The Use of Different Diols in the Synthesis of Low-Molecular-Weight Lactic-Acid-Based Telechelic Prepolymers

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ABSTRACT: The synthesis of low-molecular-weight ($\bar{M}_w$ (GPC) < 72000 g mol) lactic-acid-based telechelic prepolymers by condensation polymerization of *L*-lactic acid was investigated. All polymerizations were carried out in the melt, using tin(II)octoate as catalyst, different diols, and different polymerization temperatures. The products were characterized by differential scanning calorimetry (DSC), gel permeation chromatography (GPC), titrimetric methods, and ^{13}C nuclear magnetic resonance (NMR). According to NMR, the resulting polymers contained less than 1 mol % of lactic acid monomer and less than 8.5 mol % of lactide. The weight-average molecular weights of prepared prepolymers determined by GPC varied from 3800 to 72,000 g mol, depending on the diol and the polycondensation conditions. In DSC studies, the glass transition temperatures of the resulting polymers varied from 27 to 50°C, and the crystallinity from 0 to 51.8%. When aromatic diols were used in polymerizations, the location of hydroxyl groups had a strong effect on the properties of the final prepolymer. According to our results, the aromatic diols produced higher-molecular-weight prepolymers when the hydroxyl groups were located so that the polyester chains could grow in opposite directions. The introduction of a heteroatom raised the glass transition temperature of the prepolymer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 1017–1023, 1998

INTRODUCTION

Lactic acid is an attractive monomer in the synthesis of biodegradable polymers. Poly(lactic acid) can be produced by the condensation polymerization of lactic acid, or by the ring opening polymerization of lactide, which is the dilactone of lactic acid. The direct polycondensation of lactic acid does not produce high-molecular-weight polyester unless a special catalyst and long polymerization times are used.[1] Furthermore, during the polycondensation, the molecular weight of poly(lactic acid) is reduced by depolymerization where the lactide is formed.[2]

We have studied a two-step process for lactic acid polymerization. In the first step, the lactic acid is condensation-polymerized to a low-molecular-weight prepolymer, which contains one kind of end group. In the second step, the molecular weight is raised by joining prepolymer chains together using difunctional substances, such as diisocyanates, as the chain extenders. In our previous studies,[3–7] we have used 1,4-butanediol in the synthesis of hydroxyl-terminated prepolymer. The diol acts as the functionalizing substance, and the resulting prepolymer contains mainly hydroxyl end groups. According to our studies, 1,4-butanediol produced prepolymers with quite good molecular weights; but the prepolymers were amorphous, and their glass transition temperatures were quite low. When 2 mol % of 1,4-butanediol was used in the polycondensation of lactic acid, the resulting prepolymer has a weight-average molecular weight of 11900 g mol and a glass transition temperature of 41°C. This amorphous pre-

polymer contained 29.5 mol % of *D*-lactic acid structures [determined with ^{13}C nuclear magnetic resonance (NMR)]. In this article, we study the effect of different diols on the properties of the final prepolymers. In the polymerizations, we have used aliphatic diol, several aromatic diols with different structures, and an aromatic diol that contains a heteroatom. The purpose of this work was to prepare prepolymers with higher molecular weights and higher glass transition temperatures. Aromatic diols were used in order to get some stiffness in the polyester chains and to study how this stiffness affects the glass transition temperature and the crystallinity of the polymers prepared. In the aromatic diols, we used, where possible, two different hydroxyl groups locations in order to eliminate the possible effects of, for example, steric hindrance. The basic synthesis and characterization work of prepolymers was presented in our previous study.[7]

EXPERIMENTAL

Materials

L-Lactic acid (LA) from Fluka (Switzerland, Buchs) was a 90% aqueous solution of the monomer, 99% optically pure according to the manufacturer. The excess water was removed before use by distillation under reduced pressure at 100°C. The following products were used without further treatment: 2-ethyl-1,3-hexanediol, 1,5- and 2,7-dihydroxynaphtalene, 1,4- and 1,8-dihydroxyanthraquinone, 4,4-isopropylidenediphenol, 4-hydroxyphenyl sulfone, and 4,4′- and 2,2′-dihydroxybiphenyl from Fluka; tin(II)octoate from Sigma Chemical Co. (Germany, Deisenhosen); chloroform from Fluka; and chloroform-d$_1$ with tetramethylsilane (TMS) (1%), and a deuteration degree not less than 99.5%, from Merck (Germany, Darmstadt).

Characterizations

Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersities ($\bar{M}_w/\bar{M}_n$) were determined with respect to polystyrene standards by gel permeation chromatography (GPC). The system from Waters Associates used was equipped with a Waters 700 Satellite wisp injector, a Waters 510 high-performance liquid chromatography (HPLC) solvent pump, four linear PL gel columns (10^4, 10^5, 10^3, and 100 Å) connected in series, and a Waters 410 dif-

ferential refractometer. All samples were analyzed at room temperature. Chloroform was used as the eluent and was delivered at a flow rate of 1.0 mL min. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 μL.

For NMR measurements, the samples were dissolved in chloroform-d$_1$ in 5 mm NMR tubes at room temperature. The sample concentration was about 10% by weight. Proton-decoupled ^{13}C-NMR spectra with nuclear Overhauser effect (NOE) were recorded on a Varian Unity 400 NMR spectrometer, working at 100.577 MHz for carbon-13.

Differential scanning calorimetric (DSC) measurements were made on a PL Thermal Sciences DSC. The measurements were run from −50 to 200°C, at a heating rate of 10°C/min and at a cooling rate of 1°C/min. The glass transition temperatures and crystallinity data were determined from the second heating period. The crystallinity of different polymers was evaluated from the heat of fusion. By integrating the normalized area of the melting endotherm, determining the heat involved, and rating it to the reference 100% crystalline polymer (93.6 J g),[8] the relative crystallinity of the polymer was assessed. In this article, the relative degree of crystallinity is referred to as crystallinity, and T_m is the melting temperature.

Acid number was determined by a standard titrimetric method DIN 53 402. Every titration was repeated four times, and the reported result is an arithmetic average of these titres.

Synthesis of Lactic Acid Polymers

All polymerizations were carried out in the melt, using 20 mL test tubes. For every polymerization, 7 g of *L*-lactic acid was accurately added to the test tube. Then, 2 mol % of diol and 0.05 wt % of tin(II)octoate was added to the test tube, and the tube sealed with Glisseal laboratory grease. A continuous nitrogen gas flow was maintained under the surface of the polymerization mixture. The tube was placed in an oil bath, and the temperature was raised from room temperature to 180°C over a period of 4 h. Depending on the required polymerization temperature, the temperature was kept constant or raised over a period of 2 h. The total polymerization time in every experiment was 24 h, and one sample was taken after 8 h of polymerization at the final polymerization temperature. After 24 h of polymerization, the molten polymer was poured into an aluminium pan and placed in a desiccator to cool down. After

cooling, the resulting polymer was pulverized and analyzed.

RESULTS AND DISCUSSION

A detailed description of the low-molecular-weight lactic acid polymer analysis was presented in our previous study,[7] and the analysis results for prepolymers prepared at 180°C are collected in Table I. The GPC was calibrated with narrow polystyrene standards; therefore, GPC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. Table I lists the polymerizations, diols used, and characterization results for prepolymers prepared at 180°C.

The amount of lactic acid and lactide was calculated using the ^{13}C-NMR spectra methine area peak integrals. Figure 1 shows the structures of the tested diols.

Polymerization Results

At 180°C, 2-ethyl-1,3-hexanediol produced an amorphous prepolymer, which had an increased molecular weight when the polymerization was carried on from 8 to 24 h. Logically, the acid number decreased, and the glass transition temperature increased at the same time. The amount of D-lactic acid structures increased, showing that during polycondensation the ester interchange, reactions happen; and the longer the polymerization time, the higher the amount of D-lactic acid structures. It appears that tin(II)octoate and 2-ethyl-1,3-hexanediol produce a polycondensation system in which the ester interchange reactions happen through the breaking of the oxygen−alkyl bond, leading to racemization. When the polymerization temperature was raised to 200 and 220°C, the resulting polyesters had lower molecular weights than the polymers produced at 180°C. The amount of D-lactic acid structures and lactide also increased when the polymerization temperature was increased. The glass transition temperatures decreased, and the acid numbers increased when the polymerization temperature was increased. For 2-ethyl-1,3-hexanediol, the optimum polymerization temperature was 180°C. The polymerization time should be longer than 24 h because the acid number should be less than one if these polyesters are to be used in poly(ester-urethane) synthesis.

In the case of 1,5-dihydroxynaphtalene, the weight-average molecular weight of the prepolymer at 180°C was higher after 8 h of polymerization than after 24 h of polymerization. In 8 h, this prepolymer had reached a weight-average molecular weight of 13300 g mol and it showed slight crystallinity. After 24 h of polymerization, the weight-average molecular weight had decreased, and the acid number had increased. This showed that the prepolymer had already degraded thermally or that the ester interchange reactions had decreased the molecular weight. The 15 mol % increase in D-lactic acid structures shows that there are strong ester interchange reactions during polycondensation. Like 2-ethyl-1,3-hexanediol, the 1,5-dihydroxynaphtalene seems to produce a mechanism in which the ester interchange reactions happen through the breaking of the oxygen−alkyl bond, leading to racemization. When the polymerization temperature was raised to 200 and 220°C, the molecular weight of the prepolymer increased dramatically. At 200°C, the weight-average molecular weight was 16,300 g mol; and at 220°C, it was 71,800 g mol. Unlike the polymerization at 180°C, the molecular weight of the resulting prepolymers was higher after 24 h of polymerization than after 8 h of polymerization. The glass transition temperature of the prepolymers that were produced at higher temperatures was about 52°C. The amount of D-lactic acid structures was about equal to that for the polymers prepared at 180°C. The acid number decreased when the molecular weight of the prepolymer increased. The polymer that was produced at 220°C had an acid number of 3.4, which is quite a good value. The amount of lactide was less than 2 mol % for every polymerization temperature.

The polymerization results with 2,7-dihydroxynaphtalene were totally different to those for the 1,5-dihydroxynaphtalene polymerizations. At 180°C, the weight-average molecular weights were smaller; and the molecular weight of the prepolymer increased when the polymerization was carried on from 8 h to 24 h. After 24 h of polymerization at 180°C, the amount of lactide was 2.1 mol %; and the acid number was 8.8. The prepolymer contained only 8.2 mol % of D-lactic acid structures, and the polymer was still amorphous. It appears that D-lactic acid structures are randomly divided in the polymer chains; therefore, the polymer chains cannot form crystals. When the polymerization temperature was raised to 200 and 220°C, the molecular weight of the prepolymer increased, but not as dramatically as in the 1,5-dihydroxynaphtalene polymerizations. At 200°C,

Table I   The Polymerization Results at 180°C with 2 Mol % of Diol and 0.05 Wt % of Tin(II)octoate

| Polymer	Diol	Temperature and Time (°C/h)	$\bar{M}_w$ (GPC) (g/mol)	PD (GPC)	D-Lactic Acid Struc (^{13}C-NMR) (mol %)	Lactide (^{13}C-NMR) (Mol %)	Acid Number (titr)	T_g (°C)	T_m (°C)	Crystallinity (%)
1	2-ethyl-1,3-hexanediol	180/8	18,000	1.5	12.0	3.5	21.6	41	nd	0
2	2-ethyl-1,3-hexanediol	180/24	22,400	1.5	19.7	3.6	10.3	45	nd	0
3	1,5-dihydroxynaphtalene	180/8	13,300	2.2	10.3	1.4	9.2	48	139	1.6
4	1,5-dihydroxynaphtalene	180/24	10,100	2.5	25.4	1.5	11.3	45	nd	0
5	2,7-dihydroxynaphtalene	180/8	9500	2.3	6.2	2.0	9.8	44	145	7.1
6	2,7-dihydroxynaphtalene	180/24	11,000	2.4	8.2	2.1	8.8	45	nd	0
7	1,4-dihydroxyanthraquinone	180/8	7100	1.6	5.3	0.5	11.5	40	140	45.8
8	1,4-dihydroxyanthraquinone	180/24	18,900	1.7	7.5	2.5	20.4	45	156	43.2
9	1,8-dihydroxyanthraquinone	180/8	19,200	2.4	7.3	2.6	20.1	45	155	51.8
10	1,8-dihydroxyanthraquinone	180/24	18,300	1.8	20.3	2.9	22.0	43	126	11.2
11	4,4-isopropylidenediphenol	180/8	13,500	2.6	5.9	2.1	10.2	42	148	6.6
12	4,4-isopropylidenediphenol	180/24	15,200	2.2	22.7	2.4	7.3	43	nd	0
13	4-hydroxybiphenyl sulfone	180/8	7100	2.0	4.9	1.3	40.7	41	136	4.5
14	4-hydroxybiphenyl sulfone	180/24	30,100	1.7	11.4	2.5	25.1	49	nd	0
15	4,4'-dihydroxybiphenyl	180/8	8400	1.8	24.7	2.1	7.4	42	nd	0
16	4,4'-dihydroxybiphenyl	180/24	17,100	1.8	27.9	2.8	2.1	46	nd	0
17	2,2'-dihydroxybiphenyl	180/8	3800	1.5	22.5	2.0	40.8	27	nd	0
18	2,2'-dihydroxybiphenyl	180/24	15,600	2.1	27.9	2.3	20.9	37	nd	0

nd = not detectable.
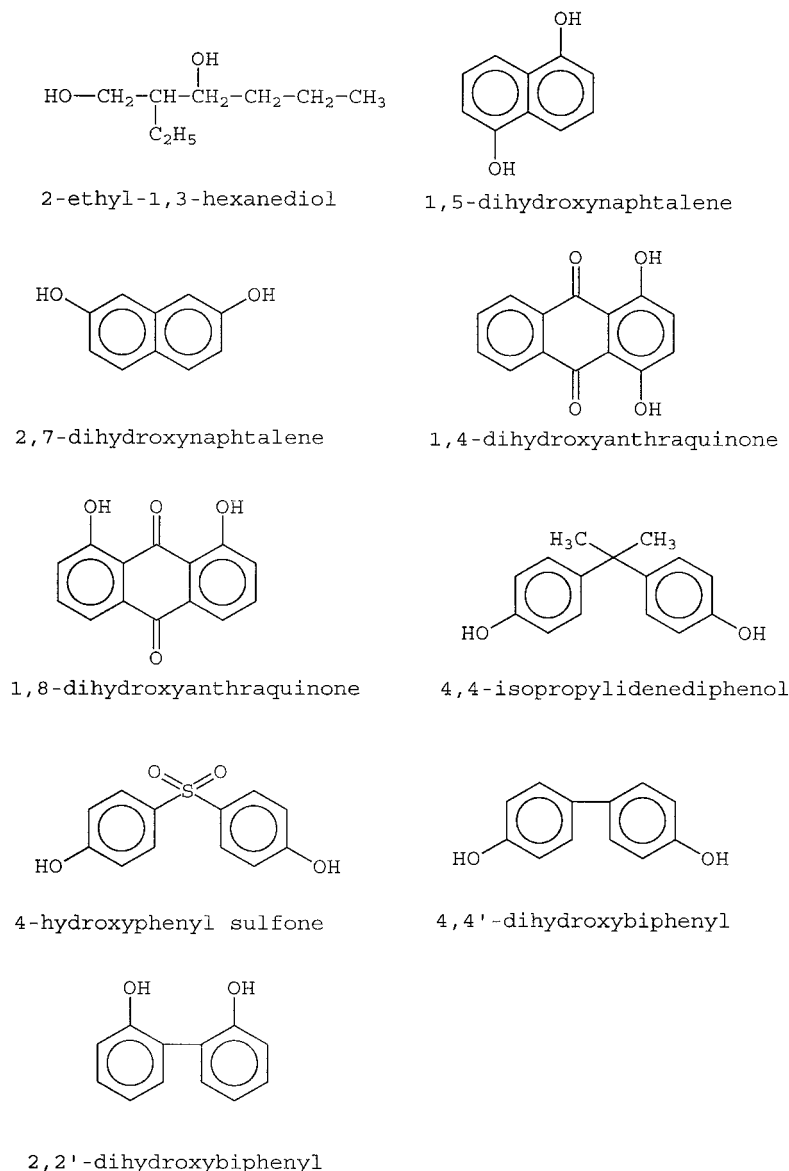
Figure 1 The structures of tested diols.

the weight-average molecular weight was 16,400 g mol; at 220°C, it was 23,100 g mol. The glass transition temperature of the prepolymers that were produced at higher temperatures was about 46°C. The amount of *D*-lactic acid structures was about equal to that for the polymers prepared at 180°C. The acid number decreased when the molecular weight of the prepolymer increased. The polymer that was produced at 220°C had an acid number of 1.9, which is a very good value. The amount of lactide was about 2 mol % for every polymerization temperature.

At 180°C 1,4-dihydroxyanthraquinone produced a crystalline prepolymer that had a weight-

average molecular weight of 18900 g mol after 24 h of polymerization. After 8 h of polymerization, the prepolymer had a molecular weight of 7100 g mol, and it contained only 5.3 mol % of *D*-lactic acid structures. When the polymerization was carried on from 8 to 24 h, the amount of *D*-lactic acid structures increased to only 7.2 mol %, and the corresponding crystallinity decreased from 45.8 to 43.2 mol %. 1,4-dihydroxyanthraquinone and tin(II)octoate seem to produce the mechanism in which the possible ester interchange reactions happen mainly through the breaking of the oxygen-carbonyl bond, leading to optically pure polyester chains. The glass transition tempera-

ture was 45°C after 24 h of polymerization at 180°C. When the polymerization temperature was raised to 200 and 220°C, the molecular weight of the prepolymer almost doubled. At 200°C, the weight-average molecular weight was 26800 g mol; at 220°C, it was 37800 g mol after 24 h of polymerization. The glass transition temperature of the prepolymers that were produced at higher temperatures was about 46°C. The amount of *D*-lactic acid structures and crystallinity was about equal to that for the polymers prepared at 180°C. The polymer that was produced at 220°C had an acid number of 2.3, which is a good value. The amount of lactide was about 2.5 mol % after 24 h of polymerization for every temperature.

The polymerization results with 1,8-dihydroxy-anthraquinone were totally different from those for the 1,4-dihydroxyanthraquinone polymerizations. At 180°C, the weight-average molecular weight after 8 h of polymerization was higher; and the molecular weight did not increase when the polymerization was carried on from 8 to 24 h. After 8 h of polymerization at 180°C, the weight-average molecular weight was 19200 g mol; and the prepolymer had 51.8% crystallinity. When the polymerization was carried on from 8 to 24 h, the prepolymer molecular weight decreased to 18300 g mol; and the crystallinity decreased to 11.2%. After 8 h of polymerization at 180°C, the amount of lactide was 2.6 mol %; and the acid number 20.1. The amount of *D*-lactic acid structures increased from 7.3 to 20.3 mol % when the polymerization was carried on from 8 to 24 h. When the polymerization temperature was raised to 200 and 220°C, the molecular weight of the prepolymer increased, but not as much as in the 1,4-dihydroxyanthraquinone polymerizations. At 200°C, the weight-average molecular weight was 25,000 g mol; at 220°C, it was 30,400 g mol after 24 h of polymerization. There was only a slight difference in molecular weights after 8 and 24 h of polymerization. The glass transition temperature of the prepolymers that were produced at higher temperatures was about 45°C. The amount of *D*-lactic acid structures was about equal to that for the polymers prepared at 180°C. The acid number decreased when the molecular weight of the prepolymer increased. The polymer that was produced at 220°C had an acid number of 3.1, which is quite a good value. The amount of lactide was less than 3 mol % for every polymerization temperature.

4,4-isopropylidenediphenol produced a prepolymer whose weight-average molecular weight increased from 13,500 to 152,00 g mol when the polymerization was carried on from 8 to 24 h at 180°C. The 8 h sample showed a slight crystallinity; but after 24 h polymerization, the polymer was totally amorphous. The acid number of the final prepolymer was 10.2, and it contained 22.7 mol % of *D*-lactic acid structures. The amount of lactide was about 2.4 mol %. The polymerization results at 200 and 220°C were almost identical to the results at 180°C; except that, at 220°C, the weight-average molecular weight of the resulting prepolymer was 13,400 g mol after 24 h of polymerization.

4-hydroxybiphenyl sulphone contains a sulphur atom between two aromatic groups. The effect of this structure can be seen from the high glass transition temperature of the prepared prepolymer. After 24 h of polymerization at 180°C, the resulting prepolymer had a weight-average molecular weight of 30,100 g mol and a glass transition temperature of 49°C. The prepolymer showed slight crystallinity after 8 h of polymerization; but after 24 h of polymerization, the resulting prepolymer was amorphous. The acid number of the final prepolymer was 25.1, which showed that the polymerization time was not long enough. The amount of lactide was 2.5 mol % at the end of the polymerization. When the polymerization temperature was raised to 200 and 220°C, the molecular weight of the prepolymer decreased. The higher the polymerization temperature, the lower the molecular weight. At 200°C, the molecular weight was 13,300 g mol; at 220°C, it was 11800 g mol after 24 h of polymerization. The glass transition temperatures of these prepolymers were 46 and 45°C. At higher temperatures, the resulting prepolymers were all amorphous.

At 180°C, 4,4′-dihydroxybiphenyl produced a prepolymer that had an acid number as low as 2.1 after 24 h of polymerization. In this polymerization, the weight-average molecular weight increased from 8400 g mol to 17,100 g mol when the polymerization was continued from 8 to 24 h. Both polymer samples were amorphous, and they contained over 24 mol % of *D*-lactic acid structures. The glass transition temperature of the final prepolymer was 46°C, and the amount of lactide was 2.8 mol %. When the polymerization temperature was raised to 200 and 220°C, the molecular weights of the resulting prepolymers were lower than for the polymerization at 180°C. At 200°C, the prepolymer had a weight-average molecular weight of 16,700 g mol; at 220°C, it was 11,200 g mol. The other properties were also lower than for

the polymerization at 180°C. The lower molecular weights were probably caused by the thermal degradation reactions, which were faster at 200 and 220°C than the polycondensation reactions. The optimum conditions for 4,4′-dihydroxybiphenyl seem to be 180°C and 24 h of polymerization.

At 180°C, 2,2′-dihydroxybiphenyl produced a prepolymer whose weight-average molecular weight was 15,600 g mol after 24 h of polymerization. Although the molecular weight of the prepolymer was almost equal to that for the prepolymer produced with 4,4′-dihydroxybiphenyl, the acid number was as high as 20.9. The reason for this could be that the structure of 4,4′-dihydroxybiphenyl worked more efficiently in the functionalizing of lactic acid prepolymers. The glass transition temperatures of the prepolymers that were produced with 2,2′-dihydroxybiphenyl were exceptionally low. For the prepolymer that was produced at 180°C, the glass transition temperature was 37°C, which is 9°C lower than for the 4,4′-dihydroxybiphenyl prepolymer. The amount of *D*-lactic acid structures was equal to that for the 4,4′-dihydroxybiphenyl polymer. When the polymerization temperature was raised to 200 and 220°C, the molecular weights of the resulting prepolymers were lower than for the polymerization at 180°C. At 200°C, the prepolymer had a weight-average molecular weight of 12,400 g mol; at 220°C, it was 9300 g mol. The other properties were also lower than for the polymerization at 180°C. The lower molecular weights were probably caused by the thermal degradation reactions, which were faster at 200 and 220°C than the polycondensation reactions.

CONCLUSIONS

In this study we used 2 mol % of different diols in order to prepare hydroxyl-terminated prepolymers. In previous studies, we have used 1,4-butanediol as functionalizing substance. When 2 mol % of butanediol was used in the polycondensation of lactic acid, the resulting prepolymer had a weight-average molecular weight of 11,900 g mol and a glass transition temperature of 41°C. Aliphatic 2-ethyl-1,3-hexanediol produced a higher-molecular-weight prepolymer, which had a glass transition temperature of 45°C. The higher glass transition temperature could be caused by ethyl and propyl side groups on this diol. These groups can prevent the flow of prepolymer chains. When aromatic diols were used in polymerizations, the location of the hydroxyl groups had a strong effect on the properties of the final prepolymer. According to our results, the aromatic diols produced higher-molecular-weight prepolymers when the hydroxyl groups were located so that the polyester chains could grow in opposite directions. This kind of diol (1,5-dihydroxynaphtalene, 1,4-dihydroxyanthraquinone, and 4,4′-dihydroxybiphenyl) produced prepolymers with molecular weights and glass transition temperatures that were clearly higher than for 1,4-butanediol polymers under the best conditions. When the diol contained a sulphur atom, the resulting prepolymer had a glass transition temperature of 49°C and a weight-average molecular weight of 30,100 g mol. 1,4-dihydroxyanthraquinone was the only diol that produced, with tin(II)octoate, an ester interchange mechanism where the possible ester interchange reactions happen mainly through the breaking of the oxygen-carbonyl bond. This mechanism leads to optically pure polyester chains. The highest weight-average molecular weight, 71,800 g mol, was achieved when 1,5-dihydroxynaphtalene was used in polymerization.

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