Polymers of Carbonic Acid. 20. High Molecular Weight Poly(Decamethylene Carbonate) by Ring-Opening Polymerization Initiated with BuSnCl$_3$ or SnOct$_2$

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POLYMERS OF CARBONIC ACID. 20. HIGH MOLECULAR WEIGHT POLY(DECAMETHYLENE CARBONATE) BY RING-OPENING POLYMERIZATION INITIATED WITH BuSnCl₃ OR SnOct₂

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ABSTRACT

Cyclobis(decamethylene carbonate), $(DMC)_2$, was prepared by polycondensation of 1,10-decane diol and diethylcarbonate followed by thermal depolymerization in vacuo. Two series of polymerizations were conducted in bulk at 120°C with $BuSnCl_3$ as initiator. Either the reaction time was varied at a constant monomer/initiator (M/I) ratio or the M/I ratio was varied at constant reaction time. Two analogous series of polymerizations were conducted with Sn(II)-2-ethylhexanoate, $SnOct_2$. Both initiators showed almost equal reactivities, but the highest yields (up to 98%) and the highest molecular weights (M_w up to 88,000) were obtained with $BuSnCl_3$. Both initiators yielded polyDMC free of ether groups. DSC measurements revealed that polyDMC is a rapidly crystallizing material with a melting temperature (T_m) of 67 ± 1°C. A comparison with poly(alkylene carbonate)s having fewer CH_2 groups demonstrated that the rate of crystallization increases with an increasing number of CH_2 groups.

INTRODUCTION

In recent years aliphatic polycarbonates and copoly(ester-carbonate)s derived from lactones and aliphatic cyclocarbonates have attracted increasing interest as potentially biodegradable materials. However, in contrast to six-membered cyclo-carbonates such as trimethylene carbonate [1–5] or substituted trimethylene carbonates [6–10], cyclocarbonates of longer α,ω-diols have not been studied in detail. To the best of our knowledge, cyclocarbonates of 1,10-deanediol have not been described. Therefore, the present work reports on the synthesis and polymerization of cyclobis(decamethylene carbonate), $(DMC)_2$, as part of a broader study of cyclocarbonates. Another purpose of this work was to broaden the evaluation of $BuSnCl_3$ and Sn(II)-2-ethylhexanoate ($SnOct_2$) as initiators. $BuSnCl_3$ has recently been found to be an efficient initiator for the ring-opening polymerization of smaller cyclocarbonates [5, 10–13]. $SnOct_2$ is an established and widely used initiator for lactones and particularly for lactides [14–20].

EXPERIMENTAL

Materials

1,10-Decanediol, diethylcarbonate, nBuSnCl$_3$, and Sn(II)-2-ethylhexanoate ($SnOct_2$) were all purchased from Aldrich Co. (Milwaukee, WI, USA). $SnOct_2$ was dried over P_4O_{10} in vacuo prior to use.

Cyclobis(decamethylene Carbonate)

1,10-Decanediol (3 mol), diethylcarbonate (3.3 mol), and potassium carbonate (1 g) were weighed into a 2-L round-bottom flask equipped with a fractionation column of 0.5 m length. The reaction vessel was placed in an oil bath preheated to 120°C. The temperature was slowly raised to 140°C over a period of 10 hours to remove most of the ethanol. The temperature was then gradually raised to 190°C (3 hours), and finally vacuum was applied to remove the excess of diethylcarbonate. After cooling, the waxy polycarbonate was dissolved in CH_2Cl_2 (1 L) and successively washed with 1 N HCl (500 mL) and four 500-mL portions of water. The CH_2Cl_2 solution was dried with Na_2SO_4 and evaporated. The residue was placed in an oil bath at 130°C, a vacuum of $\sim 10^{-1}$ mbar was applied, and the temperature was gradually raised to 200°C. After cooling, the crude polycarbonate was transferred to a short-path apparatus with a receiver cooled to $-80°C$. The temperature was raised from 200 to 310°C over a period of 12 hours. The product collected in the receiver was recrystallized from ethyl acetate, yielding 55.4 g (0.14 mol) cyclobis(decamethylene carbonate), mp 102–104°C. $m = 400$ g/mol as determined by mass spectroscopy.

Analyses. Calculated for $C_{22}H_{40}O_6$ (400.55): C, 65.97; H, 10.06%. Found: C, 65.86; H, 9.87%. ^{1}H NMR (CDCl$_3$/TMS), δ: 1.5 (m, 32H), 4.17 (t, 8 H, $J = 5.5$ Hz) ppm. ^{13}C NMR (CDCl$_3$/TMS), δ: 25.77, 28.63, 28.83, 29.01, 68.04, 155.43 ppm.

When the ethyl acetate filtrate was worked up, the following observations were made. Upon concentration and after cooling to $+4°C$ overnight, 1.6 g of a

nonidentified compound with mp 67°C was isolated. The ^{1}H- and ^{13}C-NMR spectra along with a GPC measurement in tetrahydrofuran suggested that the main product remaining after evaporation of the ethyl acetate was the monomeric cyclo(decamethylene carbonate). However, all attempts to obtain a pure product either by crystallization or distillation over a short-path apparatus failed. When the crude product was subjected to distillation over a 10-cm Vigreux column in a vacuum of 10^{-2} mbar, gradual decomposition took place.

Polymerizations

Cyclobis(decamethylene carbonate) (10 mmol) was weighed into a 25-mL Erlenmeyer flask with silanized glass walls (pretreatment with Me_2SiCl_2 in Et_2O), and the initiator was injected by means of a syringe in the form of a 1 M solution in toluene. The reaction vessel was closed with a glass stopper and steel spring and completely immersed into the oil bath thermostated at 120°C. When the reaction time was over, the cold reaction product was dissolved in CH_2Cl_2, precipitated into cold methanol, and dried at 40°C in vacuo. The reaction mixture was prepared in an atmosphere of dry nitrogen.

^{1}H NMR (CDCl$_3$/TMS), δ = 1.29 (m, 12 H), 1.66 (t, 4 H), 4.12 (t, 4 H, J = 0.65). ^{13}C NMR (CDCl$_3$/TMS), δ = 25.68, 28.66, 29.18, 29.39, 68.00, 155.42 ppm.

Measurements

The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20°C.

The IR spectra were obtained from KBr pellets on a Nicolet SXB-20 FT-IR spectrometer. The 360 MHz ^{1}H-NMR spectra were recorded with a Bruker AM 360 FT-NMR spectrometer in 5 mm o.d. sample tubes in TMS containing CDCl$_3$. The 25.4 MHz ^{13}C-NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 10 mm o.d. sample tubes.

The WAXS powder patterns were recorded on a Siemens D-500 diffractometer using Ni-filtered CuKα radiation.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The GPC curves were measured with a Kontron Anacomb HPLC apparatus combined with a Waters differential diffractometer Md 410. A combination of four Ultrastyragel columns with pore sizes of 10^2, 10^3, 10^4, and 10^5 Å was used, and tetrahydrofuran served as the eluent.

The thermogravimetrical analyses were conducted with a NETZSCH STA-apparatus 409 at a heating rate of 3°C/min combined with a BALZERS QM6 421 quadrupole mass-spectrometer.

The mass spectrum of the monomer was recorded with a V6 76SE using EI ionization.

RESULTS AND DISCUSSION

Synthesis of the Monomer

Quite analogous to the syntheses of cyclocarbonates of shorter α,ω-dihydroxyalkanes, a monomer derived from 1,10-decanediol was prepared by thermal degradation of the low molecular weight polycarbonate [11–13]. The low molec-

ular weight poly(decamethylene carbonate) was prepared by K_2CO_3-catalyzed transesterification of 1,10-decanediol with diethylcarbonate. Thermal degradation in vacuo was conducted after removal of the catalyst. The volatile degradation products were fractionated by crystallization from ethyl acetate. The cyclobis(decamethylene carbonate), $(DMC)_2$, was isolated as the least soluble compound in 9.3% yield. The filtrate contained ~20% of the monomeric cyclo(decamethylene carbonate). Unfortunately, all attempts to purify this monomer by recrystallization or distillation failed. Therefore, the cyclic dimer was used as the monomer for all polymerizations of this work. The structure of $c(DMC)_2$ was characterized by mass spectroscopy and elemental analyses (see Experimental section).

The IR spectrum of $(DMC)_2$ exhibits the band of the CO-stretch vibration at 1745 cm^{-1} (Fig. 1) whereas the "CO-band" of the poly(decamethylene carbonate), polyDMC, shows up at 1741 cm^{-1} (Fig. 2). This difference is small but suggests that the conformations of the $c(DMC)_2$ ring are not identical with those of polyDMC. Interestingly, the ^{13}C-NMR CO signal of cyclic dimer and polymer have identical chemical shifts (see Experimental section). However, the signals of two CH_2 groups exhibit shift differences around 0.3 ppm, which are outside the margin of error. These different chemical shifts confirm the existence of different conformations, albeit the ring of DMC_2 is made up of 26 ring-members. The fact that DMC_2 reacts as a monomer giving high yields and high molecular weights (Tables 1–4) indicates that the conformations of DMC_2 are energetically somewhat less favorable than those of polyDMC.

The ^{1}H-NMR spectra of $c(DMC)_2$ and polyDMC do not display any difference when measured at 100 MHz (see Experimental section). In contrast, the WAXS powder patterns of $c(DMC)_2$ and polyDMC look quite different (Figs. 3 and 4), which suggests that these compounds adopt considerably different crystal lattices. A detailed study of this aspect was not intended in this work, but the WAXS powder pattern of polyDMC is also of interest because it demonstrates that this polymer
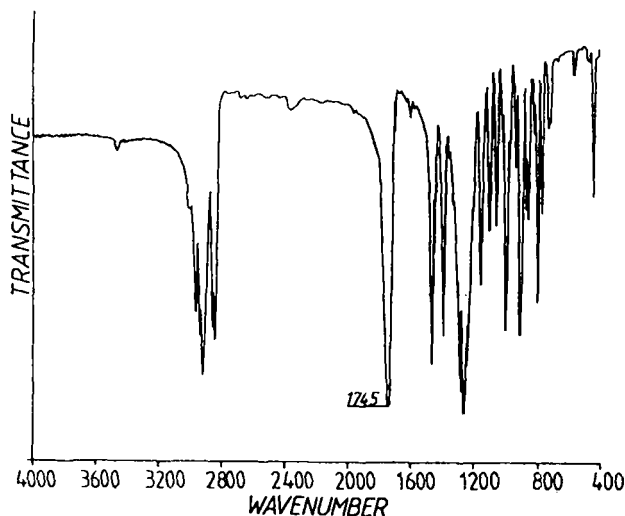
FIG. 1.   IR spectrum (KBr pellets) of cyclobis(decamethylene carbonate).
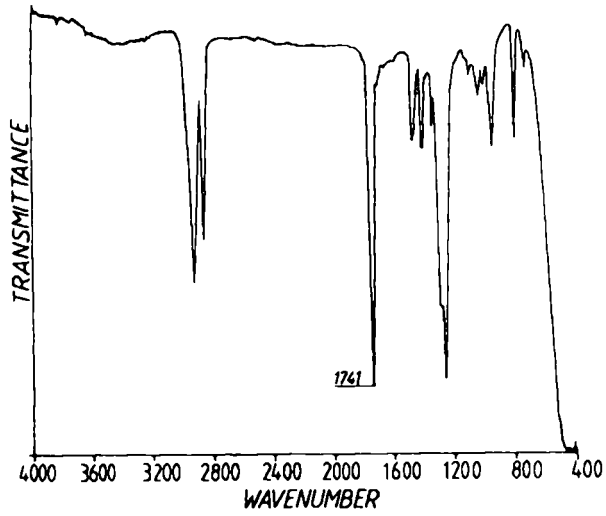
FIG. 2.   IR spectrum (KBr pellet) of poly(decamethylene carbonate).
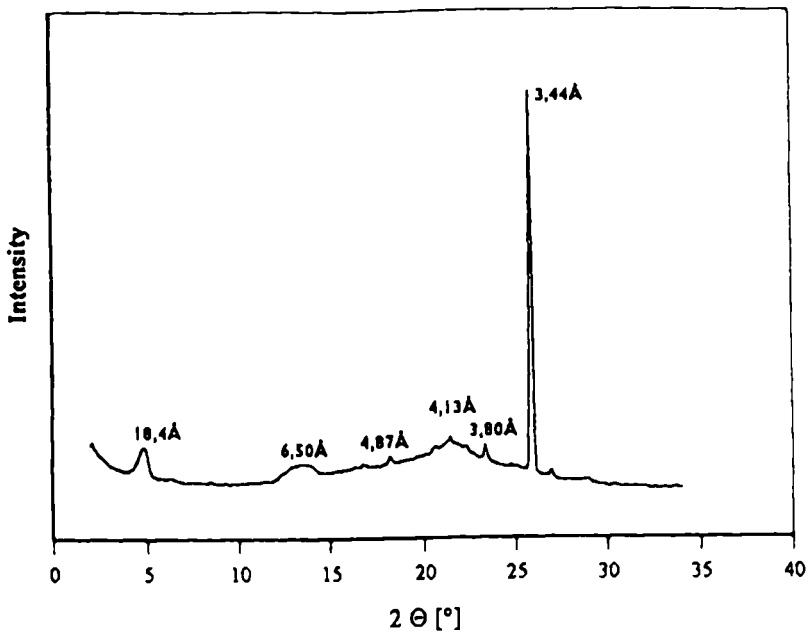
FIG. 3.   WAXS powder pattern of cyclobis(decamethylene carbonate).
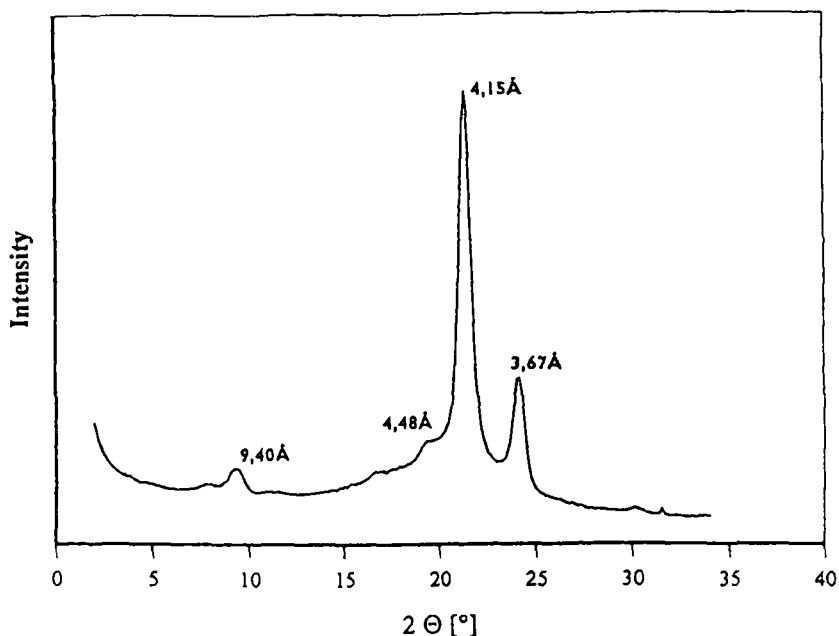
FIG. 4.   WAXS powder pattern of poly(decamethylene carbonate).

(No. 3, Table 1) has a crystallinity below 50% despite long annealing at 40°C. In the case of linear polyethylene, the degree of crystallinity may be as high as 60–70%.

$$HO-(CH_2)_{10}-CH + OC(OC_2H_5)_2 \xrightarrow[-2EtOH]{K_2CO_3}$$

$$H\left[O-(CH_2)_{10}-O-CO\right]_x H \qquad (1)$$

$$\Delta T$$

(2)
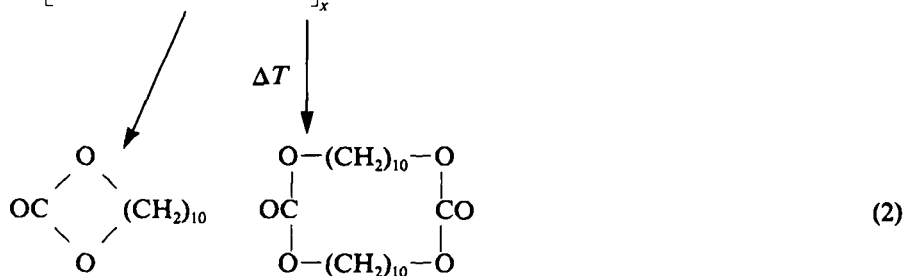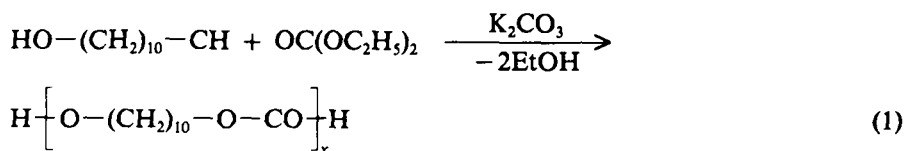
Polymerizations

Quite analogous to previous studies of other aliphatic cyclocarbonates (4, 5, 10–13], all polymerizations of c(DMC)$_2$ were conducted in bulk. nBuSnCl$_3$ was used as initiator (Tables 1 and 2) or SnOct$_2$ (Tables 3 and 4). The polymerizations were conducted in bulk not only for a better comparability with previous studies but also because nBuSnCl$_3$- or SnOct$_2$-initiated polymerizations of c(DMC)$_2$ and other

aliphatic cyclocarbonates in solution (e.g., in tolune $\leq 100°C$) are far too slow for preparative purposes. Even in bulk a reaction temperature of 120°C and reaction times ≥ 20 hours are required to reach a quantitative conversion.

In a first series of polymerizations the monomer/initiation ratio was fixed at 200/1, and the reaction time was varied. The data summarized in Table 1 demonstrate that the yield (and conversion) reaches its maximum at reaction times ≥ 20 hours and also the viscosities pass a maximum at 20 hours. In addition to these nBuSnCl$_3$-initiated polymerizations, a blind test with c(DMC)$_2$ free of initiator was conducted, which proved that the neat monomer is stable under these reaction conditions. Similar results were obtained with all other dimeric cyclocarbonates studied so far [11, 13]. Yet monomeric aliphatic cyclocarbonates, such as cyclo(trimethylene carbonate) or cyclo(tetramethylene carbonate), may be unstable upon heating above 100°C and undergo spontaneous polymerizations which may yield high molecular weight polycarbonates. The rapid polymerization of the crude monomeric cDMC upon attempted distillation in vacuo suggests that this monomer is also capable of spontaneous thermal polymerization.

A second series of polymerizations was conducted in such way that the reaction time was fixed at 20 hours and the M/I ratio was varied (Table 2). An almost quantitative conversion with yield around 97-98% was obtained for M/I = 50-300. At higher M/Is the reaction time is obviously not long enough to reach quantitative conversions. In contrast to the yields, the inherent viscosities increased with higher M/I ratios and passed a maximum at M/I = 300.

Two analogous series of polymerization were conducted with SnOct$_2$ as initiator. When the reaction time was varied with a M/I ratio fixed at 200/1 (Table 3), the highest yield and the highest viscosity were again obtained at a time of 20 hours. Variation of the M/I ratio at a fixed reaction time of 20 hours (Table 4) again gave constant yields for M/I = 50-300, whereas the viscosity passed through a maximum at M/I = 300. In the case of SnOct$_2$ it was also obvious that M/I ratios above 300 require longer reaction times. Characteristic differences observed for nBuSnCl$_3$-initiated polymerizations, on the one hand, and SnOct$_2$-initiated ones, on the other hand, are the somewhat lower yields and molecular weights resulting from initiation with SnOct$_2$. The same trends were found for all dimeric cyclocarbonates

TABLE 1. BuSnCl$_3$-Initiated Polymerizations
of (DMC)$_2$ in Bulk at 120°C (M/I = 200/1)
with Variation

Polymerization	Time, hours	Yield, %	η_{inh},[a] dL/g
1	4	68	0.35
2	8	92	0.83
3	20	96	0.91
4	48	97	0.74
5[a]	48[a]	0[b]	—

[a]Measured at 20°C with c = 2 g/L in CH$_2$Cl$_2$.
[b]Blind test without initiator.

TABLE 2.   BuSnCl₃-Initiated Polymerizations of (DMC)₂ in Bulk at 120°C/20 hours with Variation of the M/I Ratio

Polymerization	Monomer Initiator	Yield, %	η_{inh},[a] dL/g
1	50	97	0.51
2	100	98	0.72
3	200	97	0.90
4	300	97	1.02
5	500	71	0.81
6	800	46	0.36
7	1200	13	—

[a]Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

TABLE 3.   SnOct₂-Initiated Polymerizations of (DMC)₂ in Bulk at 120°C (M/I = 200/1) with Variation of the Time

Polymerization	Time, hours	Yield, %	η_{inh},[a] dL/g
1	4	56	0.28
2	8	88	0.44
3	20	94	0.69
4	48	91	0.35
5	72	85	0.28

[a]Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

TABLE 4.   SnOct-Initiated Polymerizations of (DMC)₂ in Bulk at 120°C/20 hours with Variation of the M/I Ratio

Polymerization	Monomer Initiator	Yield, %	η_{inh},[a] dL/g
1	50	94	0.46
2	100	94	0.56
3	200	93	0.67
4	300	93	0.71
5	500	85	0.52
6	800	43	0.34
7	1200	0	—

[a]Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

studied so far, namely: cyclobis(tetramethylene-) [11], cyclobis(hexamethylene-) [12], and cyclobis(octamethylene carbonate) [13]. Therefore, these trends may now be considered to be well reproducible and characteristic for the Sn initiators under investigation. The slightly lower molecular weights obtained in most polymerizations initiated by $SnOct_2$ are at least partially a consequence of stoichiometric reactions of the initiator with the cyclocarbonates. As demonstrated several times in previous publications of this series [10–13], $SnOct_2$ reacts with cyclocarbonates in such a way that the octoate groups are incorporated into the polycarbonate chain in the form of ester endgroups (Eqs. 3–6). Also in the case of $(DMC)_2$, octoate endgroups were detected before and after reprecipitation from methanol. Furthermore, $\sim CH_2-OH$ endgroups were found, in good agreement with the reaction scheme outlined in Eqs. (3–6).

OctO—Sn—OOct

$$\longrightarrow \quad OctO-Sn-O-(CH_2)_{10}-O-CO-O-OOct \quad (3)$$

$$-CO_2 \qquad (4)$$

$$OctO-Sn-O-(CH_2)_{10}-O-OOct$$

$$+n(DMC)_2 \qquad (5)$$

$$OctO-Sn-O-(CH_2)_{10}\left[O-(CH_2)_{10}-O-CO\right]_n OOCt$$

$$(+CH_3OH) \qquad (6)$$

$$HO-(CH_2)_{10}-O\left[(CH_2)_{10}-O-CO\right]_n OOct$$

In order to obtain at least a crude idea of the maximum molecular weight obtained in the present study, the sample with the highest viscosity value (No. 4, Table 1) was subjected to GPC measurements in tetrahydrofuran. The GPC curve was evaluated with the K and a values of the Mark–Houwink equation (7) published for polystyrene in tetrahydrofuran. In this way a number-average molecular weight of 50,000, a weight-average molecular weight of 88,000, and correspondingly a polydispersity of 1.77 was obtained.

$$[\eta] = 1.25 \times 10^{-4} M_w^{0.717} \qquad (7)$$

Thermal Properties of PolyDMC

The polyDMC with the highest molecular weight was examined by DSC measurements with a heating rate of 20°C/min. A glass-transition temperature (T_g) of −41°C was found which is, as expected, close to that of poly(octamethylene car-

bonate) ($-44\,^{\circ}C$) [12] and poly(hexamethylene carbonate) ($-42\,^{\circ}C$) [13]. Due to the higher concentration of polar groups (per unit volume), poly(tetramethylene carbonate) obviously has a somewhat higher T_g of $-27\,^{\circ}C$ [11]. Owing to the relatively rapid crystallization of polyDMC (see below), the T_g step was only detectable after quenching a sample from its melt at $90\,^{\circ}C$. The low T_g of polyDMC has the consequence that storage at room temperature has an annealing effect. The heating trace of the sample stored at room temperature displayed a melting endotherm at $67\,^{\circ}C$ (Fig. 5), with a good reproducibility in the second heating curve. In order to obtain a crude idea about the rate of crystallization, four cooling curves were recorded with a variation of the cooling rate. When compared to other unsubstituted aliphatic polycarbonates, a relatively weak supercooling effect of the crystallization was found. In other words, an increasing number of CH_2 groups in the repeating unit enhances the flexibility of the chain and increases the rate of crystallization.

Finally, the thermal stability of polyDMC was studied by thermogravimetric analyses conducted either in an atmosphere of nitrogen or oxygen. The results obtained at a heating rate of $3\,^{\circ}C$ under nitrogen are illustrated in Fig. 6. The maximum rate of degradation was found at $350\,^{\circ}C$. However, in contrast to poly(tetramethylene carbonate) [11] or poly(hexamethylene carbonate) [12], the thermal degradation of polyDMC involves two steps. On-line analyses of the volatile degradation products by mass spectroscopy (limited to masses below 200 g/mol) revealed
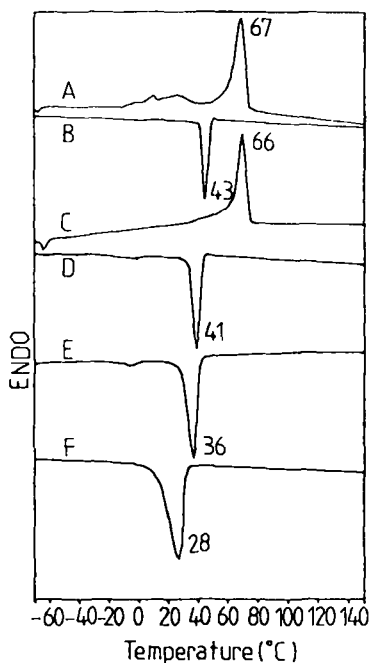

FIG. 5. DSC measurements of polyDMC, No. 3, Table 1. (A) 1st heating (rate $+$ $20\,^{\circ}C/min$); (B) 1st cooling ($-10\,^{\circ}C/min$); (C) 2nd heating ($20\,^{\circ}C/min$); (D) 2nd cooling ($-20\,^{\circ}C/min$); (E) 3rd cooling ($-40\,^{\circ}C/min$); (F) 4th cooling ($-80\,^{\circ}C/min$).
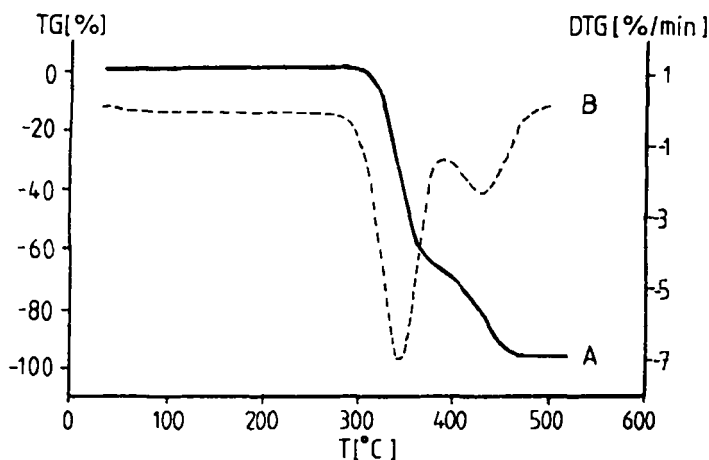
FIG. 6.   Thermogravimetric analysis (and differential thermal analysis) of polyDMC, No. 3, Table 1.

the evolution of CO_2 as the main degradation product in the temperature range of 300 to 360°C. Interestingly, no monomeric cycloDMC was found. TGA measurements in O_2 revealed an uptake of O_2 above 200°C and the formation of H_2O and CO_2 as the main degradation products up to 400°C where the oxidative degradation was almost complete.

CONCLUSIONS

The thermal degradation of low molecular weights polyDMC in a good vacuum and in the absence of a catalyst yields monomeric and dimeric cycloDMC as volatile degradation products in significant amounts. The higher melting point, higher chemical stability, and lower solubility allow an easier isolation of $(DMC)_2$. $(DMC)_2$ is an interesting monomer which may give high molecular weight polyDMC in high yield upon $BuSnCl_3$-initated polymerization in bulk. $SnOct_2$ proved to be a somewhat less efficient initiator. High molecular weight polyDMC is a rapidly crystallizing polymer which undergoes rapid thermal degradation above 300°C under a normal pressure of nitrogen, but it is sensitive to oxidation by O_2 above 200°C.

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