

Lactic Acid Based Poly(ester–urethane)s: The Effects of Different Polymerization Conditions on the Polymer Structure and Properties

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ABSTRACT: A two-step process for lactic acid polymerization is studied: in the first step the lactic acid is condensation-polymerized to a low-molecular-weight hydroxyl-terminated prepolymer; and then the molecular weight is raised by joining prepolymer chains together using diisocyanate as the chain extender. The resulting polymer is a thermoplastic poly(ester–urethane). In this study, we synthesized three different prepolymers and used three different diisocyanates as chain extenders. All of the prepolymers were hydroxyl-terminated, and their weight average molecular weights were 5,500 g/mol, 11,900 g/mol, and 26,000 g/mol. One of the diisocyanates was aliphatic, and the other two were stiff cycloaliphatic diisocyanates. The results indicate that of the tested diisocyanates, high weight average molecular weight can be achieved only by using aliphatic 1,6-hexamethylene diisocyanate. The cycloaliphatic diisocyanates produced poly(ester–urethane)s with weight average molecular weights which were quite low, but due to the stiffness of the polymer chains the glass transition temperatures can be as high as 60°C. The 1,6-hexamethylene diisocyanate (HDI) results also indicate that the molecular weight and network formation can be controlled independently by the amount of diisocyanate used and the polymerization conditions. Only the poly(ester–urethane)s which were produced with HDI had good mechanical properties, while the stiff diisocyanates produced very brittle polymers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 865–873, 1997

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INTRODUCTION

The feasibility of production processes and the possibility of using renewable raw materials have made lactic acid an attractive monomer for biodegradable polymers. However, poly(lactic acid) must have a relatively high molecular weight in order to have acceptable mechanical properties in many applications.¹ Conventional condensation polymerization of lactic acid does not increase the molecular weight enough, or the polymerization time must be very long.² In condensation polymer-

ization, the yield of cyclic side products such as lactides is often too high. Acceptable molecular weights can also be achieved through ring-opening polymerization of lactides.

Polyurethanes are polymers which typically are synthesized by the addition reaction of an alcohol with an isocyanate group. They contain the urethane group as a characteristic structural element ($R-NH-CO-O-R'$).³ In the preparation of poly(ester–urethane)s, hydroxyl-terminated macroglycols with a low acid number and low water content⁴ react with diisocyanate. The polyaddition reaction is influenced by the structure (e.g., steric hindrance) and functionality of the monomers, nature of the hydroxyl group, polymerization temperature, and OH/NCO ratio.

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Ahn and colleagues⁵ studied the changes in the properties of elastomer polyurethanes when one of the components was altered. They noticed that when the flexible 1,4-butanediol was replaced by stiff isophoronediamine the modulus was increased, perhaps because of the stiff structure of isophoronediamine. Smith and Magnusson⁶ examined the effects of diisocyanate type, urethane content, and degree of crosslinking on the properties of elastomeric urethane polymers made by reaction of diisocyanates with a combination of poly(oxypropylene)glycol of molecular weight about 2,000 g/mol, dipropylenglycol, and trimethylolpropane. By varying the relative proportions of the three hydroxylated components they were able to vary the urethane content and degree of crosslinking independently. Elastomers were made from 2,4-toluenediisocyanate (TDI) and from 1,6-hexamethylene diisocyanate (HDI), and it was shown that the glass transition temperature (T_g) increased with increasing urethane content but was unaffected by the degree of crosslinking over a wide range. Smith and Magnusson found that the difference in T_g s between the HDI and TDI series was largely due to the effect of the phenylene group of TDI which increased the chain stiffness and reduced flexibility. The increase in T_g with increasing urethane content for the HDI-based series must be a consequence of the effect of the urethane group, as the hexamethylene unit would not be expected to increase chain stiffness.

The influence of diisocyanates is also important in the biodegradability of poly(ester-urethane)s. Linear diisocyanates are less resistant to biodegradation than cyclic diisocyanates and a linear structure of polymer chains has a higher biodegradability than the corresponding branched structure.^{7,8} Commercially obtainable methylene and toluene (TDI) diisocyanates have found limited use as surgical materials, since the hydrolysis products have been found to be toxic or suspected carcinogens.⁹ Storey and associates¹⁰ used ethyl 2,6-diisocyanatohexanoate and poly(ester triol)s synthesized from DL-lactide, ϵ -caprolactone, or comonomer mixtures of the two, with glycerol as initiator. Their urethane segments hydrolyze completely into ethanol and L-lysine, which are biocompatible.

In 1992, Seppälä and colleagues¹¹ reported one route for converting lactic acid to high molecular weight polymers through the condensation oligomerization of pure lactic acid followed by isocyanate linking.¹²⁻¹⁴

In this article, we report on the linking of different molecular weight lactic acid based hydroxyl-

terminated prepolymers with different diisocyanates, and also investigate the effects of the isocyanate/hydroxyl ratio on the molecular weights and polymer structure. The synthesis and characterization of the low-molecular-weight hydroxyl-terminated prepolymers was presented in our previous work.^{15,16}

EXPERIMENTAL

Materials

L-Lactic acid from Fluka (Germany) was a 90% aqueous solution of the monomer, 99% optically pure (according to the manufacturer). The excess water was distilled off under reduced pressure and at a temperature of 100°C. The following products were used without further treatment: 1,4 butanediol (+98%) from Fluka Chemika (Germany); tin(II) octoate from Sigma Chemical Co. (Germany); chloroform (stabilized with 1% ethanol) from Riedel-de Haen Ag (Germany); chloroform- d_1 with TMS (1%), deuteration degree not less than 99.5%, from Merck (Germany); hexamethylenediisocyanate from Fluka Chemika (Germany); isophorone diisocyanate (Vestanat IPDI) from Hüls AG (Germany); 4,4'-dicyclohexylmethane diisocyanate (DES; Desmondur) from Bayer AG (Germany); and potassiumbromid (spectroscopy grade) from Riedel-de Haen Ag (Germany).

Characterizations

Molecular weights (\bar{M}_n and \bar{M}_w) and polydispersity (\bar{M}_w/\bar{M}_n) were determined with respect to polystyrene standards by gel permeation chromatography. The Waters Associates system that was used was equipped with a Waters 700 Satellite wisp injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10^4 Å, 10^5 Å, 10^3 Å, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature. Chloroform was used as the eluent, which was delivered at a flow rate of 1.0 mL/min. The samples were dissolved in chloroform at a concentration of 1.0% (wt/vol). The injection volume was 200 μ L.

For nuclear magnetic resonance (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 were recorded on a Var-

ian Unity 400 NMR spectrometer working at 100.577 MHz for carbon-13.

Differential scanning calorimetry measurements were made on a PL Thermal Sciences DSC. The measurements were run from -50 to 200°C , at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Synthesis of Prepolymer

The L-lactic acid was condensation-polymerized with 1, 2, and 4% 1,4-butanediol to produce hydroxyl-terminated telechelic prepolymers. The synthesis and characterization of these prepolymers was described in our previous studies.^{15,16} The amounts of 1,4-butanediol used produced prepolymers with number average molecular weights from 1,500 to 6,600 g/mol (determined by ^{13}C -NMR).

Synthesis of Poly(ester-urethane)s

The typical small-scale polyurethane synthesis procedure was carried out as follows: 40 g of prepolymer was accurately weighed into a 300-mL glass reactor and the reactor was sealed with gis-seal laboratory grease. The system was purged with a continuous flow of argon. The reactor was placed in an oil bath and the temperature was raised to 150°C . The temperature was kept constant until the prepolymer had melted. The amount of isocyanate to be added was calculated using the molecular weight of the prepolymer (determined by ^{13}C -NMR) and the desired isocyanate hydroxyl ratio. The accurate amount of diisocyanate was added, and the temperature was raised to the polymerization temperature of 150 or 180°C . The polymerization was followed by taking samples every 15 min. After polymerization, the molten polymer was poured into an aluminium pan and placed in a desiccator to cool. After cooling, the resulting polymer was pulverized and analyzed.

RESULTS AND DISCUSSION

Prepolymer Analysis

The detailed analysis of the prepolymers was described in our previous study,^{15,16} but a summary of the results is shown in Table I.

All prepolymers were hydroxyl-terminated telechelic polymers with quite low molecular weights. The molecular weights determined by gel permeation chromatography (GPC) were system-

Table I Summary of Prepolymer Analysis Results

Polymer	Lactic Acid (mol)	Butanediol (mol)	\bar{M}_n (GPC) (g/mol)	\bar{M}_w (GPC) (g/mol)	T_g ($^{\circ}\text{C}$)	Hydroxyl Number	Acid Number	\bar{M}_n (titr.) (g/mol)	\bar{M}_n (NMR) (g/mol)	Lactide (NMR) (mol %)	D-Lactic Acid Structures (NMR) (mol %)
P-1	5	0.2	3800	5500	27.9	69.0	1.0	1600	1500	2.1	27.4
P-2	5	0.1	7900	11900	40.8	33.4	1.6	3200	3000	2.4	29.5
P-3	5	0.05	18000	26000	46.0	15.6	1.4	6600	6600	2.8	29.0

atically higher than those determined by ^{13}C -NMR. It seems that the higher the molecular weight of the polymer, the greater the difference between the results of these tests. The GPC was calibrated with narrow polystyrene standards, and therefore the GPC results were used only as a qualitative tool to check the peak shape, size distribution, and molecular weight order of the different polymers. The molecular weights determined by ^{13}C -NMR were then used as quantitative values for the calculation of the amounts of isocyanate required.

All prepolymers were amorphous and their T_g s were below 46°C . According to tests, the polymer chain length had a significant effect on T_g s in the studied range of molecular weight. The higher the molecular weights, the higher the T_g s of these prepolymers. Besides the end-group analysis, ^{13}C -NMR was a useful tool in the quantitative analysis to determine remaining lactic acid, formed lactide, and different DL-lactic acid combinations in the polyester chain. The amounts of lactic acid and lactide were calculated using the methine area peak integrals. Different DL-lactic acid combinations caused four clear peaks in the carbonyl area, and the identification of these peaks will be reported later. It should be noted that the determined amount of DL-lactic acid structures represents the number of different DL-lactic acid combinations, and not the total amount of D-lactic acid units in the prepolymer chains.

Preparation of Poly(ester-urethane)

The complete reaction scheme for different lactic acid-based poly(ester-urethane)s is shown in Figure 1. In the tests we used non-aromatic diisocyanates, because the biodegradation products of the prepared poly(ester-urethane)s should be as harmless as possible. We chose HDI in tests because it is aliphatic and both isocyanate groups have equal reactivity; DES was a stiff cycloaliphatic diisocyanate, and it also had equally reactive isocyanate groups. Isophorone diisocyanate was a stiff cycloaliphatic diisocyanate, with one isocyanate group more reactive than the other. With these diisocyanates, the aim was to study the effect of the structure of the diisocyanate on the properties of the resulting poly(ester-urethane)s. The basic poly(ester-urethane) synthesis with HDI was described in our previous study.^{13,14}

Table II lists polymerizations, raw materials used and their molar ratios, polymerization temperatures, and the molecular weights and polydis-

persities of the resulting polymers. There are three series in Table II: P-1, P-2, and P-3. The numbers 1, 2, and 3 denote the prepolymer used in polymerization, corresponding to number average molecular weights determined by ^{13}C -NMR of 1,600, 3,200, and 6,600 g/mol, respectively.

HDI Polymerizations

In HDI polymerizations with an NCO/OH ratio of unity and a temperature of 150°C , every prepolymer produced linear poly(ester-urethane), but the molecular weights of these polymers were quite low. According to weight average molecular weights determined by GPC, the isocyanate linked on average 23, 7, and 3 prepolymer chains together at this temperature. The T_g s of these poly(ester-urethanes) were raised when the length of the ester chain increased. When the polymerization temperature was raised to 180°C , the HDI produced crosslinked poly(ester-urethane) when the lowest molecular weight prepolymer was used with both NCO/OH ratios. Other prepolymers (prepolymers P-2 and P-3) produced linear and quite high molecular weight poly(ester-urethane) when the NCO/OH ratio was unity. The short prepolymer chains are more mobile than longer chains, and therefore the reactions between the isocyanate and the urethane group are more probable. When the isocyanate was used in excess, the resulting poly(ester-urethane)s had smaller molecular weights but about the same T_g s as the poly(ester-urethane)s produced with a NCO/OH ratio of unity. The explanation could be that when the diisocyanate was used in excess the isocyanate groups also react with the urethane groups, and the result of this reaction is branched polymer chains or, ultimately, the crosslinking of the polymer. This branching or beginning of crosslinking could be the reason why these polymers have about the same T_g s as higher molecular weight polymers produced with an equimolar NCO/OH ratio. The development of the weight average molecular weights of these polymers during the polymerization process is shown in Figure 2.

When the lowest molecular weight prepolymer was used, the behavior of the weight average molecular weight curves was quite interesting. When the NCO/OH ratio was unity and the polymerization temperature 150°C , the behavior of the weight average molecular weight curve was as reported earlier.¹⁴ First the molecular weight increases quite rapidly to a certain level, and after that the molecular weight increases slowly or has

Table II Poly(ester-urethane) Synthesis and Analysis Results

Polymerization	Diisocyanate	NCO/OH Mole Ratio	Temperature (°C)	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PD	T_g (°C)
Series P-1							
P11	HDI	1/1	150	26,000	128,000	4.9	45.8
P12	HDI	1/1	180	insoluble to chloroform			47.5
P13	HDI	1.25/1	180	insoluble to chloroform			50.4
P14	VEST	1/1	150	8,000	14,900	1.9	52.4
P15	VEST	1/1	180	8,700	17,700	2.0	53.4
P16	VEST	1.25/1	180	8,600	17,600	2.0	54.0
P17	DES	1/1	150	9,500	18,000	1.9	52.1
P18	DES	1/1	180	9,600	18,600	1.9	52.7
P19	DES	1.25/1	180	7,300	12,800	1.8	44.6
Series P-2							
P21	HDI	1/1	150	29,000	78,000	2.7	53.6
P22	HDI	1/1	180	44,800	211,000	4.7	53.9
P23	HDI	1.25/1	180	32,000	195,000	6.1	52.1
P24	VEST	1/1	150	15,000	28,900	1.9	57.8
P25	VEST	1/1	180	20,200	38,300	1.9	59.6
P26	VEST	1.25/1	180	9,700	19,200	2.0	55.1
P27	DES	1/1	150	7,100	18,900	2.7	55.9
P28	DES	1/1	180	13,200	30,700	2.3	58.2
P29	DES	1.25/1	180	11,300	21,200	1.9	53.9
Series P-3							
P31	HDI	1/1	150	30,300	52,000	1.7	53.8
P32	HDI	1/1	180	45,900	82,600	1.8	51.9
P33	HDI	1.25/1	180	34,700	82,600	2.4	54.4
P34	VEST	1/1	150	20,000	35,500	1.8	58.3
P35	VEST	1/1	180	19,600	35,500	1.8	59.2
P36	VEST	1.25/1	180	20,800	38,500	1.9	59.2
P37	DES	1/1	150	21,200	37,400	1.8	57.7
P38	DES	1/1	180	18,800	35,200	1.9	58.6
P39	DES	1.25/1	180	19,300	35,300	1.8	58.9

HDI, 1,6-hexamethylenediisocyanate; VEST, isophorone diisocyanate; DES, 4,4'-dicyclohexylmethane diisocyanate.

lecular weight development curves. Both curves had a rapid period of molecular weight increase at the end of the polymerization. An NCO/OH ratio of unity produced higher molecular weight poly(ester-urethane) than the ratio of 1 : 1.25, but the polymerization time was 15 min longer.

When the weight average molecular weight of the prepolymer was 26,000 g/mol, NCO/OH ratios of unity at both polymerization temperatures (150 and 180°C) produced similar weight average molecular weight development curves. In both cases, the weight average molecular weight first increases and, after 15 min, stays at a constant level (P31) or decreases slowly (P32). In these cases it appears that there was too small an amount of HDI present. When the diisocyanate was used in excess, the weight average molecular weight first

increased smoothly, then after 60 min reached a constant value which was higher than that produced with an NCO/OH ratio of unity.

Isophorone Diisocyanate Polymerizations

When isophorone diisocyanate was used as diisocyanate, the molecular weights of the resulting poly(ester-urethane)s were quite low. The weight average molecular weight of these poly(ester-urethane)s increased when the molecular weight of the prepolymer increased. However, the molecular weights of polymers which were produced with isophorone diisocyanate were below 52,000 g/mol in every case. The final polymers were very brittle.

The reason why the weight average molecular

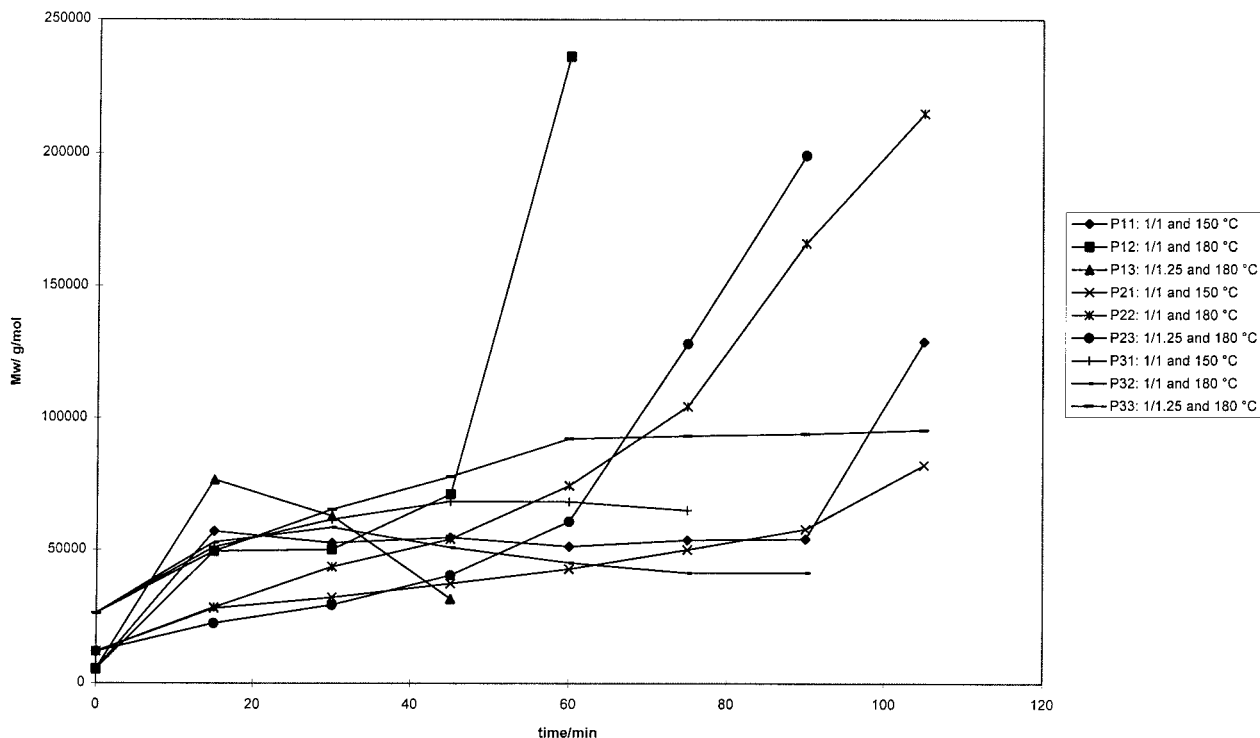


Figure 2 Development of weight-average molecular weights in hexamethylene diisocyanate polymerizations. The polymerizations were carried out until the viscosity of the polymerization mixture was raised too high, or until the viscosity was very low. For crosslinked polymer P12, the last totally soluble sample was the one which was taken after 15 min polymerization. The last weight average molecular weight point of polymer P12 represents the weight average molecular weight of the last totally soluble sample.

weights of these polymers were so low could be that the isocyanate compound produced very stiff poly(ester-urethane) chains. These stiff chains cannot react with each other because after they reach a certain chain length the stiff chains cannot move freely in the polymerization mixture, and the probability of end-group reactions becomes very low. The stiffness of these polymer chains can also be seen in the T_g s. Although the weight average molecular weights are very low, their T_g s are quite high. If the T_g of polymer P25 and the corresponding HDI polymer P22 are compared, the difference is 5.7°C, though the weight average molecular weight of hexamethylenediisocyanate polymer P22 is 5 times greater than that of polymer P22. The development of the weight average molecular weights of isophorone diisocyanate polymers during the polymerization process is shown in Figure 3.

When the lowest molecular weight prepolymer was used, the behavior of the weight average molecular weight curves was very similar: at first, the weight average molecular weight increases

quite quickly to a certain level, then the weight average molecular weight stays near constant to the end of the polymerization. When the prepolymer P-2 or P-3 was used in the polymerization, the weight average molecular weight curves also had a fast increase at the beginning of the polymerization; after that period the weight average molecular weight increased slowly. Higher polymerization temperatures (over 190°C) did not increase the molecular weight of the resulting poly(ester-urethane)s.

DES Diisocyanate Polymerizations

When DES was used as diisocyanate, the results were similar to those for the isophorone diisocyanate polymerizations. The weight average molecular weights were low, and the final poly(ester-urethane)s very brittle. The T_g s were, however, higher than the polymers which were produced with HDI but about the same as the isophorone diisocyanate polymers. According to the T_g s, DES seemed to produce very stiff poly(ester-ure-

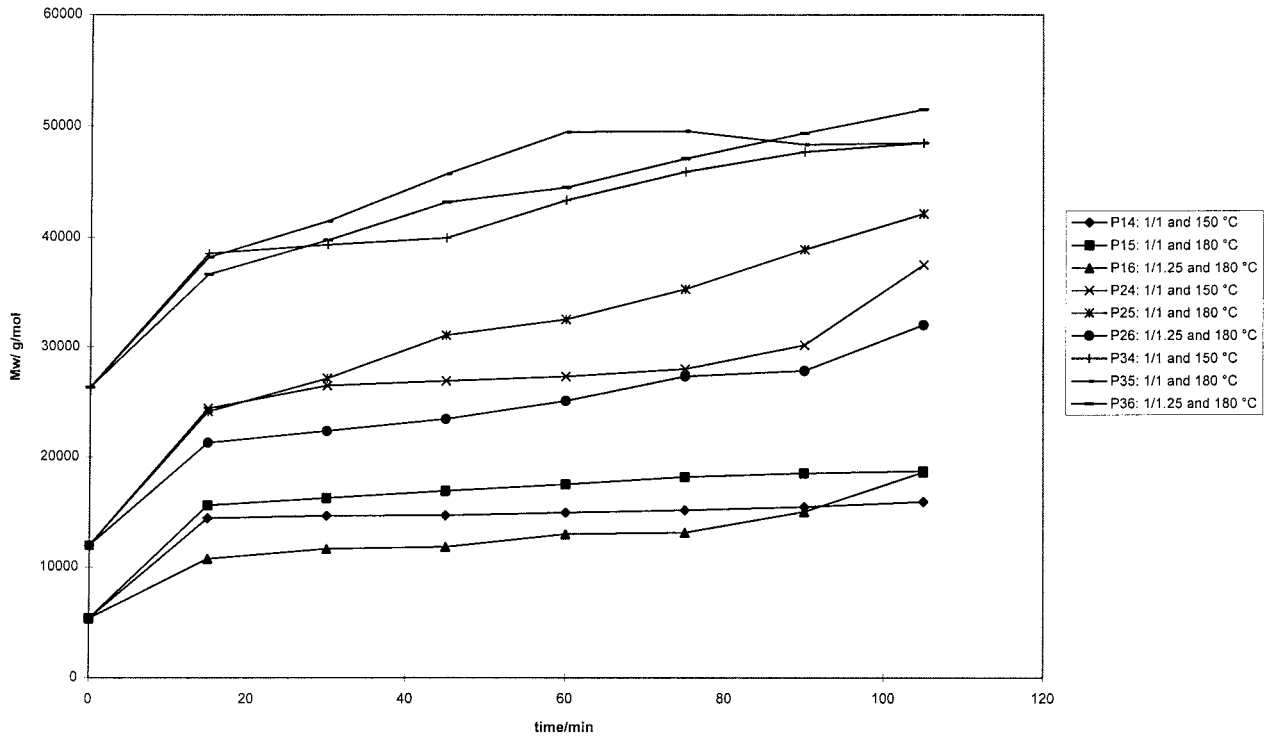


Figure 3 Development of weight average molecular weights in Vestanat IPDI polymerizations.

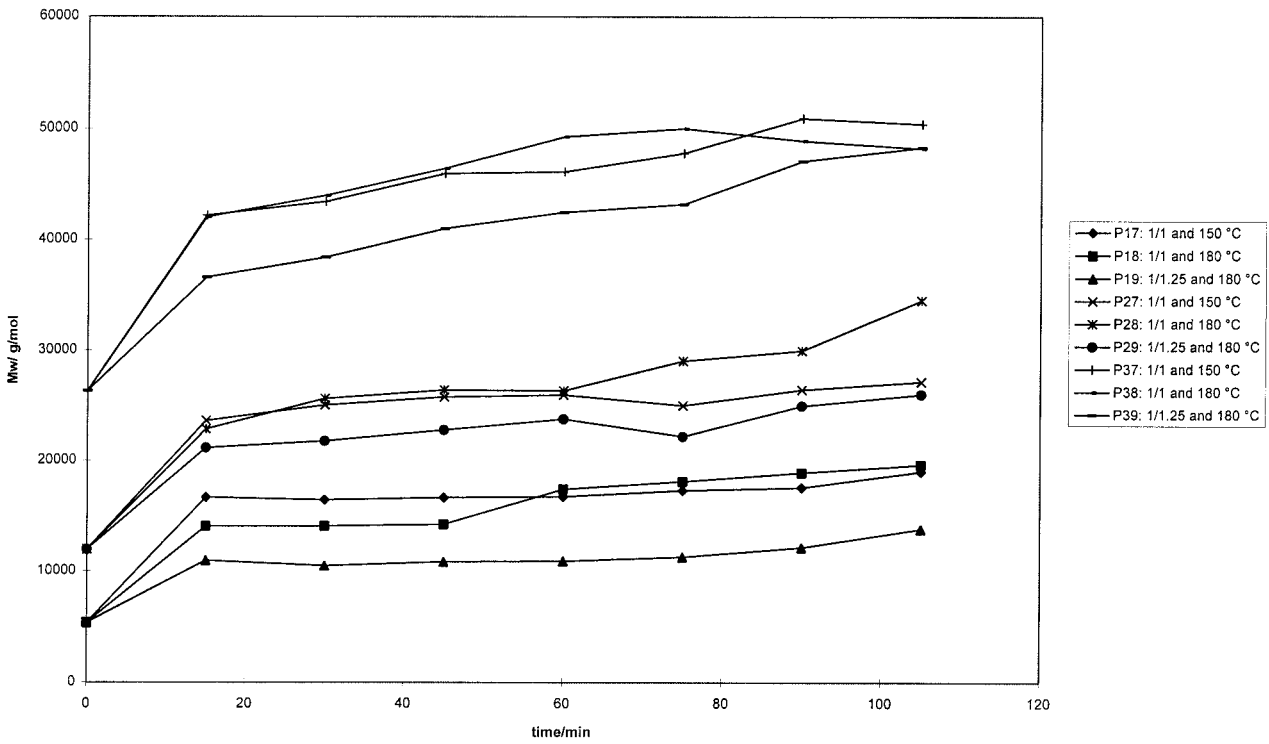


Figure 4 The development of weight average molecular weights in Desmondur polymerizations.

thane) chains. The development of the weight average molecular weights of dicyclohexylmethane diisocyanate polymers during the polymerization process is shown in Figure 4.

The weight average molecular weight curves behave in a similar way to the isophore diisocyanate curves. At first the weight average molecular weights increase quite quickly to a certain level, but after 15 min polymerization the weight average molecular weight stays near constant or increases slowly. Higher polymerization temperatures (over 190°C) did not increase the molecular weight of the resulting poly(ester-urethane)s.

CONCLUSIONS

The results indicate that the structure of the diisocyanate has a significant effect on the properties of the final poly(ester-urethane)s. When the prepolymer, with a weight average molecular weight of 12,000 g/mol, was linked with flexible HDI the highest weight average molecular weight of the resulting poly(ester-urethane) was 215,000 g/mol, and the T_g 54°C. Under the same conditions, the stiff diisocyanates isophorone diisocyanate and dicyclohexylmethane diisocyanate produced poly(ester-urethane)s with weight average molecular weights below 42,000 g/mol, but the T_g s were over 5°C higher than for the urethane produced with HDI. These stiff diisocyanates produced linear poly(ester-urethane) chains, which cannot react with each other after a certain chain length. The stiffness of these poly(ester-urethane) chains could be the reason why the weight average molecular weights of these polymers were so low.

At the lower polymerization temperature, the resulting polyesterurethanes were linear and the weight average molecular weights were quite low. When HDI was used in polymerization, the increase in the isocyanate/hydroxyl ratio seemed also to increase the polydispersity of the polymers prepared. This polydispersity behavior was also detected in our previous studies. According to this

study, only the poly(ester-urethane)s which were produced with HDI were hard, while the stiff diisocyanates produced very brittle polymers. The HDI results also indicate that the molecular weight and network formation can be controlled independently by the amount of diisocyanate used and the polymerization conditions. The resulting poly(ester-urethane)s were all thermoplastic.

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