Cyclic and Noncyclic Polycarbonates of Isosorbide (1,4:3,6-Dianhydro-D-glucitol)

Saber Chatti,[†] Gert Schwarz,[‡] and Hans R. Kricheldorf*,[‡]

Institut National de Recherche et d'Analyse Physico-Chimique (INRAP), Pôle Technologique Sidi Thabet, 2020 Sidi Thabet, Tunisia, and Institut für Technische und Makromolekulare Chemie der Universität, Bundesstrasse 45, D-20146 Hamburg, Germany

Received March 17, 2006; Revised Manuscript Received October 30, 2006

ABSTRACT: Three different synthetic methods were studied with respect to their usefulness for the preparation of poly(isosorbide carbonate) (PIC). Thermal polycondensations of isosorbide with dimethyl- or diethyl carbonate in bulk proved unsuccessful, regardless of the transesterification catalyst. Polycondensations of isosorbide with diphosgene in pyridine gave polycarbonates, the molecular weights of which depended largely on the excess of diphosgene. In all experiments, OH-terminated linear chains were the main products. Similar results were obtained from pyridine-promoted phosgenations in dioxane. However, polycondensations of equimolar mixtures of isosorbide and isomannide mainly yielded cyclic polymers. Pyridine-promoted polycondensations of isosorbide with isosorbide bischloroformate only gave low molar mass polycarbonates. At low temperatures, even-numbered linear chains were the main products, but higher temperatures gave even-numbered cycles. SEC measurements with triple detection evidenced the formation of high molar mass polycarbonates in the phosgenation experiments and a Mark−Houwink equation was elaborated. The glass transition temperatures varied between 115 and 165 °C depending on the molar mass.

Introduction

Isosorbide is technically produced from glucose in large quantities. It is thus one of the few difunctional building blocks that is not based on oil or coal chemistry. Therefore, numerous polyesters and polycarbonates containing isosorbide were prepared and characterized by several research groups[1−10] (mainly summarized in the review article of ref 1). A first attempt to prepare the homopolycarbonates of isosorbide and isomannide (1,4:3,6-dianydro-D-mannitol) was reported in a patent of Courtaulds Ltd.[11] This approach was based on the transesterification and polycondensation of isosorbide with diphenylcarbonate or on the polycondensation of the bisphenylcarbonates of the "sugar diols". Yet, it was demonstrated in a later patent of Bayer AG[12] that, due to the high reaction temperatures (220 °C or higher), only colored gels were obtained when neat isosorbide or isomannide were used as monomers. In the same patent, it was also demonstrated that interfacial (co)-polycondensations of isosorbide are unsuccessful because its solubility in water is too high and its acidity too low.

Successful syntheses of numerous copolycarbonates of isosorbide were achieved by interfacial polycondensations of isosorbide bischloroformate (IBC) with various diphenols.[10−13] Most of these copolycarbonates had a cholesteric liquid-crystalline character with interesting optical properties. Yet, the homopolycarbonate was not prepared in this way. A seemingly successful synthesis of poly(isosorbide carbonate) (PIC) was reported by Braun et al.[14] based on the polycondensation of isosorbide with diphosgene in pyridine. However, those authors did not explain why a 40% excess of diphosgene was needed, and neither yields nor viscosity data nor elemental analyses nor a spectroscopic characterization was provided. In this context, it was the purpose of the present work to study syntheses and properties of poly(isosorbide carbonate) in more detail.

Experimental Section

Materials. Isosorbide was purchased from ACROS Chemicals (Gel, Belgium), crystallized from acetone, and dried over P_4O_{10} in vacuo. Isomannide (Aldrich Co., Milwaukee, WI) was used as received but dried over P_4O_{10}. Diphosgene was purchased from Lancaster Clariant (Mühlheim-Main, Germany) and used as received. Dimethyl carbonate, diethyl carbonate, potassium *tert*-butoxide, tin(II)2-ethylhexanoate ($SnOct_2$), and titanium tetrabutoxide were all purchased from Aldrich Co. (Milwaukee, WI) and used as received. Dioxane was refluxed and distilled over sodium. Pyridine was refluxed and distilled over freshly powdered calcium hydride. Dichloromethane was refluxed and distilled over P_4O_{10}.

Polycondensations of Isosorbide. (1) With dialkyl carbonates, isosorbide (50 mmol), dimethyl carbonate, or diethyl carbonate (200 mmol) and KOtBu (0.25 mmol) were weighed into a cyclindrical glass reactor equipped with a mechanical glass stirrer, gas-inlet, and gas-outlet tubes. The reactor was placed into an oil bath preheated to 100 °C, and after 0.5 h, the temperature was raised to 200 °C in steps of 20 °C/0.5 h. Stirring to 200 °C was continued for 2 h, whereby part of the dialkylcarbonate distilled off. After cooling, the reaction mixture was diluted with toluene, and the insoluble powder was filtered off and identified as unreacted isosorbide. Analogous experiments were conducted with $SnOct_2$ or $Ti(OBu)_4$ as catalysts. (2) With diphosgene in pyridine (Table 2), isosorbide (20 mmol) was dissolved in dry pyridine (20 mL), and triethylamine (0.05 mL) was added. A solution of diphosgene (10 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise with cooling so that the temperature did not exceed 10 °C. After stirring for 24 h at 20 °C, the reaction mixture was poured into methanol, and the precipitated polycarbonate was isolated by filtration. (3) With diphosgene in dioxane (Table 3), isosorbide (20 mmol) and diphosgene (10 mmol) were dissolved in dry dioxane (20 mL), and a solution of pyridine (50 mmol) in dioxane (5 mL) was added dropwise. After stirring for 24 h at 20 °C, the reaction mixture was poured into methanol. Analogous experiments were conducted with a slight excess of diphosgene.

Copolycondensation of Isosorbide and Isomannide (Table 4). Isosorbide (20 mmol), isomannide (20 mmol). and diphosgene (20 mmol) were dissolved in dry dioxane (40 mL), and a solution of pyridine (100 mmol) in dioxane (10 mL) was added dropwise. After stirring for 24 h at 20 °C, the reaction mixture was poured into

---

* Corresponding author. E-mail: kricheld@chemie.uni-hamburg.de.

[†] Institut National de Recherche et d'Analyse Physico-Chimique (INRAP).

[‡] Institut für Technische und Makromolekulare Chemie der Universität.

10.1021/ma0606051 CCC: $33.50

Table 1. Masses of K-Doped PIC Species Labeled According to Scheme 1

Pn	C	**La**	**Lb**	**Lc**
5	899.8	1045.95	932.0	990.0
6	1071.96	1218.09	1104.16	1162.16
7	1244.12	1390.23	1276.32	1334.32
8	1416.28	1562.37	1448.48	1506.48
9	1588.44	1734.51	1620.64	1678.64
10	1760.6	1906.65	1792.8	1850.8
11	1932.76	2078.79	1964.96	2022.96
12	2104.92	2250.93	2137.12	2195.12
13	2277.08	2423.07	2309.28	2367.28
14	2449.24	2595.21	2481.44	2539.44
15	2621.4	2767.35	2653.6	2711.6
16	2793.56	2939.49	2825.76	2883.76
17	2965.72	3111.63	2997.92	3055.92
18	3137.88	3283.77	3170.08	3228.08
19	3310.04	3455.91	3342.24	3400.24
20	3482.2	3628.05	3514.4	3572.4

Table 2. Polycondensations of Isosorbide with Diphosgene in Pyridine

expt no.	excess of diphosgene (mol %)	yield (%)	η_{inh}^a (dL/g)	T_g^b (°C)	M_n^c	PD^c
1	0	73	0.11	117.0	4500	1.7
2	10	93	0.37^c	155.5	13 500	2.6
3	20	96	0.80	163.5	$50\ 000^d$	7.0^d
4	40	87	0.18	140.0	7500	2.0
5	60	83	0.13	125.0	6000	1.8

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] DSC measurements with a heating rate of 10 °C/min. [c] SEC measurements in dimethyl acetamide (0.05 M LiCl). [d] Bimodal distribution with ~70 wt % of high molar mass material.

Table 3. Polycondensations of Isosorbide with Diphosgene in Dioxane

expt no.	excess of diphosgene (mol %)	yield (%)	η_{inh}^a (dL/g)	T_g^b (°C)	M_n^c	PD^c
1	0	93	0.62	141.0	27 000	3.0
2	5	90	0.78	146.0	30 000	3.1
3	10	95	0.57	140.0	25 000	2.8
4	15	86	0.22	128.0	4000	8.0
5	20	88	0.08	115.0	3000	2.5

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] DSC measurements with a heating rate of 10 °C/min. [c] SEC measurements in dimethyl acetamide (0.05 M LiCl).

Table 4. Polycondensations of Isosorbide and Isomannide (1:1) by Means of Diphosgene and Pyridine

expt no.	excess of diphosgene (mol %)	yield (%)	η_{inh}^a (dL/g)	T_g (°C)
1	0	90	0.28	165
2	2	91	0.25	163
3	5	81	0.17	

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

methanol, and the precipitated copolymer was isolated by filtration.

Polycondensation of Isosorbide Bischloroformate (Table 5). Isosorbide (10 mmol) and isosorbide bischloroformate (10.1 mmol) were dissolved in a mixture of dioxane (20 mL) and dichloromethane (15 mL), and pyridine (25 mmol) diluted with dichloromethane (5 mL) was added dropwise. Temperature and time were varied according to the values listed in Table 5. Finally, the reaction mixture was concentrated to approximately 50% of its original volume and poured into methanol.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MH ^1H NMR spectra and the 100.4 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer in 5 mm o.d. sample tubes. Chloroform-containing TMS served as solvent (and shift reference). The MALDI-TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions using dithranol as matrix and K-trifluoroacetate as dopant. The masses of the various reaction products found in the mass spectra were listed in Table 1. The DSC measurements were performed with a Mettler Toledo MD 821 in aluminum pans under nitrogen at a heating rate of 10 °C/min. The SEC measurements were performed on a Knaur apparatus equipped with a RT detector and PSS Wing PC software. Three GRAM columns of PSS were used at −50 °C with a flow rate of 1 mL/min. A 0.05 M solution of LiCl in DMAC served as eluent.

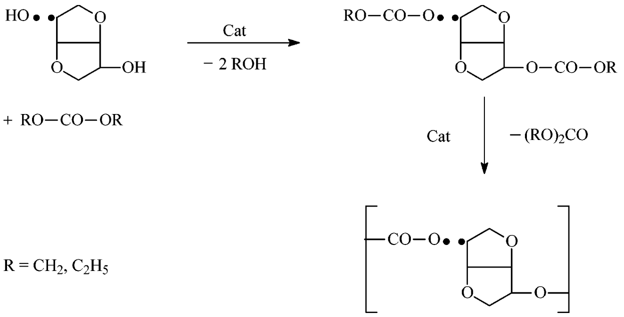
Table 5. Polycondensations of Isosorbide with Isosorbide Bischloroformate (IBC)

expt no.	excess of diphosgene (mol %)	temp (°C)	time (d)	yield (%)	η_{inh}^a (dL/g)
1	1	−10	7	27	0.12
2	1	−20	2	53	0.17
3	1	20	7	63	0.14
4	1	70	7	27	0.11
5	2	70	7	14	0.12
6	4	70	7	11	0.12

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

Results and Discussion

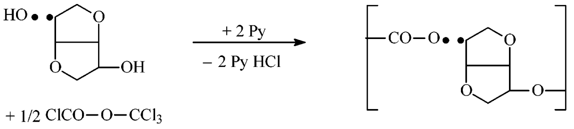
Polycondensations with Dialkylcarbonates. As reported in a patent of Bayer AG, polycondensations of isosorbide with diphenyl carbonate were unsuccessful because the high temperatures caused an intensive side reaction, resulting in a brown color and crosslinking. Therefore, it seemed to be promising to modify this approach by using dialkyl carbonates at lower temperatures (eqs 1 and 2). For instance, transesterifications and polycondensations of oligo(ethylene glycol)s with dimethyl carbonates were described in several patents and papers (although without isolation of the resulting polycarbonates). In this work, isosorbide was mixed with a fourfold excess of dimethyl or diethyl carbonate, and KOtBu, $SnOct_2$, or $Ti(OBu)_4$ were added as catalyst. These reaction mixtures were refluxed for 6 h, but unreacted isosorbide was recovered from all six experiments and no polycarbonate was obtained.



(1)

(2)

Polycondensations with Diphosgene in Pyridine. A first small series of polycondensations was conducted according to the procedure given in the literature (eq 3). Diphosgene was



(3)

added dropwise to a cooled solution of isosorbide in pyridine,

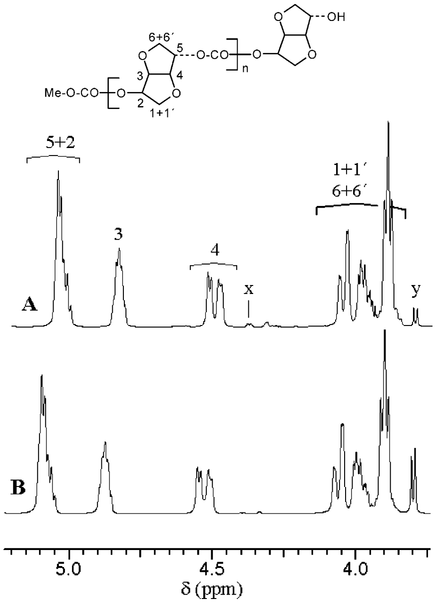


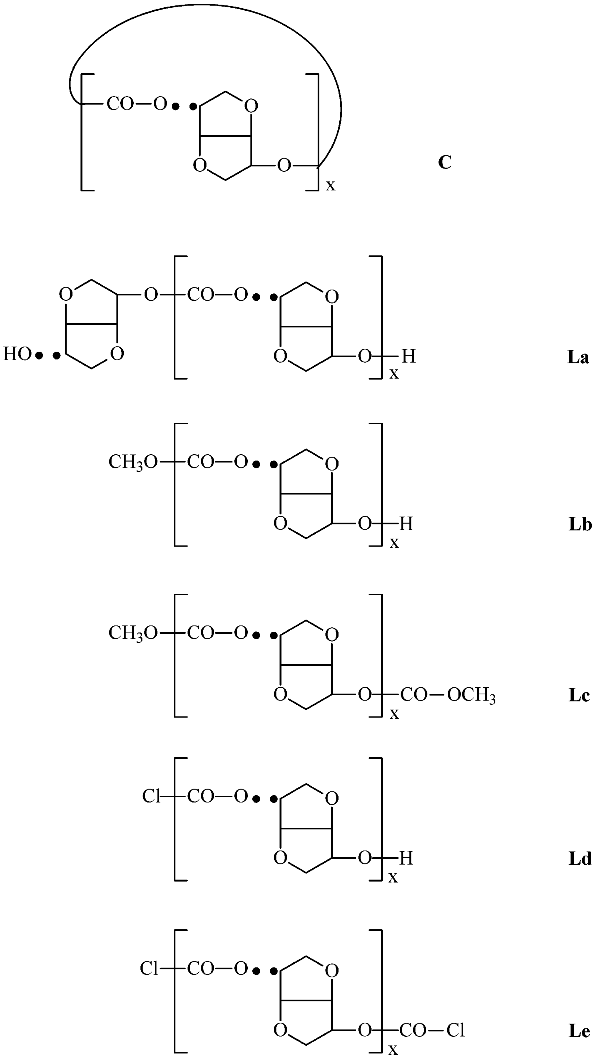
Figure 1. ^{1}H NMR spectra (400 MHz) of PICs prepared with diphosgene in dioxane: (A) no excess of diphosgene (no. 1, Table 3), (B) 15 mol % excess of diphosgene (no. 4, Table 3).

and the feed ratio was varied. As indicated by the viscosity data (Table 2), the molecular weight increased with the excess of diphosgene up to 20 mol %. This finding justifies a large excess of diphosgene, but not the 40% used in the published procedure. However, it was also observed in a separate experiment that pyridine decomposes diphosgene, and this side reaction caused a brownish color of the polycarbonate, which intensified with higher feed ratios of diphosgene. In other words, the large excess of diphosgene, which is needed for optimization of the molecular weight, results from side reactions with pyridine. This finding is not quite new and agrees with similar observations made for syntheses of poly(bisphenol-A carbonate).[15]

The poly(isosorbide carbonate)s prepared in pyridine were characterized by ^{1}H and ^{13}C NMR spectroscopy and also by MALDI-TOF mass spectrometry with respect to their chemical structure. The ^{1}H NMR spectra did not reveal clearly detectable end group signals. Yet, two weak signals around 4.4 ppm were found (see x in Figure 1), which could not be assigned.

The ^{13}C NMR spectra displayed three CO signals having intensity ratios of 1:2:1. This signal pattern results from a random sequence of exo−endo, endo−exo, and exo−exo connected carbonate groups. The MALDI-TOF proved that the main reaction products were polycarbonate chains having two OH end groups (**La** in Scheme 1), as examplarily illustrated in Figure 2. The absence of cyclic polycarbonates in most samples is surprising. Only in the PIC with the highest molar mass (no. 3, Table 2) were small peaks of cyclocarbonates clearly detectable. These results deviate from the theory of kinetically controlled polycondensations recently published by Kricheldorf et al.[16] This theory predicts that cyclization competes with chain growth at any concentration and at any stage of the polycondensation. Any optimization in the direction of higher molar masses favors cyclization. To shed more light on this problem to reduce decomposition of diphosgene by pyridine and to obtain results comparable with analogous polycondensations of bisphenol-A, a second series of polycondensations of isosorbide was performed in dioxane.

Scheme 1. Potential Reaction Products of Polycondensations of Isosorbide with Diphosgene (Lb and Lc After Precipitation into Methanol)



Polycondensations with Diphosgene in Dioxane. The second series of polycondensations was conducted in such a way that both isosorbide and diphosgene were dissolved in dioxane and a solution of pyridine was added dropwise. This procedure prevented that diphosgene was exposed to an excess of pyridine, which as reported recently,[17] decomposed diphosgene and chloroformate groups. As demonstrated by the results listed in Table 3, the viscosities passed again through a maximum when the excess of diphosgene was varied. However, this maximum was located between 0 and 5 mol % excess of

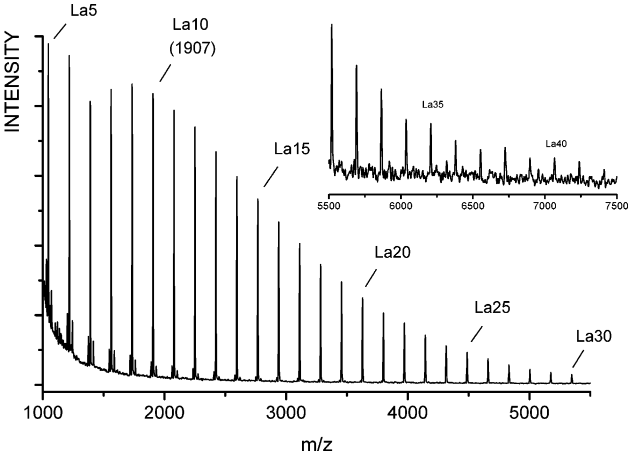


Figure 2. MALDI-TOF mass spectrum of PIC prepared in pyridine with 10 mol % excess of diphosgene (no. 2, Table 2).

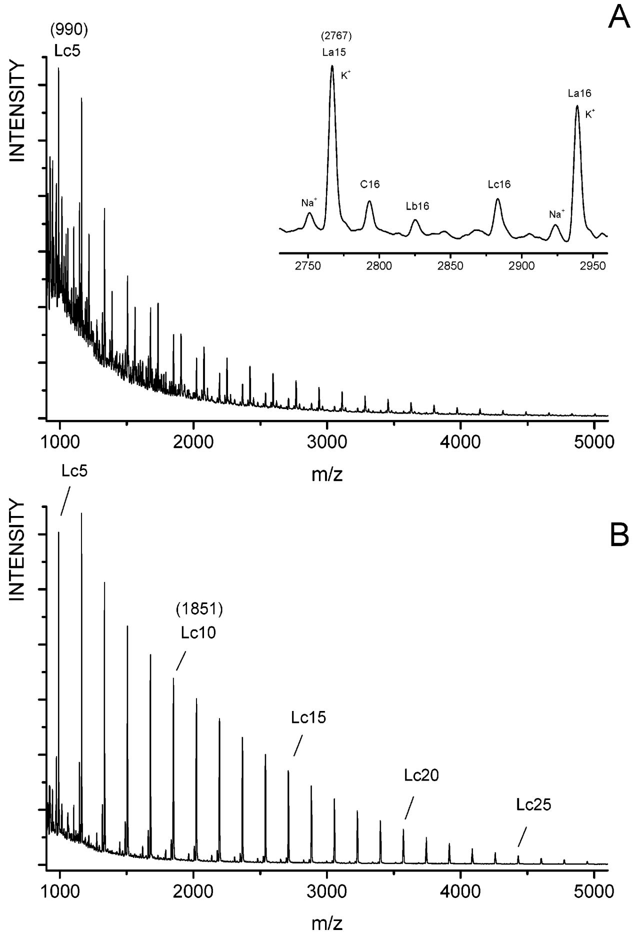


Figure 3. MALDI-TOF mass spectra of PIC prepared with diphosgene in dioxane: (A) 5 mol % excess of diphosgene (no. 2, Table 3), (B) 20 mol % excess of diphosgene (no. 5, Table 3).

diphosgene (in contrast to 20% in pyridine), indicating that the extent of side reactions was significantly reduced. The maximum of the molar mass over the variation of the feed ratio was broader than in the case of pyridine (Table 2), and the viscosity values suggest that the maximum molecular weight obtained in dioxane (no. 2, Table 3) was slightly lower.

The ^{1}H NMR spectra revealed two sharp signals around 3.8 ppm (labeled y in Figure 1), which by comparison with the ^{1}H NMR spectrum of dimethylcarbonate may be assigned to methylcarbonate end groups. The existence of two signals having somewhat different intensities may be ascribed to the exo−endo positions. This hypothesis is supported by the observation that the intensity of the methylcarbonate (y) signals increases when a larger excess of diphosgene was used and the average molecular weights decreased (Table 3).

The MALDI-TOF mass spectra confirmed this interpretation of the ^{1}H NMR spectra. With 0 or 5 mol % excess of diphosgene (nos. 1 and 2, Table 3), the OH-terminated **La** chains were the main reaction products. However, in the case of experiment no. 2, Table 3, strong peaks of **Lc** chains appeared below 2000 Da (Figure 3A). Furthermore, weak peaks of **Lb** chains and cyclic polycarbonates were detectable (insert of Figure 3A). With increasing excess of diphosgene, the peaks of **La** or **Lb** chains and the mass peaks of cycles faded away, as illustrated by Figure 3B. In the case of sample no. 5, the vast majority of the reaction product consisted of chains having two methyl carbonate end groups (**Lc**). When the number-average molecular weight (M_n) of this sample was calculated from the ^{1}H NMR end group signals (y) in Figure 1, a value of 2800 ± 1000 Da was obtained, which was in satisfactory agreement with the M_n of 3000 Da found by SEC (see below). The formation of methylcarbonate end groups is a consequence of the workup procedure. The **Lb** and **Lc** chains (Scheme 1) were formed upon precipitation of the virgin reaction mixture containing chains with chloroformate end groups (**Ld** and **Le**) into methanol. Therefore, this workup procedure allows for an indirect detection of chloroformate end groups that is not feasible when water is used for the precipitation of the polycarbonate. It is a characteristic difference between the polycondensations in pyridine and dioxane that, in the former case, only a few CH_3OCO end groups were formed, seemingly due to the decomposition of diphosgene by the excess of pyridine.

However, both series of polycondensations have in common that the formation of cyclic polycarbonates was suppressed relative to predictions of our theory[16] and relative to analogous polycondensations of bisphenol-A.[17] These polycondensations conducted at a somewhat lower concentration yielded cyclic polycarbonates of bisphenol-A with η_{inh} around 0.50−0.55 dL/g under optimized reaction conditions. The MALDI-TOF MS exclusively displayed peaks of cycles up to the technical limit of 6000 Da.[17] These findings suggested that PIC forms under the given reaction conditions a rather stiff and immobile conformation that hinders cyclization but not chain growth. A conformation that meets these requirements is a helical secondary structure. However, a helix structure is in conflict with several experimental findings. PIC is amorphous, as indicated by DSC measurements and wide-angle X-ray scattering. It is made up by a random sequence of exdo−endo, endo−exo, and exo−exo carbonate groups, as indicated by three CO peaks having intensity ratios of 1:2:1 in the ^{13}C NMR spectra. Moreover, the viscosity data and SEC measurements discussed below suggest a compact coil form in solution and not a rodlike form.

Co-condensations of Isosorbide and Isomannide. The assumption that PIC adopts in solution at temperatures ≤20 °C compact, immobile conformations hindering cyclization prompted us to synthesize copolymers with isomannide. Incorporation of comonomer into the PIC chain should somehow modify the special conformation and easy cyclization. Isomannide was selected as comonomer because a copolymer of isomeric repeat units looks like a homopolymer from the view point of MALDI-TOF mass spectrometry and thus facilitates the interpretation of the mass spectra. The three copolycondensations conducted with variation of the excess of diphosgene are compiled in Table 4. A first conspicuous result is the rather low viscosity values relative to the optimum experiments in Tables 1 and 2. Despite the lower molar masses, all three copolymers contained a significant fraction of cyclic polycarbonates. The maximum content of cycles was found for sample no. 2. Its mass spectrum is presented in Figure 4 and illustrates the tremendous difference between these copolycarbonates and the homo PICs, exemplarily characterized by the mass spectra of Figures 2 and 3A. Therefore, these results support the hypothesis that a disturbance of the special conformation of homo PIC improves its segmental mobility in such a way that efficient cyclization can take place in agreement with our theory of kinetically controlled polycondensations.

This interpretation is substantiated by further experiments. In a previous publication,[2] pyridine-promoted polycondensations of isosorbide and suberoyl chloride were described. The polyesters obtained under optimized reaction conditions exclusively displayed mass peaks of cycles in their MALDI-TOF spectra. Furthermore, random and alternating polycarbonates of

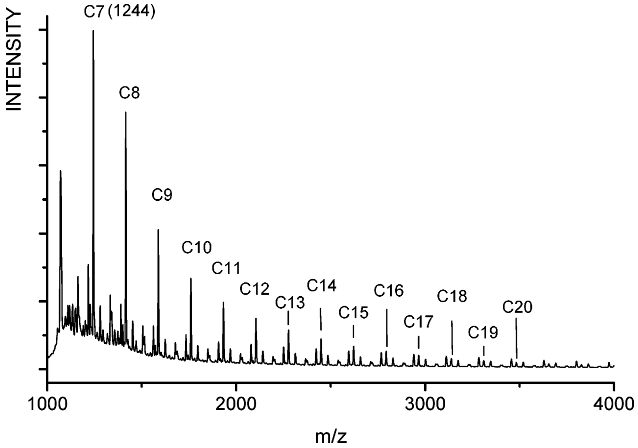
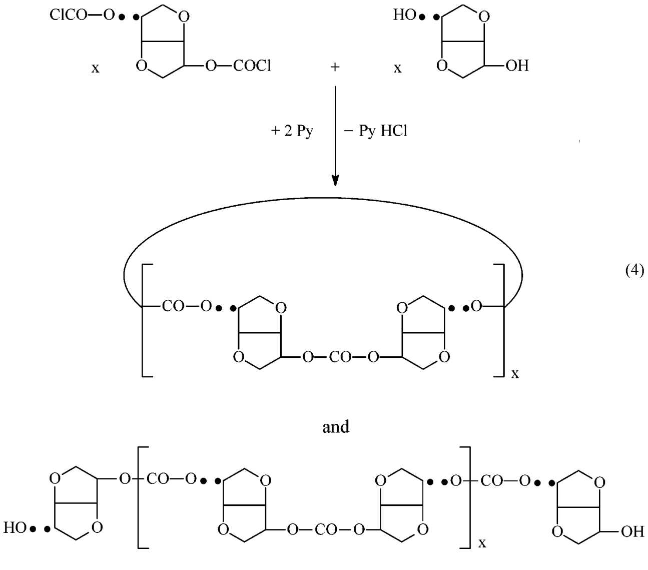


Figure 4. MALDI-TOF mass spectrum of a copolycarbonate prepared from an equimolar mixture of isosorbide and isomannide (no. 2, Table 4).

isosorbide and bisphenol-A were prepared by three different methods, as described in a recent publication.[18] Regardless of the synthetic method, all copolycarbonates prepared under optimized reaction conditions mainly consisted of cycles at least in the mass range below 7000 Da. Therefore, all results together clearly indicate that the syntheses of PICs listed in Tables 2 and 3 are exceptions with respect to the suppression of cyclization.

Polycondensations of Isosorbide and its Bischloroformate (IBC). A third approach to the preparation of PIC was studied in this work namely the polycondensation of isosorbide with its bischloroformate catalyzed by pyridine (eq 4). Dioxane served as a reaction medium, and the conditions were comparable to those of the experiments summarized in Table 3. Furthermore, the polycondensation of IBC should allow for a comparison with polycondensations of bisphenol-A and bisphenol-A bischloroformate (BABC), which were described in a recent paper.[15]



(4)

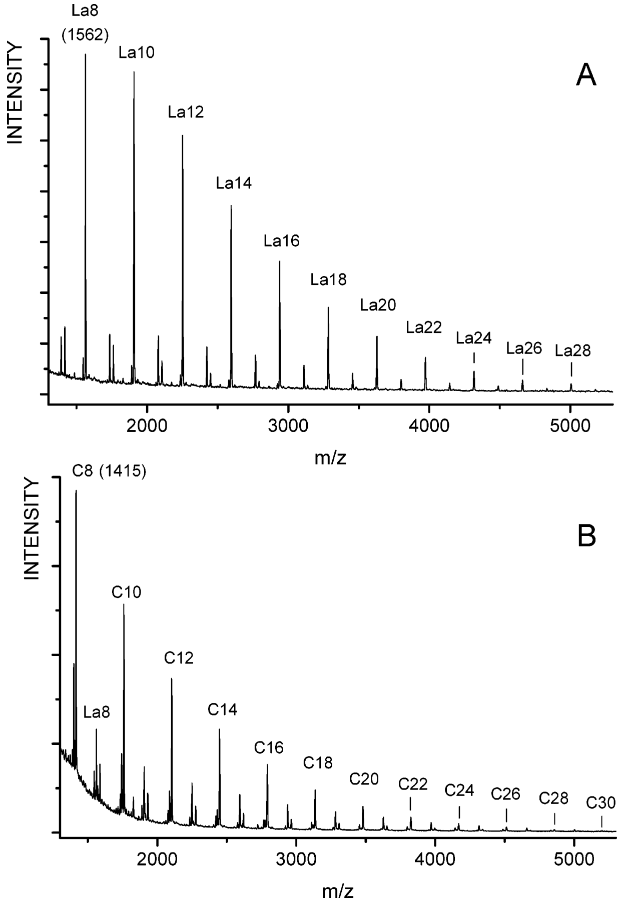


Figure 5. MALDI-TOF mass spectra of: (A) PIC prepared with IBC at −10 °C (no. 1, Table 5), (B) PIC with ICB at +70 °C (no. 5, Table 5).

A first series of three polycondensations were performed at 20 °C or below using 1 mol % excess of IBC (nos. 1−3, Table 5). Regardless of the reaction conditions, low molar masses were obtained in all three cases. The ^{1}H NMR spectra did not exhibit methyl carbonate end groups. In agreement with these NMR spectra, the MALDI-TOF mass spectra almost exclusively displayed peaks of OH-terminated **La** chains, as exemplarily documented in Figure 5A. However, these mass spectra also revealed an unexpected result because almost all **La** chains consisted of an even number of isosorbide, as demonstrated by a comparison of Figure 5A with Figures 2 and 3A and outlined in eq 4. In principle, predominant formation of OH-terminated chains can be explained by an excess of isosorbide (e.g., due to an incorrect feed ratio) or by a partial hydrolysis of IBC. Yet, both scenarios will have the consequence that equal numbers of odd- and even-chains are formed or that odd-numbered chains prevail. Therefore, the even-numbered **La** chains found in all three experiments of Table 5 definitely prove that a poor handling of the reactants, and their purification cannot be responsible for these results. At first glance, the polycondensations of nos. 1−3 suggest that isosorbide and IBC form a reactive dimer, which is in turn responsible for the further chain growth. This hypothesis needs, of course, a careful, more detailed investigation.

When the polycondensations were repeated at 70 °C to speed up the conversion and to reduce the selectivity for even-numbered chains, again the same low molar masses were obtained as those at low temperatures (nos. 4−6, Table 5). However, the MALDI-TOF mass spectra revealed a different peak pattern. Considerable amounts of cyclic polycarbonates were now found in all three samples, and the content of cycles increased with the excess of diphosgene. Figure 6B demonstrates that, with an excess of 2 mol % (no. 5), the cycles were the largely prevailing products in the mass range up to 5000 Da. Furthermore, the even-numbered cycles dominated largely over the odd-numbered ones. With an excess of 4 mol % diphosgene, the peaks of **La** chain were so small that even the weak peaks

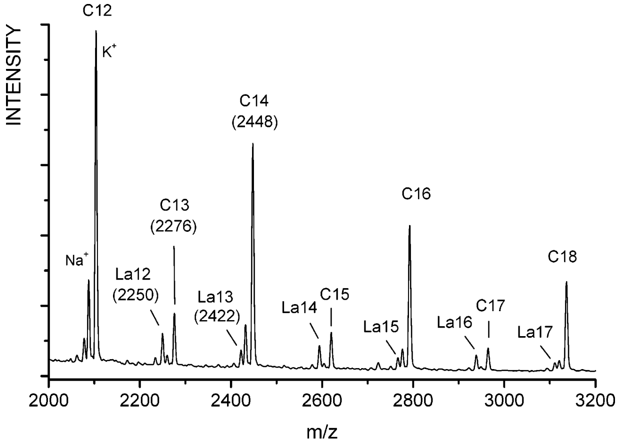


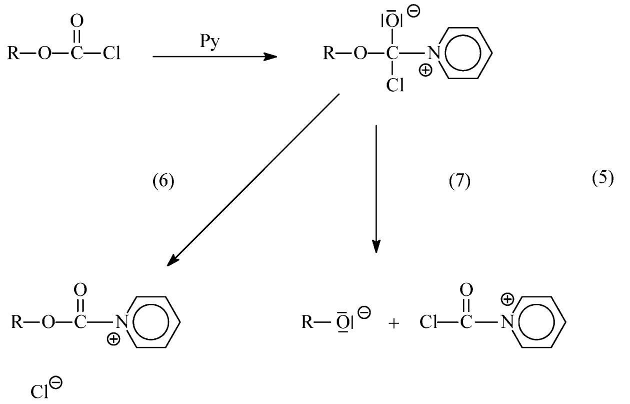
Figure 6. MALDI-TOF mass spectrum (section) of the PIC prepared with 4 mol % excess of IBC at 70 °C (no. 6, Table 5).

of the odd-numbered cycles were stronger (Figure 6). This observation means first that the conversion was rather close to completion and that the cyclization has played a key role for the limitation of the chain growth.

In contrast to the formation of even-numbered linear chains (nos. 1−3, Table 4), the formation of even-numbered cycles is a quite normal consequence of a clean polycondensation according to eq 4. Here, the question needs to be answered how the odd-numbered cycles were formed. When pyridine-promoted polycondensations of bisphenol-A and its bischloroformate (BABC) were conducted in dioxane, a similar result was obtained.[15] In addition to the prevailing even-numbered cycles, odd-numbered cycles were formed and their content was even higher than in the case of isosorbide. On the basis of the model reaction, it is concluded that pyridine reacts with chloroformates according to eqs 5−8. The primarily formed pyridinium complex (eq 5) can decompose in two ways. In addition to the predominant elimination of chloride ions (eq 6), phenoxide or alkoxide ions may liberated (eq 7), which in turn react with chloroformiates to yield carbonate groups (eq 8). Because

$$R-\overline{\underline{O}}|^{\ominus} + ClCO-OR \xrightarrow[-Cl^{\ominus}]{} R-O-CO-O-R \tag{8}$$

phenoxide ions are more stable than alkoxide ions, this side reaction is more likely in the case for bisphenol-A than for isosorbide. Therefore, this hypothesis provides a consistent explanation of all experimental observations.



SEC Measurements of PICs. Because all PICs samples prepared in this work were soluble in CH_2Cl_2, the first SEC measurements were conducted in this solvent and calibrated with polystyrene. Most samples yielded bimodal, and in two cases, even trimodal, molecular weight distributions (MWDs). Furthermore, for two samples (no. 2, Table 2 and no. 2, Table 3) weight-average molecular weights (M_ws) close to or above 10^6 Da were found. Furthermore, the shapes of the distribution curves strongly depend on the concentration. These results suggested that the elution curves were affected by aggregation phenomena, resulting from the high polarity of the repeat units (compared to poly(bisphenol-A) carbonate). Therefore, SEC measurements were repeated in dimethyl acetamide containing LiCl to suppress aggregation. All the molecular weight data listed in Tables 2 and 3 were obtained in this way. In this polar solvent, all PIC samples, with exception of no. 3, Table 2, yielded monomodal elution curves. Figure 7A provides an examplary illustration of a monomodal MWD, whereas Figure 7B displays the curve of no. 3, Table 2. These findings and the lower M_w values suggest that aggregation was indeed suppressed. Although calibration with polystyrene certainly did not provide accurate number-average (M_n) or M_w values, these SEC measurements yielded a couple of useful informations. First, high molar mass samples were indeed obtained despite the simple polycondensation procedure and despite side reactions of diphosgene with pyridine. Second, both narrow and broad MWDs were obtained without any systematic correlation to individual experimental parameters. The relatively low M_n of no. 3, Table 2, relative to the M_ns of samples nos. 2 and 3 of Table 3 is, of course, a consequence of the low molar mass fraction evident in the elution curve of Figure 7B. Third, the molar masses scatter over a broad range. This finding is in satisfactory agreement with the DSC measurements listed in Tables 2 and 3. The glass-transition temperatures (T_g's) also scatter over an unusually broad range from values around 115−117 °C to values around 165 °C. Such a broad range of T_g's can only be explained by a correspondingly broad range of the molar masses.

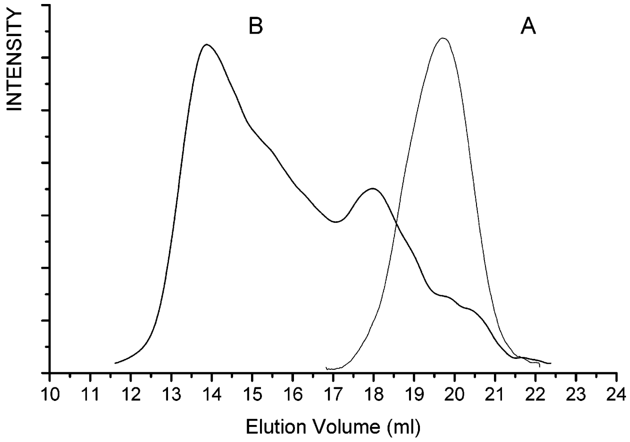


Figure 7. SEC elution curves of: (A) PIC, no. 1, Table 2, (B) PIC, no. 3, Table 2.

When compared to the Mark−Houwink equation (eq 9) of

$$[\eta] = 0.22 \times 10^{-4} . M_w^{0.76} \ (L/g) \tag{9}$$

poly(bisphenol-A carbonate)s dissolved in CH_2Cl_2,[19] the high molar mass samples of PICs possess relatively low solution viscosities. This finding has two consequences. First, it rules out that PICs form helices that behave as rigid rods in CH_2Cl_2 solution. Second, it suggests that PICs form dense coils, possibly involving intra- (and intermolecular) contacts between chain segments similar to the situation under ϑ conditions. Such dense coils reduce the mobility of the entire chain, whereas the chain ends may maintain a mobility comparable to that of monomers, as pointed out by Flory.[20] Because cyclization requires motions of the entire chain, this hypothesis may explain why the efficiency of cyclization is reduced but that of chain growth is not.

Conclusions

In the present work, three different synthetic methods designed to yield PIC were compared. A bundle of unexpected results were obtained that deviate largely from what has been observed for polycondensations of other aliphatic or aromatic diols under similar conditions. First, all attempts to prepare PIC by transesterification and polycondensation of isosorbide with dialkyl carbonates failed regardless which transesterification was used. Under the same conditions, α,ω-alkane diols or oligo(ethylene glycol)s yield polycarbonates of moderate molecular weight.[21−23] Second, pyridine-promoted polycondensations of isosorbide and diphosgene below 25 °C yielded high molar mass PIC almost free of cyclocarbonates. Under quite similar conditions, bisphenol-A yields polycarbonates of moderate molar mass that mainly consist of cycles. Predominantly, cyclic polycarbonates were also found when an equimolar mixture of isosorbide and isomannide or bisphenol-A was polycondensed with diphosgene. These findings suggest that PIC adopts below 25 °C a compact immobile conformation that hinders cyclization but not chain growth. Third, polycondensations of isosorbide with IBC below 25 °C yielded even-numbered linear **La** chains, whereas cyclic PIC was formed when the polycondensations were performed at 70 °C. In contrast, polycondensations of bisphenol-A and BABC yielded cyclic polycarbonates and odd-numbered linear chains (their ratio depends on the excess of BABC), even at low temperatures. A plausible explanation for the predominant formation of even-numbered linear chains cannot be offered at this time, and further studies on syntheses of homo- and copolycondensations of isosorbide and isomannide are in progress.

Acknowledgment. We thank Dr. A. Meyer (Bayer AG, Uerdingen, Germany) for financial support.

References and Notes

(1) Kricheldorf, H. R. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 599 and literature cited therein.

(2) Kricheldorf, H. R.; Chatti, S.; Schwarz, G.; Krüger, R.-P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3414.

(3) Adelman, D. J.; Charbonneau, L. F.; Ung. S. (Du Pont). U.S. Patent 6,656,577, 2003.

(4) Adelman, D. J.; Green, R. N.; Putzig, D. E. (Du Pont). U.S. Patent 0232960, 2003.

(5) Lin, Q.; Pasattie, J.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2512.

(6) Espinosa, M. A.; Cadiz, V.; Galia, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2847.

(7) Charbonneau, L. F.; Khanarian, G.; Johnson, R. E.; Witteler, H. B.; Flint, J. A. (Hna Holding, Inc.). U.S. Patent 6,063,495, 2000.

(8) Hayes, R. A. (Du Pont) U.S. Patent 6,368,710, 2000.

(9) Kricheldorf, H. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 568.

(10) Sun, S.; Schwarz, G.; Kricheldorf, H. R.; Chang, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1125.

(11) Collins, J. R. (Courtaulds, Ltd.). Br. Patent 1,079,686, 1987.

(12) Medem, H.; Schreckenberg, M.; Dhein, R.; Nouvestre, W.; Rudolph, H. (Bayer AG). German Patent DE 2938464, 1981.

(13) Kricheldorf, H. R.; Sun, S.-J.; Chen, C.-P.; Chang, T.-C. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1611.

(14) Braun, D.; Bergmann, M. *J. Prakt. Chem./Chem.-Ztg.* **1992**, *334*, 298.

(15) Kricheldorf, H. R.; Böhme, S.; Schwarz, G. *Macromolecules* **2006**, *39*, 3210.

(16) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.

(17) Kricheldorf, H. R.; Böhme, S.; Schwarz, G. *Macromol. Chem. Phys.* **2005**, *206*, 432.

(18) Chatti, S.; Kricheldorf, H. R.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3616.

(19) Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Schultz, C.-L. *Macromol. Chem. Rapid Commun.* **2002**, *23*, 803.

(20) Flory, P. *J. Chem. Rev.* **1946**, *39*, 137.

(21) Kricheldorf, H. R.; Mahler, A. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2399.

(22) Kricheldorf, H. R.; Mahler, A. *Polymer* **1996**, *37*, 4383.

(23) Kricheldorf, H. R.; Lossin, M.; Mahler, A. *Macromol. Chem. Phys.* **1997**, *138*, 3559.

MA0606051