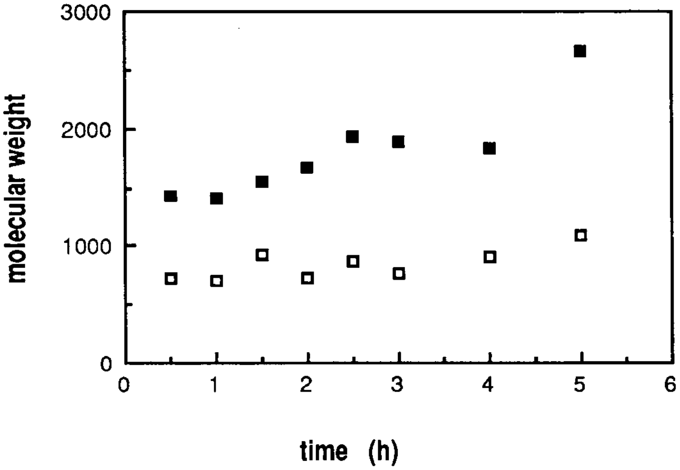


FIG. 4. Molecular weight as a function of time for the melt polymerization of adipic anhydride initiated by stannous 2-ethylhexanoate at 80°C. Open squares = M_n, filled squares = M_w.

weight. The molecular weight distribution increases from an initial narrow value and approaches the value of 2–3, indicating a Gaussian distribution. To explain this behavior, one can assume that the initially formed narrow molecular weight distribution gradually undergoes coupling reactions to yield a high molecular weight fraction. Since the weight-average molecular weight is sensitive to high molecular weight molecules and the number-average molecular weight is sensitive to low molecular weight molecules, an increase in polydispersity is expected. This behavior in the synthesis of poly(anhydrides) is in agreement with results presented by Hill and Carothers [3] and with work done by Domb and Langer [6]. At higher temperatures the increase in molecular weight is more rapid, but the leveling off after 1 h of reaction is obvious. Molecular weight curves are shown in Fig. 5 as a function of time for the melt polymerization of adipic anhydride initiated by stannous 2-ethylhexanoate at 100°C (open squares = number-average molecular weight, filled squares = weight-average molecular weight).

Initially a high molecular weight with a wide distribution (relatively high polydispersity) is formed at 100°C but after 1 h the weight-average molecular weight decreases. This behavior may perhaps be explained by the formation of monomers and low molecular weight cyclic macromers such as dimers, trimers,

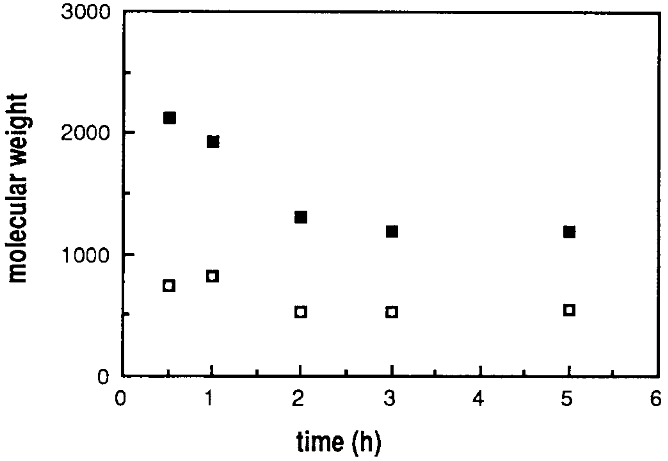


FIG. 5. Molecular weight curves as a function of time for the melt polymerization of adipic anhydride initiated by stannous 2-ethylhexanoate at 100°C. Open squares = M_n, filled squares = M_w.

etc., resulting in a more narrow molecular weight distribution. As can be seen in Fig. 6, which shows the GPC-chromatogram after polymerization of adipic anhydride at 100°C ((M)/(I) = 250), there is a shift to higher elution volumes after 5 h of reaction and also an increase in the low molecular weight fractions and a more narrow curve shape.

It is possible that after reaching a relatively high molecular weight at 100°C, the parallel depolymerization reaction becomes significant, leading to a decrease in molecular weight. This trend was investigated further by running the reaction at 120°C, which resulted in a slightly viscous dark brown liquid. This confirms that sn-oct acts as a depolymerization catalyst at elevated temperatures in the poly(anhydride) synthesis.

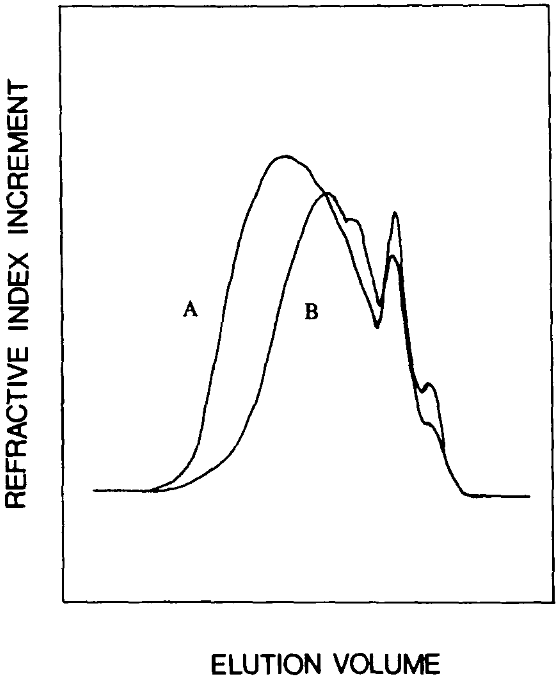


FIG. 6. GPC chromatograms after polymerization of adipic anhydride using sn-oct as a catalyst; Curve A after 0.5 h of reaction, and Curve B after 5 h of reaction at 100°C and (M)/(I) = 250.

When the ratio of monomer to initiator was varied from 100 to 1000, a slight increase in weight-average molecular weight was observed, as can be seen in Fig. 7, which shows the polymerization of adipic anhydride with different ratios of monomer to initiator at 100°C and a reaction time of 2 h (open squares = number-average molecular weight and filled squares = weight-average molecular weight). There was also a small increase in the number-average molecular weight. There is thus a tendency for a higher molecular weight to be reached by increasing the ratio of (M)/(I), which can be explained by a living character of the initiating species. If the reaction was simply an anionic insertion polymerization mechanism, the increase in molecular weight as a function of (M)/(I) ratios would be linear.

These results are in agreement with those of Hill and Carothers, who reported the formation of cyclic macromers at elevated temperatures in poly(anhydride) syntheses [3]. Similar results have also been reported by Domb and Langer [6]. They explained this behavior by the reaction of adjacent chains with themselves to produce larger and shorter chains as described in Fig. 8. Reactions at two points simultaneously will yield large rings, and these rings may continue to react by the same mechanism to produce smaller rings.

Experiments with the five-membered and six-membered cyclic anhydrides were

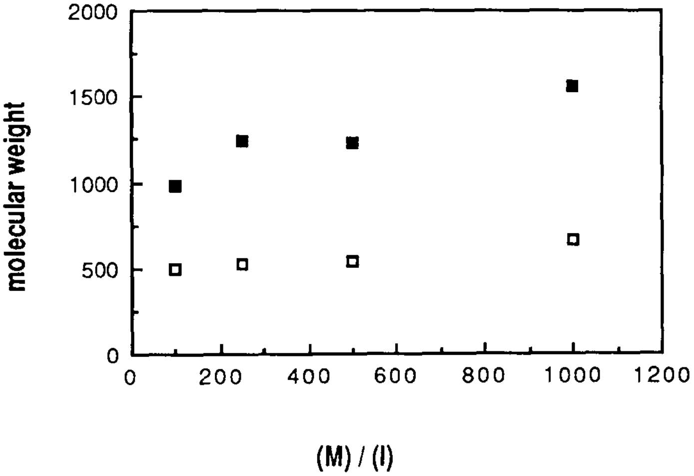


FIG. 7. Polymerization of adipic anhydride with different ratios of monomer to initiator at 100°C and a reaction time of 2 h. Open squares = M_n, filled squares = M_w.

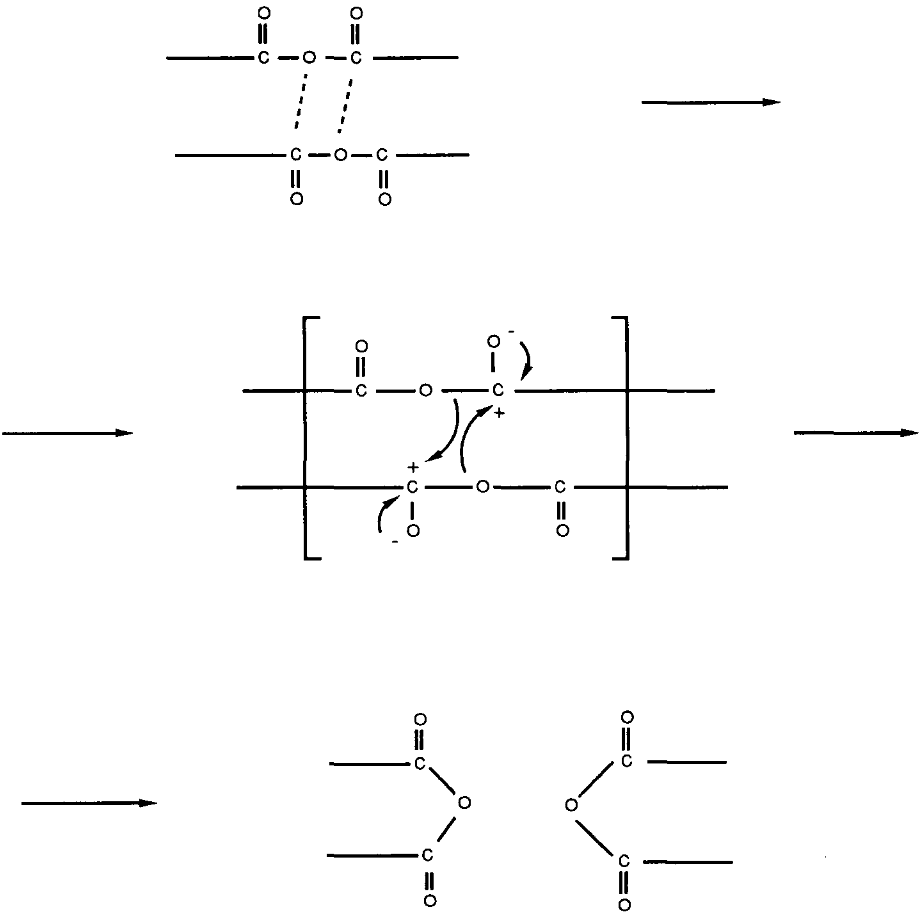


FIG. 8. Anhydride exchange reaction between adjacent chains.

also carried out in the presence of stannous 2-ethylhexanoate (Table 2), but no increase in molecular weight could be observed by GPC analysis.

The poly(adipic anhydrides) obtained were all characterized by ^{1}H-NMR analysis (triplet at 1.75 ppm and multiplet at 2.50 ppm). The infrared spectra showed doublets at 1820 and 1746 cm^{-1}, which are characteristic of the anhydride bond in an aliphatic polyanhydride.

The polymers had a melting point of 73°C and ΔH = 78 J/g as determined by DSC analysis.

Polymerization Mechanism

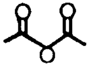
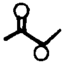
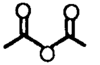
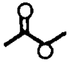
An attempt was made by IR- and ^{1}H-NMR analysis to investigate the mechanism of the initiation of oxepane-2,7-dione by sn-oct. We have measured the reaction between adipic anhydride and stannous 2-ethylhexanoate at room temperature and observed the shift in characteristic frequencies. The mole ratio of monomer to initiator was 1:1 to suppress the propagation step of the reaction. The results are shown in Table 3.

A shift in $\nu_{C=O}$ toward shorter wavelengths is indicative of a coordination of the C=O bond. Coordination of the endocyclic oxygen must shift the carbonyl band to higher wave numbers. No shift in the ν_{-CO-O-} could be observed, indicating that the ester group in sn-oct did not participate in the initiation. IR analysis showed the disappearance of the band at 930 cm^{-1} characteristic of the ring vibration [12] of the cyclic anhydride, indicating that ring-opening did occur. The ^{1}H-NMR spectra showed an instant shift in the peaks of adipic anhydride to lower ppm, which also manifests the rapid ring-opening of oxepane-2,7-dione. The intensities of the two IR bands from the anhydride bond can also be used to distinguish ring compounds from open chain compounds [13]. In small ring compounds it is found that the intensity of the lower band is always much more intense than the band at higher frequency. The opposite is the case for open-chain compounds [13]. This

TABLE 2. Results of the Bulk Polymerization in the Melt of Adipic Anhydride with Stannous 2-Ethylhexanoate with Different Mole Ratios of (M)/(I) at 100°C, Reaction Time 2 h

Experiment	Initiator	M/I	*T*, °C	Time, h	M_w
1	sn-oct	100	100	2	1000
2	sn-oct	250	100	2	1250
3	sn-oct	500	100	2	1250
4	sn-oct	1000	100	2	1700

TABLE 3. Characteristic IR Frequencies of Adipic Anhydride and Complexes with Stannous 2-Ethylhexanoate at Room Temperature: (M)/(I) = 1

			Original IR frequencies, cm^{-1}		Shifted or new IR frequencies, cm^{-1}		
Experiment	Monomer/initiator[a] mixture	Time, min	ν ()	ν ()	ν ()	ν ()	ν ()
1	AA	3	1801, 1757	—	1801, 1757	—	—
2	AA + sn-oct	3	1801, 1757	1708	1814, 1760	1708	—
3	AA + NaH	3	1801, 1757	—	1819, 1729	1563	1729
4	PAA	120	1801, 1757	—	1820, 1746	—	—

[a] Experiment 2 is a 1:1 mixture of (1) and sn-oct. Experiment 4 is the polymer. Experiment 3 is a 1:1 mixture of NaH and (1).

phenomenon could be observed after 3 min of reaction between oxepane-2,7-dione and stannous 2-ethylhexanoate.

Another way to open the cyclic anhydrides is by an anionic mechanism. By introducing NaH as an example of an anionic initiator, a new band at 1563 cm^{-1} due to carboxylate anion and another band at 1729 cm^{-} due to aldehyde formation appeared. There is also an instant shift in band intensities from the ring and open form respectively. The cleavage of the anhydride ring takes place by acyl-oxygen fission, either as a nonionic insertion polymerization mechanism, Fig. 9, at the beginning of the reaction, or after a few hours by an anhydride exchange reaction which then appears to be the dominating reaction.

The smooth degradation of the poly(anhydride)s yielding cyclic degradation products is consistent with the high mobility and reactivity of anhydrides. Hill and Carothers suggested that the formation of the γ-anhydride (Fig. 1) from the β-anhydride involves the mutual "coalescence" of the cylic molecules of the latter compounds [3]. They found that this transformation occurs under fairly rigorously anhydrous conditions and, since they could observe no terminal group in the resulting γ-anhydrides, they suggested that the transformation of α-anhydride depends upon the presence in this compound of terminal groups capable of being eliminated by condensation between adjacent molecules.

The function of sn-oct might also be just to increase the electron deficiency under the carbonyl carbon as is the case in the transesterification polymerization of polyesters. Domb and Langer [6] investigated the effects of a large number of coordination catalysts in the melt polycondensation of mixed anhydrides. They found that these catalysts were very effective in producing poly(anhydride)s in the condensation of mixed anhydrides with the removal of acetic anhydride.

There seem to be at least three possible reaction mechanisms in the ring-opening polymerization of adipic anhydride in the presence of stannous 2-ethylhexanoate: a) a nonionic insertion mechanism (initiating effect of sn-oct); b) coordination of the exocyclic oxygens in the anhydride bond of the ring, facilitating the anhydride interchange reaction that involves a nucleophilic attack on a carbonyl carbon from the endocyclic oxygen of another ring (catalytic effect from sn-oct); and c) anhydride exchange reactions between adjacent polymer chains (with or without the catalytic effect of sn-oct).

The formation of low molecular weight cylic monomers and macromers which are in equilibrium with the polymer formed at the temperatures studied might explain why only *DP* values around 10 were obtained, despite high (M)/(I) ratios.

Current investigations in our laboratory are focused on the effects of polymerization temperature and different catalysts and on the influence of solvents in the cyclic anhydride reactions, and also on the copolymerization between oxepane-2,7-dione and cyclic esters. The results of these studies will be reported soon.

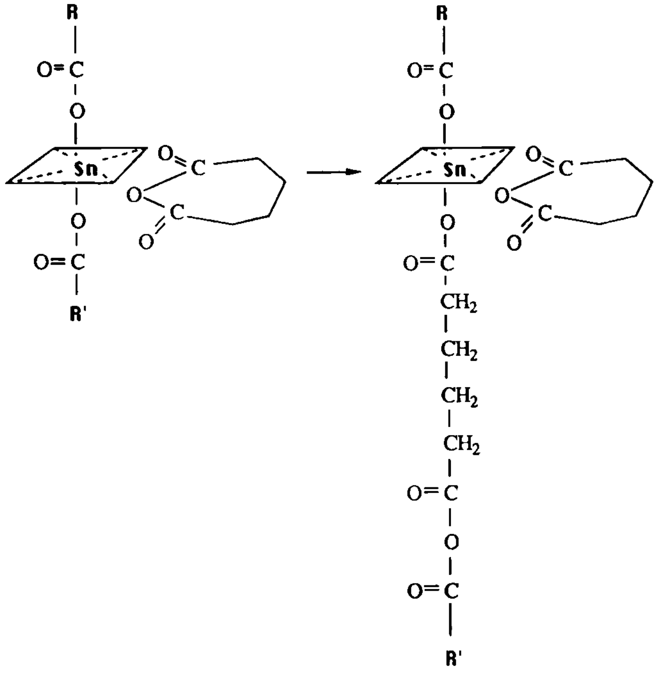


FIG. 9. Proposed mechanism for insertion-ring-opening of adipic anhydride by stannous 2-ethylhexanoate.

CONCLUSIONS

These results show that the ring-opening melt polymerization of oxepane-2,7-dione can be carried out in the presence of stannous 2-ethylhexanoate. The experimental results support a proposed nonionic insertion polymerization mechanism at the very beginning of the reaction, with sn-oct probably acting as an initiator. After 1 h of reaction, anhydride exchange, with sn-oct acting as a catalyst, is the dominating reaction which broadens the molecular weight distribution. The formation of monomers and low molecular weight cyclic macromers which are in equilibrium with the polymer formed explains why *DP* values of the order of 5–10 were obtained, despite high (M)/(I) ratios.

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