

Synthesis of Linear Aliphatic Polycarbonate Macroglycols Using Dimethylcarbonate

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ABSTRACT: A series of linear aliphatic polycarbonate polyols were synthesized using dimethylcarbonate and a linear alkane diol or specific combinations of linear alkane diols. Polyol synthesis was carried out in a two-stage process using dimethylcarbonate and a linear alkane diol to prepare a series of homopolymer polycarbonate polyols. Polyol grades were characterized using Fourier transform infrared spectroscopy, gel permeation chromatography, and differential scanning calorimetry techniques. Suitable reaction conditions were developed to yield polycarbonate polyols of

number average molecular weight between 700 and 1700. The crystallinity of the polycarbonate polyols was shown to reduce as the molecular weight of the alkane diols used in the polycarbonate synthesis was increased. These polymers offer the potential for use in the synthesis of ether free polyurethane elastomers for biomedical applications. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 217–227, 2009

Key words: polycarbonates; polyurethanes; polycondensation

INTRODUCTION

Since the introduction of polyurethane (PU) elastomers for medical applications, polyurethane elastomers remain one of the most important medical-grade polymers. Polyurethane elastomers exhibit a unique combination of tensile strength, elongation, durability, biocompatibility, and biostability. Such properties are attributed to the complex morphology that results from the microphase separation of hard and soft segment domains. Polyurethane elastomers comprise three reactive components: a di-isocyanate, a macromolecular soft segment and a chain extender. These components are combined in various ratios to yield the required phase separated structure where the hard segment domains generally comprise the di-isocyanate and chain extender. The chemical composition and ratio of the chemical components can be altered to create the desired chemical, physical, and biological performance required.

Although polyurethane elastomers continue to be used for biomedical applications, these materials remain prone to various degradation mechanisms that restrict their suitability for long-term implantation into a biological host.^{1–4}

Degradation of the polyurethane system after long-term biological implantation have been shown to occur predominantly at the soft segment component of the polymer. Several studies have reported the hydrolytic degradation of the ester soft segment of poly(ester-urethanes) group in the presence of acids, oxidants, and enzymes under *in vivo* conditions.^{5–7} Moreover, once the ester linkages begin to hydrolyze, it produces acid groups which further increase the acidity surrounding the degrading polyurethane and may autocatalyze its destruction.⁸ Although the use of polyether soft segments in the synthesis of poly(ether-urethanes) removes the susceptibility of degradation due to hydrolysis, several studies have also shown that poly(ether-urethanes) undergo oxidative degradation which leads to several mechanisms of breakdown such as environmental stress cracking (ESC) and metal ion oxidation (MIO).^{9–12} As a means of improving the *in vivo* stability of polyurethane elastomers, the susceptible ester and ether linkages have been replaced by using a polycarbonate soft segment. Investigations carried out on poly(carbonate-urethane) grades have shown great promise as long term biostable elastomers exhibiting excellent resistance to hydrolysis, ESC and MIO.^{8,10,13–17} Although poly(carbonate urethane) elastomers were shown to have superior *in vivo* stability to that of ether and ester-based polyurethanes, their inherent stiffness may limit their use for soft tissue applications.

Polycarbonate polyols used as the soft segment component in polyurethane synthesis are usually

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obtained either by polycondensation of phosgene with diols or by the transesterification of five-membered cyclic carbonate with selected diols. The later reaction is, however, accompanied by decarboxylation which gives rise to the formation of poly(ether carbonate) diols containing less than 50 mol % of carbonate units.^{18–25} This method of polycarbonate synthesis does, however, offer the potential to incorporate hydroxyl terminated groups during transesterification and subsequently modify the backbone chain of the polymer.

The removal of by-products, however, such as ethylene glycol, necessary to achieve product of sufficiently high molecular weight in polycondensation reactions may also result in the decomposition of the polyol product especially at elevated temperatures in the presence of catalysts.²⁵ Moreover, the presence of ether linkages in polyurethane elastomers will increase the susceptibility of the material to oxidative degradation under *in vivo* conditions.^{5,6,26}

The objective of this present study was to investigate an alternative means of synthesizing linear polycarbonate polyols without the presence of ether linkages in the backbone chain of the polymer and improving by-product elimination and subsequently the efficiency of the polymerization reaction. This technique involves the condensation polymerization of dimethylcarbonate with a series of linear hydroxyl terminated aliphatic diols in the presence of an appropriate catalyst with the liberation of methanol as reaction by-product.

EXPERIMENTAL DETAILS

Materials

1,2-ethanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol were vacuum distilled using a short path distillation apparatus and dried under vacuum in a desiccant oven for 12 h before use. Dimethylcarbonate, sodium stannate trihydrate, sodium metaborate hydrate, titanium isopropoxide, and calcium were used as received from Aldrich Chemical.

Synthesis of polycarbonate polyols

A series of polycarbonate polyols were synthesized using dimethylcarbonate and a linear aliphatic diol. The polymerization reaction was divided into two stages where first stage represents the condensation polymerization of the dimethylcarbonate and the glycol moiety. Second stage polymerization involves the progressive increase of temperature and reduction of reaction pressure necessary to liberate polycondensation by-products and subsequently increase the molecular weight of the polyol product.

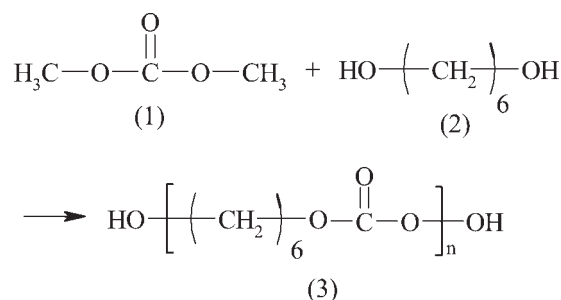


Figure 1 Reaction scheme for the polycondensation of dimethylcarbonate and hexanediol.

Synthesis of homopolymer polycarbonate polyols

Polycarbonate homopolymer polyols were prepared according to the following general method; using a hexanediol (C₆)-based polyol as example (Fig. 1).

First stage

Hexanediol (20 g, 169.5 mmol) (2) and calcium catalyst (0.18 g, 0.5 wt %) were placed in a 500-mL two neck round-bottomed flask, equipped with magnetic stirrer, Liebig condenser, and fractionating column. The temperature of the system was raised to 100°C and dimethylcarbonate (16.78 g, 186.5 mmol) (1) was added drop-wise to the system over a period of 2 h. The temperature was increased to 150°C and the reaction continued for a further 22 h under reflux. The temperature at the distillation head was maintained between 70°C and 80°C by controlling the flow rate of water through the Liebig condenser.

Second stage

The reaction was allowed to cool to room temperature, and a short path distillation head and Liebig condenser was then attached to the reaction flask. The reaction temperature was raised to 150°C for a further 2 h and a vacuum applied, reducing the pressure from 760 mmHg to 150 mmHg in 4 h. The reaction pressure was gradually lowered to a pressure of 2 mmHg and the reaction temperature progressively increased to 165°C for 8 h. The flask was returned to atmospheric pressure and a steady stream of dry nitrogen introduced into the reaction vessel for a further 2 h.

The polycarbonate polyol was dissolved in acetone and slowly filtered to remove the catalyst. Acetone was then removed from the polyol by vacuum distillation at 70°C under a pressure of 150 mmHg.

Further purification of the polycarbonate polyol was carried out by washing with boiling water to remove traces of unreacted monomer and low molecular weight polyol. Boiling water (100 mL) was added to the polymer and stirred for 10 min, allowed to settle, and then water decanted off. This

TABLE I
Reactant Concentrations and Reaction Conditions Used in the Synthesis of Homopolymer Polycarbonate Polyols Using Various Molar Excesses of Dimethylcarbonate

Polyol	Diol (g)	Carbonate (g)	Molar excess carbonate	First stage		Second stage	
				Temp (°C)	Time (h)	Temp (°C)	Time (h)
C ₂	20.0	29.0	EQU	130	24	140	14
	18.0	28.8	1.1	130	24	140	14
	18.0	31.4	1.2	130	24	140	14
	17.0	32.1	1.3	130	24	140	14
	17.0	37.0	1.5	130	24	140	14
C ₄	20.0	20.0	EQU	140	24	150	14
	18.0	19.8	1.1	140	24	150	14
	18.0	21.6	1.2	140	24	150	14
	17.0	22.1	1.3	140	24	150	14
	17.0	25.5	1.5	140	24	150	14
C ₅	20.0	17.3	EQU	140	24	155	14
	20.0	19.0	1.1	140	24	155	14
	20.0	20.8	1.2	140	24	155	14
	20.0	22.5	1.3	140	24	155	14
	20.0	26.0	1.5	140	24	155	14
C ₆	20.0	15.3	EQU	150	24	165	14
	20.0	16.8	1.1	150	24	165	14
	20.0	18.3	1.2	150	24	165	14
	20.0	19.8	1.3	150	24	165	14
	20.0	22.9	1.5	150	24	165	14

EQU represents an equal molar ratio of diol to carbonate polyols during first stage reaction.

process was repeated three times. The final polymer was then dried at 50°C under vacuum.

The influence of reactant ratio on polyol molecular weight

A number of polymerization studies were carried out to determine the influence of various molar excesses of dimethylcarbonate on the molecular weight and molecular weight distribution of the polycarbonate polyols. Monomer concentrations and reaction conditions used in the synthesis of homopolymer, polycarbonate polyols are presented in Table I.

Characterization techniques

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was carried out on a Perkin–Elmer Ff -IR 2000 system. Polyol samples were predried at 40°C under a pressure of 150 mmHg for 12 h before analysis. Scans were carried out in transmission mode, and predried polyol samples were placed on NaCl plates for bulk property analysis. Polyol samples were measured between 4000 cm⁻¹ and 500 cm⁻¹ and a minimum of 30 scans were recorded for each sample.

Gel permeation chromatography

Gel permeation chromatography (GPC) studies were performed using an integrated PERKIN ELMER GPC system comprising an isocratic LC pump, LC-

30 RI detector, and a 900 series interface. A PLgel 5 μm mixed D GPC column was used for all polyols using tetrahydrofuran (THF) as solvent carrier at an oven temperature of 35°C. The molecular weight and molecular weight distributions recorded for each polycarbonate glycol were estimated using narrow molecular weight distribution polyethylene glycol standards. Standards of number average molecular weight, 400, 960, 1470, and 4100 were used and a calibration curve of linear regression >0.997 was used to correlate molecular weight data. Calibration was carried out after every four samples due to drift and to ensure accuracy in molecular weight data recorded.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) studies were carried out on the polyurethane samples in accordance with ISO-3146 using a Perkin–Elmer 6 Series DSC unit. Polyol samples were predried at 40°C under a vacuum pressure of 150 mmHg for 12 h before analysis. The sample size was maintained at 10 mg and thermal history effects were removed by heating to 100°C before analysis. Samples were then cooled to -90°C. Enthalpy versus temperature responses were recorded for each sample over the temperature range -90°C to 100°C.

RESULTS AND DISCUSSION

The polycondensation of dimethylcarbonate (4) and a linear diol, (5) such as butanediol, was carried out

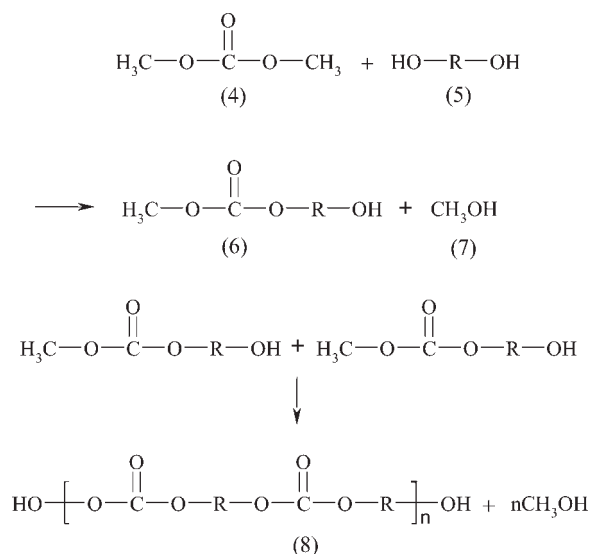


Figure 2 Reaction scheme for synthesis of low molecular weight polycarbonate.

in Stage 1 to form polycarbonate polyols of number average molecular weights between 300 and 500 (8) (Fig. 2). Methanol produced as by-product was easily removed from the reaction vessel during this stage by controlling the temperature at the fractionation head.

The temperature at the head of the column was maintained between 65°C and 75°C to prevent direct

removal of dimethylcarbonate (BP 90°C) from the reaction vessel.

Stage 2 involved the transesterification of low molecular weight polyols to form polycarbonate polyols of number average molecular weights between 700 and 2500 (Fig. 3). It is proposed that transesterification occurs similar to that described by Harris.²⁶

As this is an equilibrium reaction, low molecular weight polycarbonate oligomers (9) and small traces of dimethylcarbonate/methanol azeotropes were continuously extracted as by-product throughout second stage polymerization. By-product removal from the reaction is essential to drive the reaction in the forward direction.²⁷

The removal of low molecular weight by-product from the reaction vessel was brought about by slowly increasing the reaction temperature and gradually reducing the reaction pressure to 2 mmHg. The removal of the by-product from the reaction vessel was carried out at a controlled rate to ensure the transesterification of low molecular weight species to higher molecular weight polymers.

Using dimethylcarbonate as monomer the efficient removal of low molecular weight by-product throughout the polymerization process was possible without exposing the polymer to an excessively high temperature environment. As a result, the molecular weight of the polyol was shown to increase steadily throughout first and second stage polymerization.

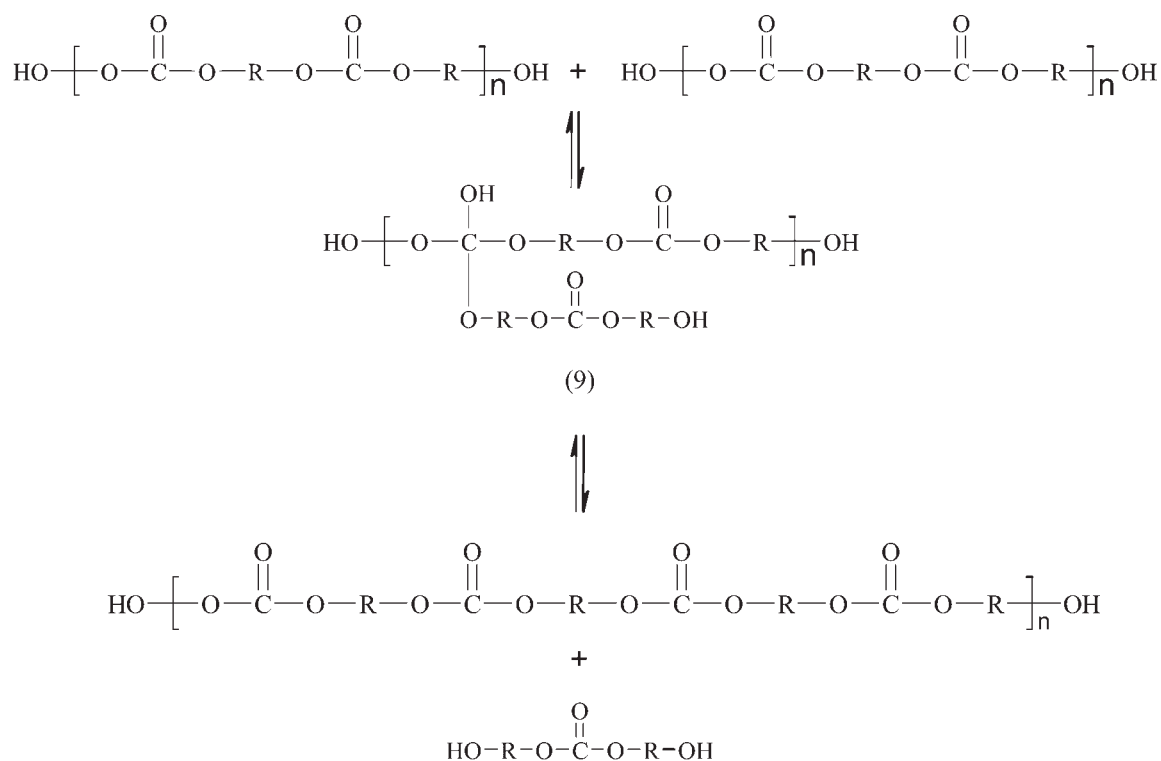


Figure 3 Reaction scheme for synthesis of low molecular weight polycarbonate polyols during first stage reaction.

TABLE II
Chemical Composition of Polycarbonate Polyols
Prepared in this Study

Diol code	Chemical structure
C ₂	$\text{HO} \left[\left(\text{CH}_2 \right)_2 \text{O} - \text{C} \left(\text{O} \right) - \text{O} \right]_n \text{OH}$
C ₄	$\text{HO} \left[\left(\text{CH}_2 \right)_4 \text{O} - \text{C} \left(\text{O} \right) - \text{O} \right]_n \text{OH}$
C ₅	$\text{HO} \left[\left(\text{CH}_2 \right)_5 \text{O} - \text{C} \left(\text{O} \right) - \text{O} \right]_n \text{OH}$
C ₆	$\text{HO} \left[\left(\text{CH}_2 \right)_6 \text{O} - \text{C} \left(\text{O} \right) - \text{O} \right]_n \text{OH}$

The chemical composition of the full range of polycarbonate grades developed in this study are presented in Table II.

Molecular weight analysis of polycarbonate polyols

Figure 4 shows GPC chromatographs of a C₄ polyol sample at various stages throughout Stage 1 polymerization. After a reaction time of 16 h, the number average molecular weight of the polyol reaches 1037 and the presence of numerous low molecular weight fractions are readily apparent. As the reaction continues, low molecular weight polyol fractions are continuously combined, reducing the molecular weight distribution of the polyol from 3.7 to 2.5 and increasing the overall molecular weight of the polyol product to 1254.

After a first stage reaction time of 24 h, low molecular weight polyol fractions still remain in the polyol product and further reaction time is required to obtain a more homogenous polyol product.

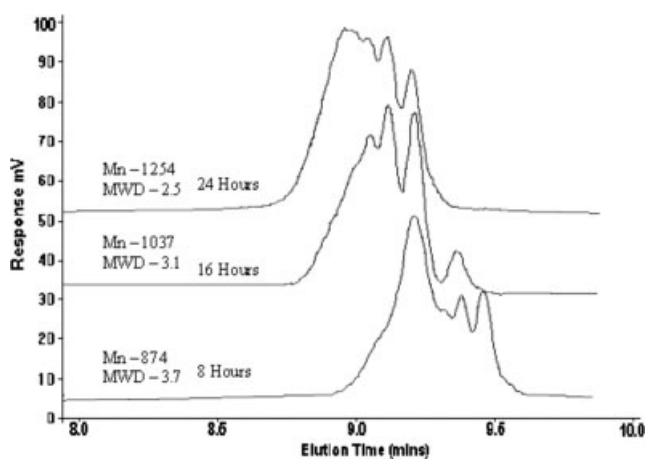


Figure 4 GPC chromatogram of a C₄ polyol throughout first stage polymerization.

GPC chromatographs for the C₄ polyol at various stages throughout second stage polymerization show that low molecular weight polyol fractions continue to amalgamate with higher molecular weight species, reducing the polydispersity from 2.0 to 1.37. As a result, the number average molecular weight of the polyol increases from 392 to 1584. The increase in molecular weight can be accounted for by transesterification reactions that involve the continuous addition of hydroxyl terminated units to larger polymer chains, with the evolution of low molecular weight by-product.

The gradual increase in reaction temperature and reduction in pressure during second stage polymerization makes the removal of by-product possible. The removal of sufficient quantities of reaction by-products is essential to the transesterification reactions and the formation of higher molecular weight polyol products of reduced molecular weight distribution.

FTIR analyses

FTIR was used to determine the chemical composition of the polycarbonate polyols. Qualitative analysis of polycarbonate polyols was carried out on each polyol grade after synthesis to ensure a reproducible chemical structure and to detect the presence of degradation products. A typical spectrum of a polycarbonate polyol is shown in Figure 5.

Polycarbonate spectra showed strong carbonyl (C=O) stretching at 1741 cm⁻¹, characteristic of the carbonate backbone. FTIR analysis was also used to detect the presence of degradation products that occurred when using high reaction temperatures. Thermal degradation of the polyol product resulted in the formation of unsaturated groups (C=C) that were generally detected at 1640 cm⁻¹. The formation of unsaturated groups also resulted in the yellowing of the polyol product.

FTIR was extensively used to determine the influence of reaction conditions on the stability and purity of polycarbonate polyols. Long reaction times

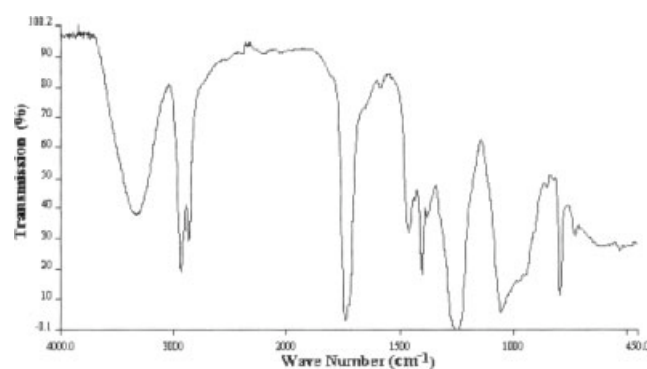


Figure 5 Characteristic FTIR of polycarbonate polyols synthesized.

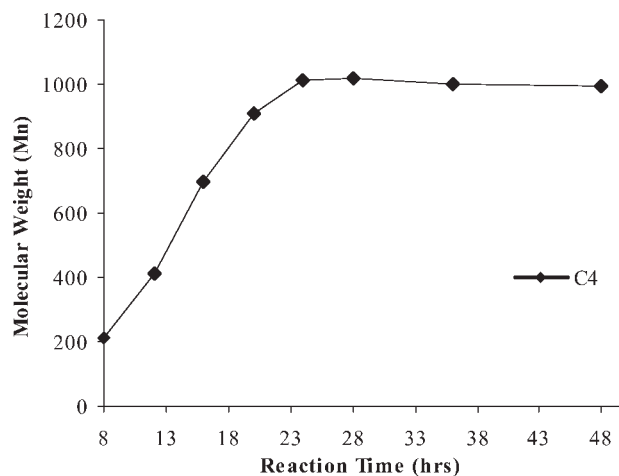


Figure 6 Number average molecular weight as a function of reaction time for a C_4 -based homopolymer polycarbonate polyol.

and high temperatures during polyol synthesis can lead to the rapid formation of degradation products. Using FTIR analysis of the polyol product at various times throughout first and second stage polymerization, reaction times and temperatures can be modified accordingly to prevent the formation of degradation products.

Molecular weight control of polycarbonate polyols

To prepare polycarbonate polyols within a desired molecular weight range of 700 to 2000, it was necessary to bring about suitable control of the polymerization process. A number of polymerization trials were carried out to optimize reaction conditions for the preparation of polycarbonate polyols of specific molecular weight and molecular weight distribution.

The influence of reaction times on polyol molecular weight

Experimental analysis carried out by Flory²⁸ and Lin and Hsieh²⁹ on step growth polymerization reactions involving diethylene glycol and adipic acid have shown that the degree of polymerization is a function of reaction time. To determine the influence of various first stage and second stage reaction times on the molecular weight of polycarbonate polyols, a number of polymerization reactions were carried out.

Figure 6 shows molecular weight data obtained for a C_4 -based polycarbonate throughout first stage polymerization. A gradual increase in molecular weight up to a reaction time of 24 h is observed. After the 24 h period, the reaction is not shown to undergo any increases in molecular weight signifying that the reaction is fully complete.

This trend was confirmed by the reduction in the quantity of by-product removed from the polymer-

ization reaction after 24 h under first stage reaction conditions. A reduction in by-product removal from the reaction suggests that polycondensation of dimethylcarbonate and diol may be fully complete. Based on these results, a first stage reaction time of 24 h was selected for the preparation of homopolymer, copolymer, and terpolymer polycarbonate polyol grades.

Using a first stage reaction time of 24 h the influence of second stage reaction time on the molecular weight for similar C_4 -based polycarbonate were investigated.

The molecular weight data recorded at regular intervals throughout second stage polymerization are presented in Figure 7. The molecular weight of the polymer was shown to increase rapidly throughout the initial stages of the reaction until a stable threshold was reached. The rapid molecular weight build-up of the polymer was also confirmed by the larger quantities of reaction by-product extracted throughout second stage polymerization.

In view of the fact that some polyol degradation occurred after extended exposure to high reaction temperatures, a second stage reaction time of 38 h was selected. After a reaction time of 38 h, a molecular weight of 1504 was recorded for homopolymer polyols.

The influence of reactant ratio on polyol molecular weight

To compensate for the removal of dimethylcarbonate and bring about suitable molecular weight control, polyols were prepared using a stoichiometric excess of dimethylcarbonate. Samples were removed from the reaction vessel at various times during the reaction and their molecular weight and molecular weight distribution determined by GPC.

Figure 8 compares the influence of molar ratio on the molecular weight of a C_2 -based polycarbonate

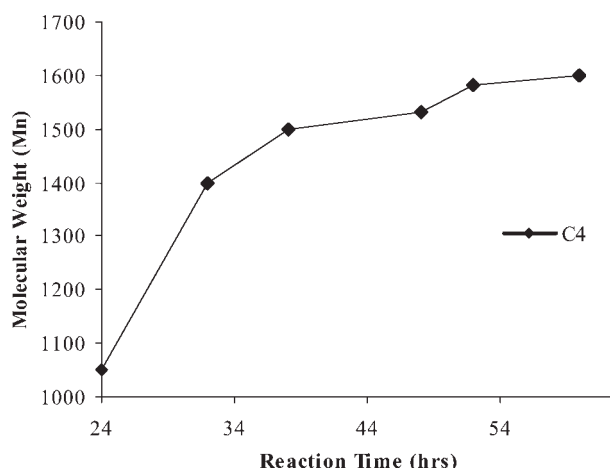


Figure 7 The influence of second stage reaction times on the molecular weights of C_4 polycarbonate polyols.

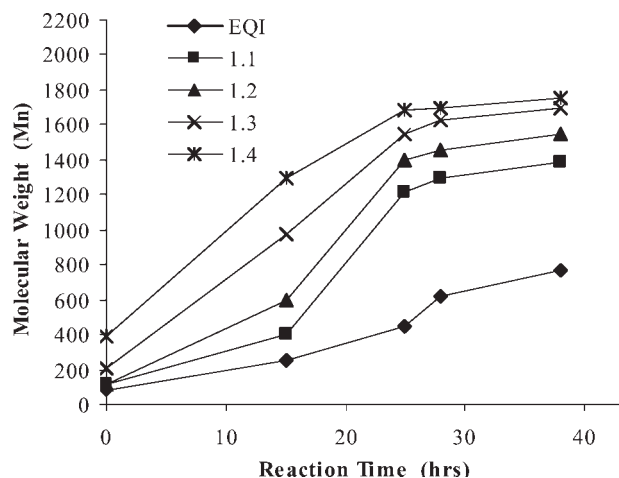


Figure 8 Molecular weight as a function of reaction time for C₂-based polycarbonate polyols using various molar ratios.

polyol. Considerable differences are observed in molecular weight values recorded for polyols prepared using different molar ratios.

As the molar ratios were increased, the rate of molecular weight build-up and the final molecular weight of the polyol product were shown to increase. The polyol prepared using an equal molar ratio of carbonate to diol shows a consistently slow rate of molecular weight build-up throughout the reaction, due to insufficient concentrations of dimethylcarbonate. Although stoichiometrically balanced, the low boiling temperature of the dimethylcarbonate may permit the loss of the monomer during the first stage polymerization.

Higher rates of molecular weight build-up, particularly throughout first stage polymerization are shown for polyols prepared using higher concentrations of the carbonate component. High polymerization rates throughout the first stage polymerization may suggest that these reactions are less affected by the quantities of dimethylcarbonate removed from the reaction as by-product.

The rate of polymerization decreases throughout second stage polymerization indicating that the transesterification reaction may be considerably slower than the polycondensation reaction involved in the first stage polymerization. The reduction in polymerization rate may also result from the increase in viscosity of the reaction mixture and a reduction in the diffusion rate of the low molecular weight by-product from the bulk of the reaction.

Molecular weight data obtained from polymerization studies were further analyzed by comparing the final molecular weight values with stoichiometric ratios used during polymerization. Figure 8 shows the molecular weight values recorded for a series of polyols using various molar excesses of dimethylcar-

bonate. As observed earlier in Figure 8, the molecular weight of the polyol increases as the molar ratio of the carbonate component increases. However, no significant increase in molecular weight was observed for polyol grades prepared using molar ratios of 1.3 and 1.5.

During first stage synthesis of the polycarbonates, careful consideration was given to maintaining the temperature at the distillation head between 70°C and 80°C. As mentioned previously, the low boiling temperature of dimethylcarbonate (90°C) may lead to traces of the monomer being removed from the reaction vessel perhaps due to the formation of an azeotropic mixture with the methanol by-product. The removal of monomer and subsequent disruption of molar ratio of reactants may account for the increase in molecular weight with increasing molar excess of dimethylcarbonate. This trend is further illustrated in Figure 8 for a series of polycarbonate grades, where the final molecular weight of the polymers were shown to increase progressively until a dimethylcarbonate molar excess of 1.2 is reached. Minor increases in molecular weight above a molar ratio of 1.2 are observed, perhaps accountable on by the large quantities of dimethylcarbonate available for reaction that compensates for loss through evaporation. The determination of the most efficient concentration of dimethylcarbonate is an important observation and particularly relevant to the efficient use of monomer in the preparation of larger quantities of polyol. In this study, a molar ratio of 1.2 provided the most efficient reaction conditions as no significant increases in molecular weight were recorded using greater concentrations of dimethylcarbonate at molar ratios of 1.3 and 1.5.

The number average molecular weight as a function of reaction times and molar excess of dimethylcarbonate for each polycarbonate polyol prepared in this study are presented in Table III.

Molecular weight distribution of polycarbonate polyols

Although the molecular weight of polycarbonate polyols prepared was shown to increase as the molar ratio of the dimethylcarbonate component exceeded that of the diol, Figure 9, an increase in molecular weight distribution was also observed above a molar ratio of 1.3. The molecular weight distribution of polyol grades prepared using various molar ratios of the carbonate component to glycol component are shown in Figure 10. These data were recorded for polyol samples after the polymerization reactions were fully complete. The molecular weight distribution of polyol grades is shown to reduce with increasing concentration of the carbonate component. This trend suggests that a more homogeneous

TABLE III
Number Average Molecular Weight Data Recorded for Homopolymer Polycarbonate Polyols Throughout Polymerization

Time (h)	EQU	Molar ratio			
		1.10	1.20	1.30	1.50
C₂					
8	217	208	261	237	384
16	268	472	620	907	1280
24	492	1260	1480	1537	1668
28	704	1352	1560	1664	1711
38	731	1380	1600	1711	1764
C₄					
8	214	210	229	298	356
16	345	598	876	921	1018
24	498	1043	1254	1372	1410
28	640	1163	1392	1513	1636
38	819	1467	1584	1735	1771
C₅					
8	241	439	497	506	685
16	502	874	1182	1213	1388
24	828	1239	1571	1583	1591
28	902	1479	1725	1763	1779
38	1108	1624	1791	1801	1810
C₆					
8	210	310	515	529	577
16	275	661	932	939	1007
24	444	1106	1256	1296	1354
28	666	1269	1567	1596	1607
38	916	1372	1589	1612	1641

polymer product is obtained using greater quantities of dimethylcarbonate and may suggest that polymerization reactions are more complete.

The molecular weight distribution of polyol grades is shown to reduce with increasing concentration of the carbonate component. This trend suggests that a more homogeneous polymer product is obtained using greater quantities of dimethylcarbonate and may suggest that polymerization reactions

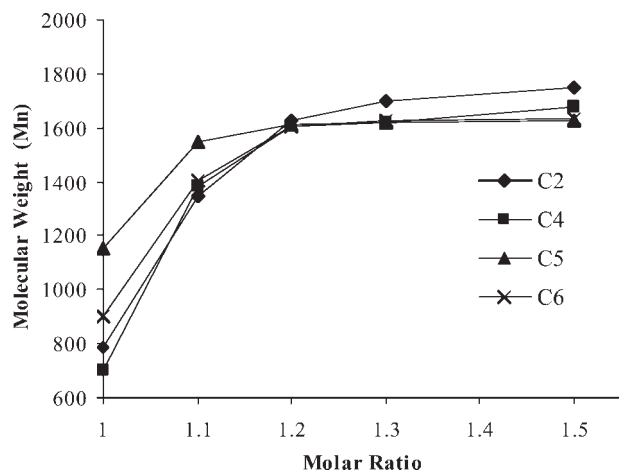


Figure 9 Molecular weight as a function of molar ratio after complete polymerization for a series of polycarbonate polyols.

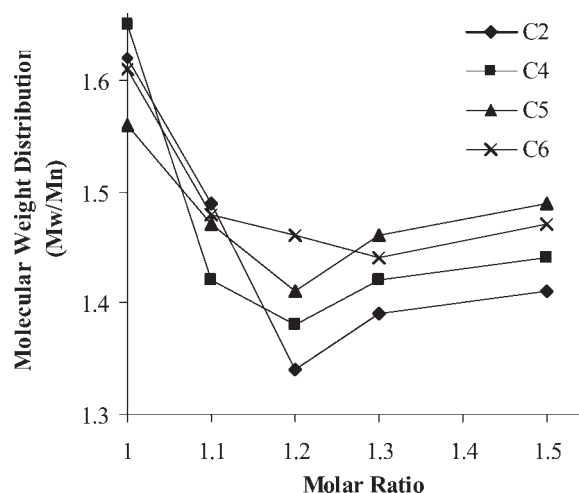


Figure 10 Molecular weight distribution as a function of molar ratio of homopolymer polycarbonate polyols after a reaction time of 38 h.

are more complete. Although the molecular weight of polycarbonate polyols prepared was shown to increase as the molar ratio of the dimethylcarbonate component exceeded that of the diol, Figures 8 and 9, an increase in molecular weight distribution was also observed above a molar ratio of 1.3. This trend may be accounted for by the chain terminating influence that the excess dimethylcarbonate has on the reaction. Although the rate of polymerization and molecular weight of the polycarbonate polyols were shown to increase with increasing molar ratio, lower molecular weight dimethylcarbonate terminated polymers that are formed throughout the initial stages of the polycondensation reaction may be unable to participate in second stage polyesterification reactions. Moreover, the loss of dimethylcarbonate due to low boiling temperature throughout the reaction may also contribute to the lower molecular weight distribution observed between a molar excess of 1.1 and 1.3.

The primary constraint placed on the involvement of the lower molecular weight polymer species throughout second stage polymerization is reaction time. Additional second stage reaction time would allow dimethylcarbonate terminated polymers to react with hydroxyl terminated groups and participate in polyesterification reactions. However, due to the formation of degradation products detected (using FTIR) at high reaction temperatures it was not possible to extend the reaction times for the synthesis of polycarbonate polyol grades. As a consequence, a high number of lower molecular weight polycarbonate species remain in the final polymer product that influences the high molecular weight distribution of the polyol product.

Furthermore, no significant improvement in the molecular weight of polycarbonate polyols was observed using a molar ratio greater than 1.3 due to

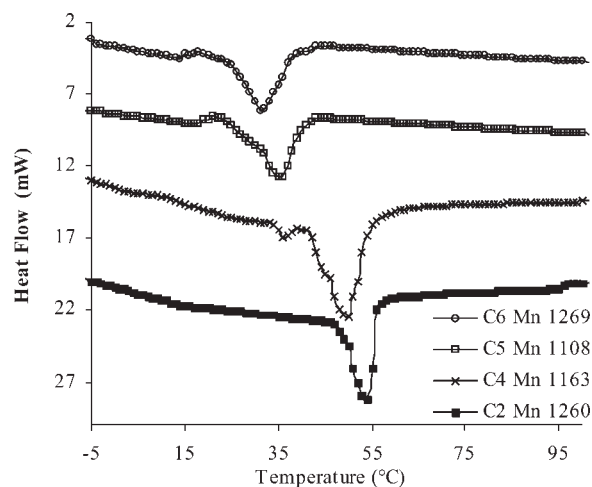


Figure 11 DSC thermograms of homopolymer polycarbonate grades with increasing hydrocarbon chain length.

the possible chain terminating effects of the dimethylcarbonate and the presence of low molecular weight species.

Experimental analysis carried out on polycarbonate polyols has shown that the step-growth polymerization mechanism can be controlled by modifying the molar ratio of reactants. The adjustment of reactant ratios was shown to yield polycarbonate polyols of number average molecular weights of 700 to 1700 and molecular weight distribution between 1.3 and 1.9. No significant increase in molecular weight and no major reduction in molecular weight distribution were observed in synthesizing polycarbonate polyols using a molar ratio greater than 1.3.

DSC analysis of polycarbonate polyols

DSC studies were carried out to monitor the endothermic response of selected polycarbonate polyol grades and to characterize the influence of the molecular weight of the diol moiety on polyol crystallinity. These studies were carried out over a wide temperature range, typically from -100°C to 100°C ; representative DSC curves recorded are presented in Figures 11 and 12.

The DSC traces in Figure 11 are typical of those recorded for polycarbonate polyols developed in this study; the curves shown here are for polyols of similar molecular weight, but with different hydrocarbon chain length. The C_2 -based polyol shows a sharp melting endotherm at 60.5°C , indicative of the presence of high crystalline order in the polyol.^{29–38} As the hydrocarbon chain length increases from C_2 to C_6 the crystalline melting point, T_m , falls progressively from 60.5°C to 35.8°C and the heat of fusion, ΔH_f , falls from 59.5 J/g to 34.1 J/g . A reduction in ΔH_f is not unexpected since the level of dipole inter-

action between carbonate groups on adjacent polyol chains will diminish as hydrocarbon chain length increases. A reduction in intermolecular interaction is also likely to reduce the level of crystalline ordering in the homopolymer and may explain the reduction observed in crystalline melting temperature with increasing hydrocarbon chain length. By modifying the molecular weight of the hydrocarbon unit between carbonate groups, the crystallinity of the polycarbonate polyols can be altered significantly to match the requirements of further applications.

The effect of molecular weight on the magnitude and position of the polycarbonate polyols is examined using a C_4 -based polycarbonate and illustrated in Figure 12. Clearly, the intensity of the melting endotherm and its position increases with increasing the molecular weight. As number average molecular weight increases from 1007 to 1467, the crystalline melting point increases from 42.9°C to 54.6°C and the heat of fusion, ΔH_f , increases from 40.7 J/g to 50.0 J/g .

The progressive increase in heat of fusion with molecular weight may be explained by greater dipole interaction of carbonate groups and a reduction in the number of chain ends in the higher molecular weight polycarbonate chains. Crystalline ordering of the polyol is therefore improved, shown by an increase in heat of fusion and melting temperature. The amplitude and sharpness of the melting peaks are also shown to increase as the crystalline order of the polyol improves. This trend also suggests an increase in the purity of the crystalline zones of the polycarbonate polymer as the molecular weight of the polymer is increased.

Further evidence of the melting point dependence on polyol molecular weight was found. As the molecular weight increases there is a significant increase in the intensity and position of the polyol

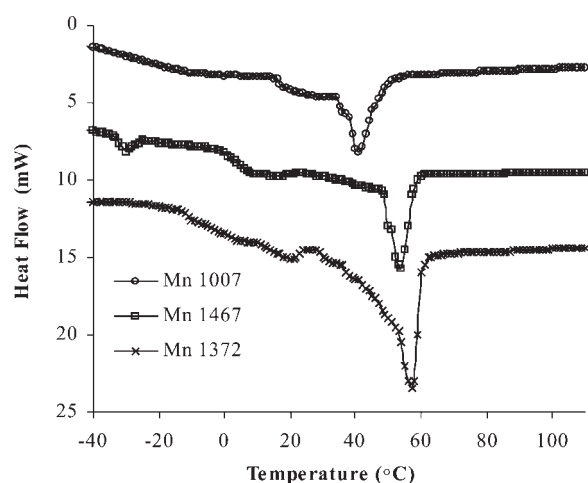


Figure 12 DSC thermograms of C_4 -based homopolymer polycarbonate grades.

melting endotherms. T_m increases from 35°C to 57°C as the number average molecular weight of the polyol increases from 598 to 1467. An increase in T_m of a similar magnitude was also recorded by Eceiza et al.³⁹ in their studies of C₆-based polycarbonate polyols. Buckley and Kovacs⁴⁰ has also shown that decreasing the molecular weight of polyethylene oxide caused the melting temperatures to shift to low temperatures and significantly broaden.

Studies carried out by Flory and Flory et al.^{31,41} on normal paraffin hydrocarbons have also shown a similar relationship between melting point and molecular weight. Flory suggested that chain ends function as diluents and therefore serve to lower the crystalline melting points, depending on their concentration. A similar argument can be made in the case of the melting behavior of the homopolymer polycarbonate polyols throughout second stage polymerization. As the molecular weight of the homopolymer polyol increases during second stage polymerization there is significant fall off in the number of chain ends present, which in turn is likely to promote a greater level of molecular ordering and a corresponding increase in the temperature at which melting occurs. These trends are in strong agreement with trends reported by Flory and Flory et al.^{31,41}

CONCLUSIONS

A series of polycarbonate polyols were successfully synthesized using dimethylcarbonate and specific combinations of linear alkane diols. A two-stage condensation polymerization technique was used to yield polycarbonate polyol grades of number average molecular weight and molecular weight distribution ranging between 700 and 1700 and 1.2 and 1.8, respectively.

It was observed that the monomer concentration and polymerization reaction conditions used during the first and second stages of the polymerization had a direct influence on the molecular weight, molecular weight distribution and quality of the polycarbonate polyol. By modifying the ratio of the dimethylcarbonate component to the diol or diol combinations, polycarbonate polyols of specific molecular weights were successfully synthesized. Although the rate of reaction throughout the first stage polymerization was greater using a dimethylcarbonate excess of 1.5, no significant improvement in molecular weight of the polycarbonate polyols were observed using molar excess above 1.2.

The morphology of the polycarbonate polyol was significantly affected by the molecular weight and the diol combination used during synthesis. Thermal analysis studies of the polycarbonate polyols showed a reduction in both heats of fusion, and crystalline

melting temperatures as the molecular weight of the diol component used in the polymerization of polycarbonate grades was increased. As the molecular weight of the diol was increased from C₂ to C₆ an accompanying reduction in melting point and crystallinity was also observed. It is suggested that the reduction in crystallinity occurs due to a reduction in packing density due to the increase in molecular weight between adjacent carbonate bonds.

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