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Poly(alkylene carbonate)s by the carbonate interchange reaction of aliphatic diols with dimethyl carbonate: synthesis and characterization[*]

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Poly(alkylene carbonate)s have been synthesized by the melt-phase interchange reaction of aliphatic diols with dimethyl carbonate. Aliphatic polycarbonates with inherent viscosities of 0.3 to 0.8 dl g^{-1} have been obtained. Polycarbonates derived from alicyclic diols show a T_g below room temperature and a T_m in the range 50–60°C. However, the polycarbonate derived from a cyclic diol, namely 1,4-bis(hydroxymethyl)-cyclohexane, shows a T_g of +35°C and a T_m of +97°C, the highest yet reported for this class of polymers.

(Keywords: poly(alkylene carbonate)s; carbonate interchange reaction; dimethyl carbonate)

INTRODUCTION

Poly(aryl carbonate)s are well known as a class of valuable engineering thermoplastics with diverse end applications[1,2]. However, poly(alkylene carbonate)s derived from aliphatic diols have attracted significantly lesser attention as structural materials on account of their poor physical properties. Nevertheless, they show potential as biodegradable and biocompatible materials[3,4], which has resulted in a resurgence of interest in their synthesis. Poly(alkylene carbonate)s have been synthesized by (a) the reaction of aliphatic diols with phosgene[5], (b) the copolymerization of epoxides with carbon dioxide in the presence of an organometallic catalyst[6], (c) the ring-opening polymerization of cyclic carbonates using nucleophilic initiation[7–10], (d) the carbonate interchange reaction of aliphatic diols with dialkyl or diaryl carbonates in the presence of alkali metals, alkali metal alkoxides or alkali metal acetates as catalysts[11–19], and (e) the direct condensation of diols with carbon dioxide or alkali metal carbonates[20–23]. Of these, (b) and (c) are not considered to be general methods: method (b) is only applicable to poly(alkylene carbonate)s derived from ethylene oxide and propylene oxide, while method (c) only works satisfactorily with trimethylene carbonate. In addition, methods (b) and (c) yield a mixture of carbonate and ether linkages in the polymers produced, with the latter arising from a facile decarboxylation occurring during the polymer forming reaction. Method (d) avoids the use of phosgene and could form the basis for a general synthetic method for poly(alkylene carbonate)s. This method has been described largely in the patent literature, but the range of molecular weights that are accessible and the extent of decarboxylation associated with it is not readily apparent from a reading of this literature.

In view of our interest in the evaluation of poly(alkylene carbonate)s as biodegradable and biocompatible matrices for parenteral drug delivery systems, we have examined the synthesis of this class of polymers by the melt-phase carbonate interchange reaction of aliphatic diols with dimethyl carbonate. This present paper reports the results of this study[24].

EXPERIMENTAL

Materials

Dimethyl carbonate (DMC) (Aldrich) was distilled and stored over molecular sieves (type 4A). 1,4-Butanediol (**1**), 1,6-hexanediol (**2**), 1,8-octanediol (**3**), 1,4-bis(hydroxymethyl)cyclohexane (**4**) (all from Aldrich), poly(tetramethylene glycol)-650 (**5**) (BASF, NJ, USA) and di-n-butyltin oxide (FASCAT-4201, M and T Chemicals, Rahaway, NJ, USA) were used as received. 1,3-Diphenoxytetra-n-butyl distannoxane was prepared according to the literature procedure[25].

General synthesis

A representative procedure for the synthesis of the poly(alkylene carbonate) derived from dimethyl carbonate (DMC) and diol **4** is described below.

In a three-necked round-bottomed flask fitted with a nitrogen inlet tube, a fractionating column connected to a liquid dividing head, and a dropping funnel was placed **4** (19.42 g, 0.134 mol) and 1,3-diphenoxytetra-n-butyl distannoxane (3.45 g, 2.6×10^{-3} mol). The mixture was heated to 120–130°C under nitrogen to dissolve the catalyst. The temperature of the flask was lowered to 90°C and DMC (24.1 g, 0.26 mol) was added dropwise. The reaction temperature was then increased to

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130–140°C, at which point a constant boiling azeotrope of methanol plus DMC began to distil. The temperature of the reaction was then gradually increased to 180°C over a period of 2 h and maintained at this temperature for 1 h to allow complete distillation of the azeotrope, as well as unreacted DMC. The resulting product was recovered by dissolving in methylene chloride, washing with 0.1% aqueous alkali solution, followed by water, and then precipitation with n-hexane. The oligomeric polycarbonate was dried in vacuum; yield: 17.1 g (88%). The oligomer (10.0 g) obtained above was subjected to post-polymerization in a separate step, in the presence of 2 mol% 1,3-diphenoxytetra-n-butyl distannoxane as the catalyst. The reaction temperature was gradually increased from 140–220°C over a period of 7 h at a pressure of 0.5 mmHg. The final polymer was recovered as above; yield: 8.6 g (86%).

*Synthesis of 1,4-bis(methyl methylenecarbonate) cyclohexane (**6**)*

In a three-necked round-bottomed flask, fitted with a nitrogen inlet tube, a fractionating column connected to a liquid dividing head, and a dropping funnel, was placed **4** (5.0 g, 0.034 mol) and 1,3-diphenoxytetra-n-butyl distannoxane (0.5 g, 3.75×10^{-4} mol). The mixture was heated to 120°C under nitrogen to dissolve the catalyst, and DMC (28.1 g, 0.31 mol) was added dropwise. Heating was continued at 120°C for a period of 3 h, during which time a constant boiling azeotrope of methanol and DMC distilled out. The resulting product was recovered by dissolving in methylene chloride, washing with aqueous alkali solution and water, and evaporating the organic layer. The product obtained (4.6 g, (92%)) was found to be a mixture of two compounds, i.e. the mono- and the biscarbonate, as evidenced by T.L.C. analysis, i.r. (1760 and 3400 cm^{-1}) and ^1H n.m.r. ($CDCl_3$/TMS; δ, ppm: 1.0–1.8 (m, -⬡-), 3.5–3.6 (2d, >$-CH_2OH$), 3.7 (s, OCH_3), and 4.0–4.2 (2d, >$-CH_2OCO$).). The biscarbonate was separated from the mixture by column chromatography using silica gel as the stationary phase and petroleum ether/ethyl acetate (3 vol%) as the eluent. Yield 5.4 g (54%); m.p. 103–105°C; i.r. ($CHCl_3$) 1760 cm^{-1}; ^1H n.m.r. ($CDCl_3$/TMS; δ, ppm: 1.0–1.9 (m, -⬡-), 3.7 (s, OCH_3), 4.0–4.2 (d, >$-CH_2OCO$)).

Analysis

^1H n.m.r. spectra were recorded on a Bruker 200 MHz instrument in $CDCl_3$ and reported in ppm (relative to TMS). I.r. spectra were recorded in $CHCl_3$ solution on a Perkin–Elmer 599B spectrophotometer. Elemental analysis was carried out on a CH analyser (Carlo–Erba EA 1108). Inherent viscosity measurements were carried out using 0.5% (wt/vol) of polymer in $CHCl_3$ at 30°C using an Ubbelhode viscometer. Vapour phase osmometry was performed on a Knauer Model 11 instrument in $CHCl_3$. X-ray analysis was performed on a Philips model PW1730 X-ray generator using nickel-filtered CuKα radiation. Gel permeation chromatography (g.p.c.) was performed using a Waters 150C instrument with μ-Styragel columns (10^5, 10^4, 10^3, 10^2 and 500 Å) in THF as solvent (0.3–0.4 wt/vol. solution, 2 ml min^{-1}) at 30°C. Thermogravimetric analysis was conducted with a Perkin–Elmer TGA-7 at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (d.s.c.) studies were carried out on a Mettler DSC-20 machine equipped with a thermal analysis data station. The parameters were determined from the heating and cooling scans; the heating (cooling) rate was +(−) 5°C min^{-1}.

RESULTS AND DISCUSSIONS

A series of diols of varying carbon numbers (**1**–**5**) was used for the syntheses of various poly(alkylene carbonate)s. The best results were obtained when the reaction was performed in two stages. In the first stage an oligomer was formed, which was then purified free of starting monomers. The purified oligomer was subjected to self-polymerisation in the second stage. The results are shown in *Table 1*. The oligomer obtained in stage I was characterized by i.r. and ^1H n.m.r. spectroscopy and elemental analysis (*Table 2*). Both the oligomer and the polymer showed no signals at $\delta = 3.4$–3.5 ppm, indicating the absence of any ether linkages in the polymer. It can be concluded that even under the high temperatures used in the melt-phase reaction, decarboxylation is not an important side reaction. The yields of recovered oligomer and polymer from both stages of the reaction never exceeded 85%. This was due to loss of some lower-molecular-weight fractions, e.g. hexane-soluble fractions.

Table 1 The carbonate interchange reaction of diols with DMC[a]

	Stage I				Stage II			
Diol	Conversion (%)	η_{inh}[b] ($dl\,g^{-1}$)	M_n[c]	M_n[d]	Conversion (%)	η_{inh}[b] ($dl\,g^{-1}$)	M_n[d]	$\frac{M_w}{M_n}$[e]
1	82	0.06	522	610	79	0.56	7960	2.4
2	78	0.07	647	850	82	0.79	9550	2.6
3	84	0.15	1161	1246	80	0.30[f]	2965	2.0
4	84	0.09	1120	1301	86	0.39	7960	2.7
5[g]	83	0.11	1700	1205	80	0.55	6125	2.3

[a] Stage I: 110–120°C, 5 h; stage II: 140–220°C, 6 h, 0.5 mmHg

[b] In $CHCl_3$ at 30°C

[c] Calculated from ^1H n.m.r. spectroscopy by taking the ratio of integration of methylene protons to the terminal OCH_3 protons

[d] From vapour phase osmometry

[e] From g.p.c.

[f] Reaction carried out for 3 h in stage II

[g] Reaction temperature was not allowed to go beyond 150°C in either of the stages

Table 2 Analytical data for the stage I oligomer

Diol	I.r.[a] (cm^{-1})	^{1}H n.m.r.[b] (ppm)	Elemental analysis, calcd/found (%)
1	1240, 1760, 2900	1.0–1.8 (m), 3.7 (s), 4.0 (t)	C = 51.72/51.76 H = 6.89/7.00
2	1240, 1745, 2900	1.0–1.8 (m), 3.7 (s), 4.0 (t)	C = 57.38/58.30 H = 8.74/8.33
3	1245, 1750, 2900	1.0–1.8 (m), 3.6 (s), 4.0 (t)	C = 62.15/62.79 H = 9.27/9.30
4	1240, 1750, 2900	1.0–1.8 (m), 3.7 (s), 4.0 (d), 4.1 (d)	C = 63.49/63.52 H = 8.58/8.23
5	1120, 1240, 1760, 2900, 3400	1.0–1.8 (m), 3.4 (t), 3.6 (s), 4.0 (t)	C = 55.38/57.06 H = 7.69/7.09

[a] In $CHCl_3$
[b] In $CDCl_3$ relative to TMS

The ^{1}H n.m.r. spectra of the polymer obtained from diol **4** showed two doublets in the region $\delta = 4.0$–4.2 ppm, in analogy with the ^{1}H n.m.r. spectra of 1,4-dimethylcyclohexane[26]. We assign the peak at $\delta = 4.0$ ppm to the equatorial methylene protons and that at 4.2 ppm to the axial methylene protons. All of the polymers after precipitation from n-hexane showed a single peak in their g.p.c. scans, with a molecular-weight distribution value between 2 and 3. The poly(alkylene carbonate)s derived from diols **1–3** show appreciable crystallinity (*Figure 1*). Of the three homologous diols, diol **3** appeared to have maximum crystallinity (~40–50%). This can be attributed to the ability of longer carbon chains ($>C_8$) to undergo crystallization. The polymer derived from diol **4** was predominantly amorphous, on account of the ring structure of the cyclohexyl groups.

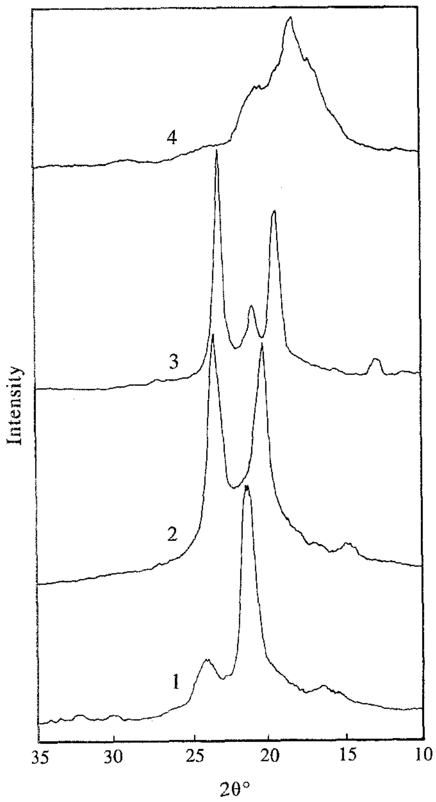
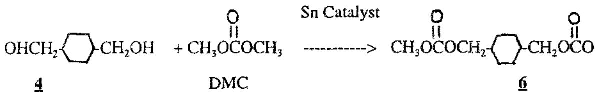


Figure 1 X-ray diffraction patterns of poly(alkylene carbonate)s derived from diols **1–4**

We have recently reported that the bis(methyl carbonate) of 4′,4′-isopropylidenediphenol (bisphenol A) undergoes facile self-polymerization in the melt phase to give high-molecular-weight poly(aryl carbonate)s[27]. With a view to synthesizing high-molecular-weight poly(alkylene carbonate)s, we prepared the bis(methyl carbonate) of **4**, by reacting **4** with excess DMC and ensuring that the reaction temperature did not exceed 120°C (equation (1)). From this reaction, **6** was isolated in 54% yield and was characterized by i.r. and ^{1}H n.m.r. spectroscopy.



(1)

The monomer (**6**) was subjected to post-polymerization in the presence of 1,3-diphenoxytetra-n-butyl distannoxane as catalyst. The polymer obtained had an inherent viscosity of 0.55 dl g^{-1} ($CHCl_3$, 30°C).

The various poly(alkylene carbonate)s synthesized in the course of this study were subjected to t.g.a. and d.s.c. investigations, and the results are shown in *Table 3*. The polymer derived from diol **4** showed a T_g of +35°C and a T_m of 97°C. The polymers derived from other aliphatic diols showed T_gs below room temperature and T_ms in the range 50–60°C. No consistent values for the T_gs of aliphatic polycarbonates are available in the literature. The T_gs of polycarbonates derived from ethylene glycol, 1,3-propanediol and 1.6-hexanediol has been reported by various authors as having values of +5°C (ref. 4), +27°C (ref. 10) or −15°C (ref. 28), and −43°C (ref. 29), respectively. In the case of a series of homologous aliphatic polyesters derived from aliphatic diols and adipic acid, it has been reported that the T_g remains

Table 3 Thermal analysis data for poly(alkylene carbonate)s

Diol	*IDT*[a] (°C)	T_g[b] (°C)	T_m[b]
1	252	−39.8	61.4
2	269	−11.4	51.4
3	270	−51.7	56.3
4	297	+35.0	97.0

[a] Initial decomposition temperature obtained from t.g.a.
[b] Obtained from d.s.c. (2nd heating scan)

practically unchanged, when the carbon number in the diol is changed from C_2 to C_{10}[29].

CONCLUSIONS

In conclusion, the carbonate interchange reaction of aliphatic diols with dimethyl carbonate offers a general route to wholly aliphatic polycarbonates. Depending on the nature of the diols, they show diverse behaviour in terms of melting, glass transition and crystallinity. The polycarbonate derived from diol **4** forms optically clear films and has the highest T_m yet reported for this class of polymers.

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