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Polymers of carbonic acid 18: polymerizations of cyclobis(hexamethylene carbonate) by means of $BuSnCl_3$ or Sn(II)2-ethylhexanoate

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Cyclobis(hexamethylene carbonate), $(HMC)_2$, was prepared from 1,6-hexane diol and diethylcarbonate by a combined polycondensation–depolymerization procedure. The recrystallized monomer was characterized by standard methods and subjected to polymerization in bulk at 140°C. Either $BuSnCl_3$ or $SnOct_2$ were used at initiator. When the reaction time was varied at constant monomer/initiator (M/I) ratio both initiators yielded the highest molecular weights at 20 h. Variation of the M/I ratio proved that the molecular weights do not parallel the M/I ratios. The best results were obtained with $BuSnCl_3$ as initiator: yields up to 89% and weight average molecular weights (M_w) around 200 000 were found. In all cases the M_w/M_n ratio was of the order of 2. Differential scanning calorimetry measurements showing that polyHMC is a rapidly crystallizing polymer, which crystallizes even at a cooling rate of $-40°C\,min^{-1}$. Thermogravimetrical analyses were conducted at a heating rate of $3°C\,min^{-1}$ under nitrogen, and under oxygen. The degradation begins around 250°C and reaches its maximum around 350°C. Under nitrogen, CO_2, H_2O and tetrahydropyran were found as low molar mass degradation products, whereas formaldehyde and the monomeric cyclocarbonate were not formed. Under an O_2 atmosphere oxidation is the main degradation process above 300°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyclobis(hexamethylene carbonate); poly(hexamethylene carbonate); ring-opening polymerization)

INTRODUCTION

Over the past ten years aliphatic polycarbonates and their copolyesters with lactones have attracted increasing interest as potentially biodegradable materials. Furthermore, copolymers of aliphatic carbonates and ϵ-caprolactone are useful as polymeric plasticizers, for instance in PVC. Cyclocarbonates may be polymerized by anionic initiators[1], cationic initiators[2,3] or by initiators of insertion mechanisms[4]. Although the polymerization mechanism is unknown, $BuSnCl_3$ has recently been found[5–7] to be a highly useful initiator for the ring-opening polymerization of six-membered aliphatic cyclocarbonates. Therefore this initiator was also used in the present work. Sn(II)2-ethylhexanoate ($SnOct_2$) which is an excellent catalyst for the polymerization of lactide and lactones[8–14] was used for comparison.

Whereas numerous papers have been devoted to the ring-opening polymerizations of trimethylene carbonate and neopentane diol carbonate, higher alkane diol carbonates have attracted little interest. The present work is concerned with the polymerization of cyclobis(hexamethylene carbonate) ($(HMC)_2$) which was selected as monomer, because it is easier to synthesize and purify than the monomeric cyclo(hexamethylene carbonate). To the best of our knowledge the synthesis of poly(hexamethylene carbonate) (polyHMC) by ring-opening polymerization has never been described before, and a fundamental characterization of this polycarbonate is also missing.

EXPERIMENTAL

Materials

1,6-Hexanediol, diethyl carbonate, *n*-butyltintrichloride and Sn(II)2-ethylhexanoate were all purchased from Aldrich Co. (Milwaukee, WI, USA) and used after distillation.

Cyclobis(hexamethylene carbonate)

1,6-Hexane diol (5 mol), diethylene carbonate (55 mol) and K_2CO_3 (1 g) were mixed and heated in a round-bottomed flask equipped with a fractionation column. The temperature was kept around 125°C for 10 h whereby most of the liberated ethanol was removed. Afterwards the temperature was raised to 190°C over a period of 2 h and finally vacuum was applied for one additional hour. After cooling the waxy solid was dissolved in dichloromethane (100 ml), washed once with 0.1 *N*-hydrochloric acid and four times with neutral water. After drying with Na_2SO_4 the methylene chloride was evaporated and the residue heated to 130°C. A

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vacuum of approximately 0.5 mbar was then applied and the temperature was raised to 200°C over a period of approximately 0.5 h. The round bottom flask was then equipped for distillation in the form of a short-path apparatus and the receiver flask was cooled with CO_2/methanol to −80°C. A vacuum of 0.1–0.5 mbar was then applied again and the temperature was raised to 280°C over a period of 10 h. The distilled product was washed with a small amount of cold ethyl acetate and finally recrystallized from ethyl acetate. Yield 11%, mp 130–131°C.

Analyses calcd for $C_7H_{12}O_3$ (144.17): C 58.32, H 8.39, found: C 58.19, H 8.22%. Mass spectroscopy revealed a peak at 282 g mol^{-1} proving the dimeric nature of the monomer. ^1H nuclear magnetic resonance (n.m.r.) ($CDCl_3$/TMS): $\delta = 1.65$ (*m*, 16 H), 4.17 (*t*, 8H). ^{13}C n.m.r. ($CDCl_3$/TMS): $\delta = 25.8, 28.0, 67.7, 155.2$ ppm.

Polymerizations

Cyclobis(hexamethylene carbonate) (20 mmol) was weighed into a 25 ml Erlenmeyer flask with ground-glass joints and silanized-glass walls (pretreatment with Me_2SiCl_2). The initiator was injected in the form of a 1 M solution in dry chloroform. The reaction vessel was closed with a glass-stopper and steel spring and completely immersed into an oil bath thermostated at 140°C. After cooling the product was dissolved in CH_2Cl_2 (50–60 ml) and precipitated into cold methanol. The precipitated polycarbonate was isolated by filtration and dried at 25°C *in vacuo*. ^1H n.m.r. ($CDCl_3$/TMS): $\delta = 1.44$ (*m*, 4H), 1.68 (*t*, 4H), 4.12 (*t*, 4H) ppm. ^{13}C n.m.r. ($CDCl_3$/TMS): $\delta = 25.3, 28.4, 67.6, 155.2$ ppm.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer, thermostated at 20°C.

The infra-red (i.r.) spectra were recorded from KBr pellets using a Nicolet SXB-20 Fourier transform infra-red (*FT* i.r.) spectrometer. The 100 MHz ^1H n.m.r. spectra were recorded on a Bruker AC-100 in 5 mm o.d. sample tubes. The same spectrometer was used for the ^{13}C n.m.r. measurements.

The differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The wide angle X-ray scattering (WAXS) powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu K_α radiation.

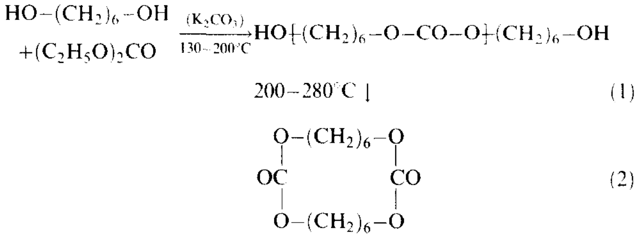
The thermogravimetrical analyses (t.g.a.) were conducted with a NETZSCH STA-apparatus 409 at a heating rate of 3°C min^{-1} combined with a Balzers QM6 421 quadrupole mass-spectrometer.

The gel permeation chromatography (g.p.c.) measurements were performed with a Kontron HPLC 420 equipped with a Waters differential calorimeter 410. Four Ultrastyragel® columns with pore sizes of 10^2, 10^3, 10^4 and 10^5 Å were used, and tetrahydrofuran served as eluent. The mass spectrum of the monomer was recorded with a VG 70 SE using EI ionization.

RESULTS AND DISCUSSION

Synthesis of the monomer

In order to prepare cyclic hexamethylene carbonate the method reported for the synthesis of monomeric and cyclic tetramethylene carbonate[7,15] was also used in the present work. 1,6-Hexanediol was reacted with diethyl carbonate under the catalytic influence of potassium carbonate up to temperatures around 280°C (equation (1)). The resulting OH-terminated low molecular weight polyHMC was purified to remove the basic transesterification catalyst. The dry pure polyHMC was then heated to 280°C *in vacuo* whereby cyclocarbonate distilled off. It was reported for the synthesis of cyclo(tetramethylene carbonate) that it is advantageous to remove the catalyst prior to the thermal degradation of the prepolymer, to avoid decomposition into CO_2 and cyclic ethers. In the absence of a catalyst the 'back-biting degradation' involving the OH-endgroups is predominant.



$$\begin{array}{l} HO{-}(CH_2)_6{-}OH \\ +(C_2H_5O)_2CO \end{array} \xrightarrow[130-200^\circ C]{(K_2CO_3)} HO{+}(CH_2)_6{-}O{-}CO{-}O{+}(CH_2)_6{-}OH \qquad (1)$$

$$200-280^\circ C \downarrow$$

$$\begin{array}{ccc} O{-}(CH_2)_6{-}O & & \\ OC \qquad\qquad CO & & \\ O{-}(CH_2)_6{-}O & & \end{array} \qquad (2)$$

When this procedure was applied to the crude polyHMC a cyclic hexamethylene carbonate was indeed isolated by distillation, but the yield was only on the order of 10% after recrystallization. The structure of this cyclocarbonate was identified by elemental analyses, i.r. spectroscopy (*Figure 1*), ^1H and ^{13}C n.m.r. spectroscopy and mass spectroscopy. The mass spectroscopy revealed that a cyclic dimer was obtained, that was quite analogous to the synthesis of cyclobis(tetramethylene carbonate)[7,15].

Surprisingly, the i.r. spectra of the cyclic dimer $(HMC)_2$ (*Figure 1*) displays a 'CO-band' at a wavelength of 1744 cm^{-1} which is almost identical with that of the polycarbonate (*Figure 2*). This means that the carbonate group of $(HMC)_2$ does not 'feel' much ring-strain. In contrast, when monomeric or dimeric cyclo(tetramethylene carbonate) was compared with poly(tetramethylene carbonate)[7] the 'CO-bands' of the cyclic carbonates displayed a distinct hypsochromic shift relative to that of the polymer. However, the ^{13}C n.m.r. signals of $(HMC)_2$ and of polyHMC (see Experimental) are slightly different, and thus, indicate different conformations. Obviously the conformations of

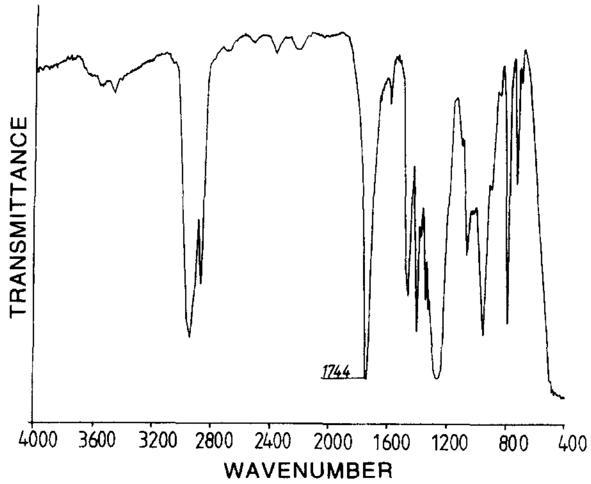


Figure 1 I.r. spectrum (KBr pellets) of $(HMC)_2$

Table 1 Polymerizations of $(HMC)_2$ initiated with $BuSnCl_3$ in bulk at 140°C (M/I = 200/1)

Exp. no.	Time (h)	Yield (%)	$\eta_{inh}{}^{a}$ ($dl\,g^{-1}$)	$M_n{}^{b}$ ($\times 10^3$)	$M_w{}^{b}$ ($\times 10^3$)	$M_n{}^{c}$ ($\times 10^3$)	$M_w{}^{c}$ ($\times 10^3$)
1	4	78	0.71	–	–	–	–
2	8	93	0.92	–	–	–	–
3	20	97	1.10	105	220	90	180
4	48	97	1.07	100	200	80	160
5	120^d	0^d	$–^d$	–	–	–	–

[a] Measured at 20°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2
[b] From g.p.c. measurements in THF evaluated with $K = 4.10 \times 10^{-4}$ and $a = 0.62$ (ref. 5)
[c] From g.p.c. measurements evaluated with $K = 2.77 \times 10^{-4}$ and $a = 0.677$ (ref. 16)
[d] Blindtest without initiator

Table 2 Polymerizations of $(HMC)_2$ initiated with $BuSnCl_3$ in bulk at 140°C, reaction time 20 h

	Mon.						
Exp. no.	Time (h)	Yield (%)	$\eta_{inh}{}^{a}$ ($dl\,g^{-1}$)	$M_n{}^{b}$ ($\times 10^3$)	$M_w{}^{b}$ ($\times 10^3$)	$M_n{}^{c}$ ($\times 10^3$)	$M_w{}^{c}$ ($\times 10^3$)
1	50	98	0.71	49	105	47	95
2	100	98	1.11	105	210	93	180
3	200	98	1.21	120	240	105	210
4	300	98	1.14	110	220	100	200
5	500	91	0.78	58	120	52	105
6	800	83	0.65	47	95	37	85
7	1200	64	0.57	30	62	28	60

[a] Measured at 20°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2
[b] G.p.c. measurements evaluated with $K = 4.1 \times 10^{-4}$ and $a = 0.62$ (ref. 5)
[c] G.p.c. measurements evaluated with $K = 2.77 \times 10^{-4}$ and $a = 0.677$ (ref. 16)
[d] Blindtest without initiator

$(HMC)_2$ are energetically less favourable than those of the polymer, so that negative polymerization enthalpy results upon the polymerization of $(HMC)_2$. The high yields and high molecular weights obtained at 140°C (see below) at least demonstrate that $(HMC)_2$ is a useful monomer and the reaction temperature of 140°C should be considerably lower than the (unknown) ceiling temperature.

Polymerizations

All polymerizations of $(HMC)_2$ were conducted in bulk, because a couple of polymerizations in toluene or CCl_4 had demonstrated that $BuSnCl_3$-initiated polymerizations in solution below 100°C are too slow for any preparative application. The temperature of 140°C used for all polymerizations was adjusted to the melting point of $(HMC)_2$ (130–131°C). With $BuSnCl_3$ as initiator one series of polymerizations was conducted in such a way that the monomer/initiator ratio (M/I) was kept constant at 200/1 and the reaction time was varied. The data compiled in *Table 1* suggest that the conversion was nearly complete after 8 h. No degradation (e.g. by 'back-biting') was detectable after 48 h. In a second series of polymerizations the reaction time was fixed at 20 h and the M/I ratio was varied (*Table 2*). In agreement with previous studies of other cyclocarbonates it was found that the molecular weights do not parallel the M/I ratio. Therefore, high M/I ratios do not have any preparative advantage. On the contrary, high M/I ratios entail a lower rate of conversion, and longer reaction times are required for a complete conversion. The highest molecular weights were obtained at a M/I of 200. The molecular weights listed in *Tables 1* and *2* are crude estimations based on g.p.c. measurements, but certainly provide the correct order of magnitude.

The g.p.c. curves were evaluated by means of the K and a values of two Mark–Houwink equations published for poly(trimethylene carbonate), equations (3)[5] and (4)[16]. The best results correspond to weight average molecular weights (M_w) around 200 000. Similar M_w values were found for $BuSnCl_3$-initiated polymerizations of cyclo(trimethylene carbonate)[5] and cyclo-(neopentanediol carbonate)[6]. This means that $BuSnCl_3$ is an excellent initiator for broad variety of aliphatic cyclocarbonates. No results have been published yet concerning $BuSnCl_3$-initiated polymerizations of lactones. In contrast $SnOct_2$ has not been used as initiator of cyclocarbonates in the past, although it has been known for many years to be an excellent initiator for lactides and other lactones.

$$[\eta] = 4.10 \times 10^{-4} M_w^{0.62} \tag{3}$$

$$[\eta] = 2.77 \times 10^{-4} M_w^{0.677} \tag{4}$$

Using $SnOct_2$ as initiator again, two series of polymerizations were conducted, one with variation of the reaction at M/I = 200 (*Table 3*) the other with variation of the M/I ratio (*Table 4*). The results listed in *Table 3* suggest that the $SnOct_2$-initiated polymerizations were a little slower than those initiated by $BuSnCl_3$. When the M/I ratio was carried at a reaction time of 20 h the optimum results were again obtained at a M/I of 200 and 300. Higher M/Is resulted in incomplete conversion. When compared to the $BuSnCl_3$-initiated polymerizations lower molecular weights were obtained under all

Table 3 Polymerizations of $(HMC)_2$ initiated with $SnOct_2$ in bulk at 140°C (M/I = 200/1)

Exp. No	Time (h)	Yield (%)	$\eta_{inh}{}^{a}$ ($dl\,g^{-1}$)
1	4	52	0.41
2	8	76	0.63
3	20	93	0.86
4	48	92	0.73

[a] Measured at 20°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2

Table 4 Polymerizations of $(HMC)_2$ initiated with $SnOct_2$ in bulk at 140°C (time 20 h)

Exp. No	Mon. / ini.	Yield (%)	$\eta_{inh}{}^{a}$ ($dl\,g^{-1}$)
1	50	92	0.69
2	100	93	0.88
3	200	95	0.90
4	300	95	0.92
5	500	86	0.71
6	800	61	0.52
7	1200	0	–

[a] Measured at 20°C with $c = 2\,g\,l^{-1}$ in $CHCl_2$

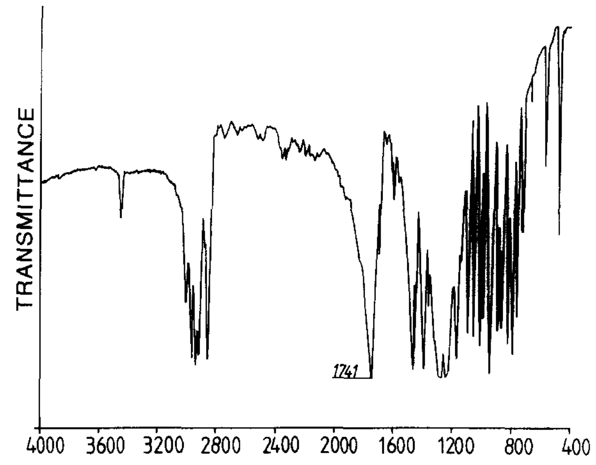
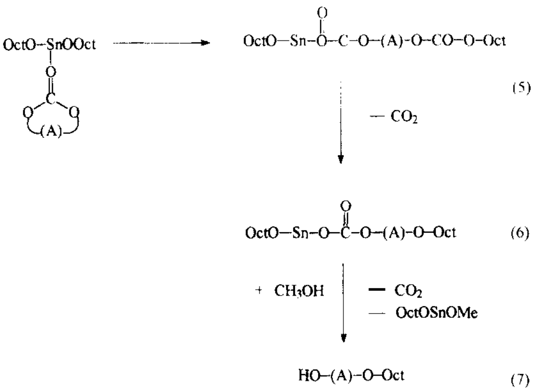


Figure 2 I.r. spectrum (KBr pellets) of polyHMC

circumstances. Thus, $SnOct_2$ is less attractive an initiator, at least for preparative purposes.

Characterization of polyHMC

In addition to the i.r. spectrum of *Figure 2* ^1H and ^{13}C n.m.r. spectra of the isolated polyHMC samples were recorded (see Experimental and *Figures 3* and *4*). These n.m.r. spectra demonstrate that all polyHMC samples of this work are free of ether groups. In contrast to cationic polymerizations the propagation steps initiated by $BuSnCl_3$ or $SnOct_2$ do not involve decarboxylation. This observation suggests that both tin compounds initiate an insertion mechanism. The ^1H n.m.r. also revealed in the case of $SnOct_2$-initiated samples that these polycarbonates possess covalently bound octoate endgroups and OH-endgroups (*Figure 3*). The OH-endgroups were identified on the basis of their chemical shift and their rapid esterification with trifluoroacetic anhydride. The reaction with trifluoroacetic anhydride has the consequence that the triplet signal of the CH_2OH endgroup at 3.7 ppm (*Figure 3*) disappears and the triplet signal of the $-CH_2O_2CCF_3$ appears at 4.3 ppm. These endgroups suggest that the $SnOct_2$-initiated polymerizations mainly follow the reaction sequences outlined in equations (5)–(7).



For a further characterization of polyHMC, d.s.c. measurements were conducted which revealed a melting endotherm at 62°C in the second heating curve (*Figure 4C*). The corresponding crystallization exotherm was detectable in the cooling traces, when the cooling rate was varied between −10°C min^{-1} and −40°C min^{-1}.

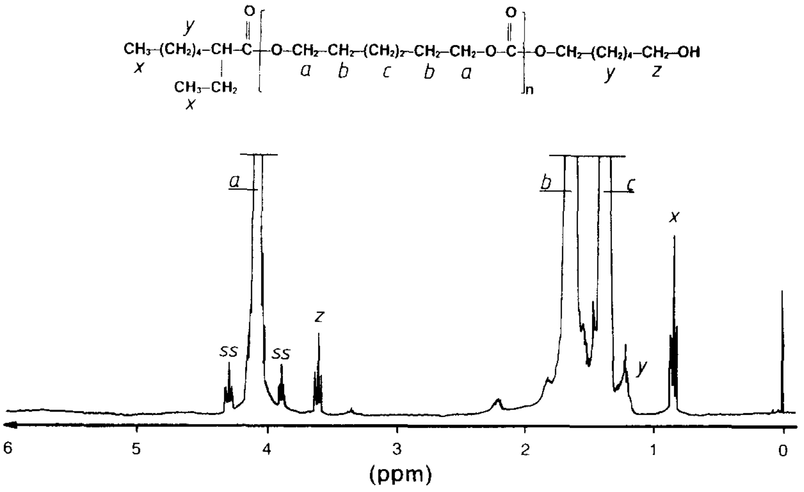


Figure 3 360 MHz ^1H n.m.r. spectrum of polyHMC in $CDCl_3$ (No. 1, Table 3)

However at a cooling rate of $-80°C\,min^{-1}$ the crystallization was suppressed (*Figure 4F*).

These results illustrate the tremendous influence of the aliphatic chain on the crystallization of aliphatic polycarbonates. Poly(trimethylene carbonate) does not crystallize at all, and crystallization of poly(tetramethylene carbonate) is so slow that a cooling rate of $-10°C\,min^{-1}$ suffices to suppress the crystallization completely[7]. In a future part of this series we will report on poly(decamethylene carbonate), and see whether a greater length of the alkane segment will cause an additional acceleration of the crystallization.

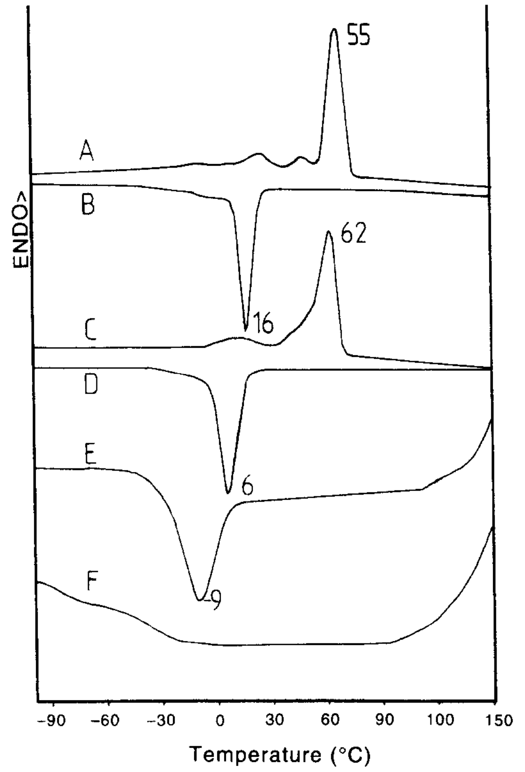


Figure 4 D.s.c. measurements (heating/cooling rate $20°C\,min^{-1}$) of polyHMC: (A) first heating; (B) first cooling with $-10°C\,min^{-1}$; (C) second heating; (D) second cooling with $-20°C\,min^{-1}$; (E) third cooling with $-40°C\,min^{-1}$; (F) fourth cooling with $-80°C\,min^{-1}$

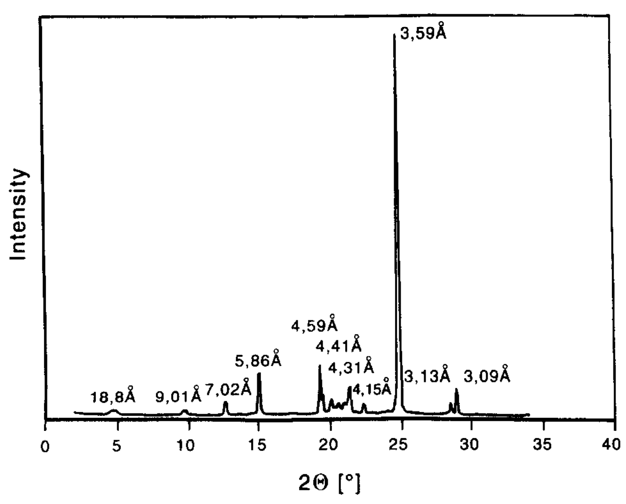


Figure 5 WAXS powder pattern of $(HMC)_2$

WAXS powder patterns of $(HMC)_2$ (*Figure 5*) and polyHMC (*Figure 6*) were recorded to complete the characterization of both compounds, although no detailed X-ray analysis was intended. The WAXS patterns suggest that the crystal lattices of both carbonates are quite different and they indicate a degree of crystallinity around 40% in the case of polyHMC.

Finally, the thermal degradation of polyHMC was investigated. The t.g.a. measurements were conducted under nitrogen at a heating rate of $3°C\,min^{-1}$. As illustrated by *Figure 7* the degradation (2–4% loss of weight) of the high molecular weight sample No. 3, *Table 2* begins around 280°C. The loss of weight reaches its maximum rate around 350°C and a residue of a few percent of charcoal is left at 400°C. These results indicate a higher thermostability than that of poly(tetramethylene carbonate) reported in the preceding part of this series[7]. In the case of poly(tetramethylene carbonate) the maximum rate of degradation was found at 280°C. Another characteristic difference concerns the nature of the degradation product. CO_2 and tetrahydrofuran were by far the most predominant degradation products of poly(tetramethylene carbonate) along with a small amount of water. In the case of poly(HMC) again CO_2 and water were found as degradation products, but only small amounts of tetrahydropyran. Interestingly, neither the

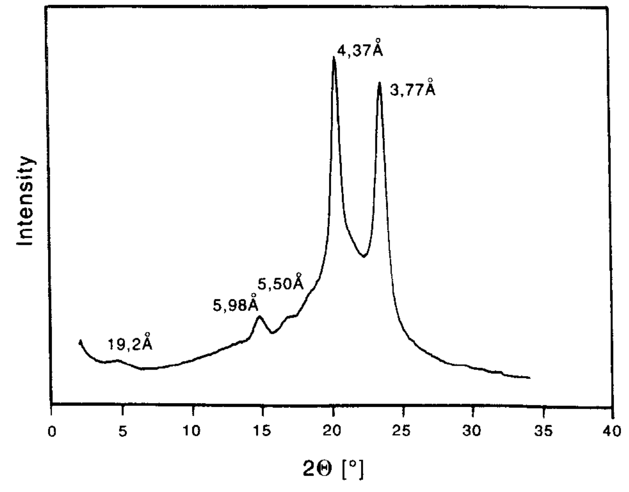


Figure 6 WAXS powder pattern of poly(HMC)

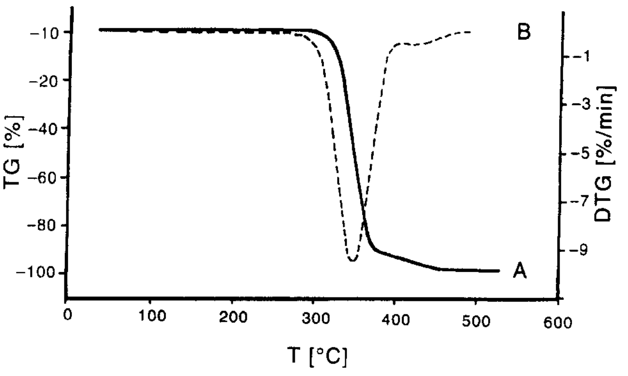


Figure 7 T.g.a. of polyHMC (No. 3, Table 2) conducted under nitrogen at a heating rate of $3°C\,min^{-1}$

monomeric cyclocarbonate nor formaldehyde were detected. Masses above 200 g mol^{-1} were not detectable for technical reasons. Clearly, the course of the thermal degradation of both polycarbonates is quite different. When the degradation was studied under a slow stream of oxygen, oxidation was the main degradation process and tetrahydropyran was never detected. It should be emphasized that these studies were conducted with re-precipitated, almost catalyst-free, polycarbonates. The addition of a transesterification catalyst may change the course of the thermal degradation.

CONCLUSION

The thermal degradation of low molecular weight and catalyst free polyHMC *in vacuo* yields the dimeric cyclocarbonate $(HMC)_2$ as a crystalline, easy to isolate degradation product. Degradation under normal pressure yields larger quantities of CO, CO_2 and H_2O. The cyclic dimer is a useful monomer for ring-opening polymerization and gives high yields of high molecular weight polyHMC when $BuSnCl_3$ is used as initiator. $SnOct_2$ gives inferior results. An interesting property of polyHMC is the relatively rapid crystallization which was observed neither for poly(trimethylene carbonate) nor for poly(tetramethylene carbonate).

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