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C o n t e n t s

Chapter 1

Polycondensation of isosorbide and various diols by means of
diphosgene characterization by a combination of MALDI and NMR
Moez A. Hani, Saber Chatti, Hans R. Kricheldorf and Hédi Zarrouk

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Polycondensation of isosorbide and various diols by means of diphosgene characterization by a combination of MALDI and NMR

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Abstract

Polycondensations of isosorbide with diphosgene in pyridine gave linear homopolycarbonates, the molecular weights of which depended largely on the excess of diphosgene. Similar results were obtained from pyridine-promoted phosgenations in dioxane. However, polycondensations of equimolar mixtures of isosorbide and isomannide or bisphenol A with

diphosgene in dioxane, mainly yielded cyclic copolycarbonates. The compositions were determined by ^1H NMR spectroscopy, the random sequences were characterized by ^{13}C NMR spectroscopy. The glass transition temperatures varied between $135\text{ }^\circ\text{C}$ and $163\text{ }^\circ\text{C}$ depending on the comonomers.

Introduction

Utilization and valorization of renewable carbon resources derivatives for polymers syntheses has been paid much attention because of the promising biodegradability and biocompatibility of the polymers from them [1-2].

Some of the most promising carbohydrates derivatives are 1,4:3,6-dihydrohexitols (Figure 1) that is 1,4:3,6-dihydro-D-glucitol (**1**) or isosorbide, 1,4:3,6-dihydro-D-mannitol (**2**) or isomannide, and 1,4:3,6-dihydro-L-iditol (**3**) or isoidide [3-4].

In particular, the former two compounds are available from D-glucose and D-mannose, respectively, by hydrogenation followed by acid-catalyzed intermolecular dehydration. These sugar-based stereoisomeric diols **1-3** represent highly useful diol components for the syntheses of various polymers such as polyethers [5-6], polyesters [7], polyurethanes [8-9], polyamides [10-11] and polycarbonates [12-14]. We have reported the syntheses of a variety of polymers based on sugar-based diols **1-3**.

As an extension of the series of our studies on polymers syntheses based on renewable resources, novel copolycarbonates containing isosorbide and isomannide or 4,4-isopropylidene diphenol (bisphenol A: **4**) as comonomers have been synthesized by polycondensation with diphosgene in a homogenous organic solution (Figure 2).

This work serves two purposes: *i*) to investigate if copolycondensations of isosorbide and isomannide or bisphenol A by means of diphosgene yield random copolycarbonates, and *ii*) to determine the formation of fraction of cyclic polycarbonates. The resulting copolycarbonates (**Copolycarb-1** and **Copolycarb-2**) were characterized by ^1H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. The glass transition temperatures (T_g) of copolycarbonates were determined by DSC measurements.

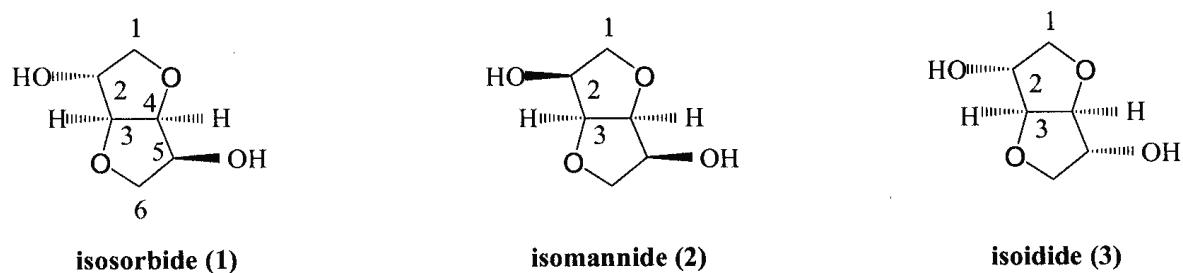


Figure 1. Chemical structures of 1,4:3,6-dihydrohexitols (**1-3**).

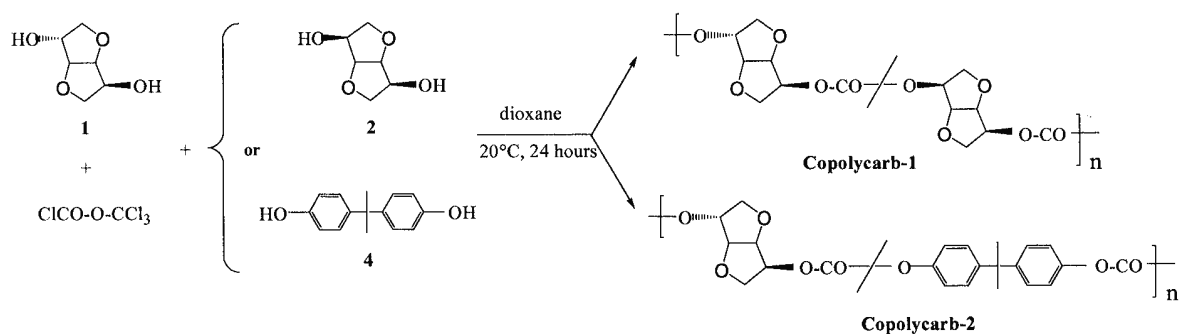


Figure 2. Polycondensation of isosorbide and diphsogene with isomannide (**Copolycarb-1**) or bisphenol A (**Copolycarb-2**) in dioxane at 20°C during 24 hours.

Results and discussion

1. Preliminary studies

The syntheses of isosorbide-homopolycarbonates (**IHC**) was reported by Braun et al. [11] based on the polycondensation of isosorbide with diphsogene in pyridine. However, those authors did not explain why a 40% excess of diphsogene was needed, and neither yields nor viscosity data, nor elemental analyses nor a spectroscopic characterization was provided. A first series of polycondensations was conducted according to the procedure given in the literature (Figure 3).

Diphsogene was added dropwise to a cooled solution of isosorbide in pyridine and the feed ratio was varied. The molecular weight increased with the excess of diphsogene up to 20 mol%. However, it was also observed in a separate experiment that pyridine decomposes diphsogene, and this side reaction caused a brownish color of the polycarbonate which intensified with higher feed ratios of diphsogene. In other words, the large excess of diphsogene which is needed for optimization of the molecular weight results from side reactions with pyridine. The MALDI-TOF [16-17] proved that the main reaction products were polycarbonate chains having two OH-endgroups (**La**).

Surprising is the absence of cyclic polycarbonates in most samples. Only in the IHC with the highest molar mass ($M_n = 50\,000$ g/mol) small peaks of cyclocarbonates were clearly detectable. These results deviate from the theory

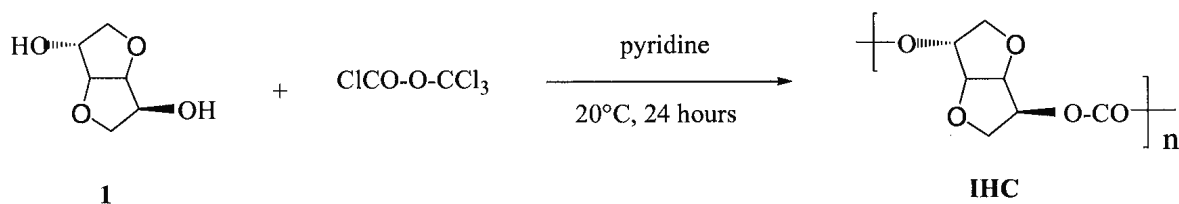


Figure 3. Polycondensation of isosorbide with diphsogene in *pyridine*.

of kinetically controlled polycondensations recently published by Kricheldorf *et al* [15]. This theory predicts that cyclization competes with chain growth at any concentration and at any stage of the polycondensation. Any optimization in direction of higher molar masses favours 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.

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 decomposed diphosgene and chloroformate groups. The viscosities passes through a maximum when the excess of diphosgene was varied. However, this maximum was located between 0 and 5 mol% excess of 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 and the viscosity values suggest that the maximum molecular weight obtained in dioxane ($M_n = 30\ 000\ \text{g/mol}$) was slightly lower.

The ^1H NMR spectra revealed two sharp signals around 3.8 ppm, which by comparison with the ^1H NMR spectrum of dimethylcarbonate, may be assigned to methylcarbonate endgroups (CH_3OCO -endgroups). 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 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 ^1H NMR spectra. With 0 or 5 mol% excess of diphosgene the OH-terminated **La** chains were the main reaction products. However, in the case of 5 mol% excess, strong peaks of **Lc** chains appeared below 2000 Da. Furthermore, weak peaks of **Lb** chains and cyclic polycarbonates (**C**) were detectable. With increasing excess of diphosgene the peaks of **La** or **Lb** chains and the mass peaks of cycles faded away. In the case of 20 mol% excess, the vast majority of the reaction product consisted of chains having two methyl carbonate endgroups (**Lc**) (Figure 4).

The formation of methylcarbonate endgroups is a consequence of the work-up procedure. The **Lb** and **Lc** chains (Scheme 1) are formed upon precipitation of the virgin reaction mixture containing chains with chloroformate endgroups into methanol. Therefore, this work-up procedure allows for an indirect detection of chloroformate endgroups which is not feasible when water is used for the precipitation of the polycarbonate. It is a characteristic difference between the polycondensations in pyridine and

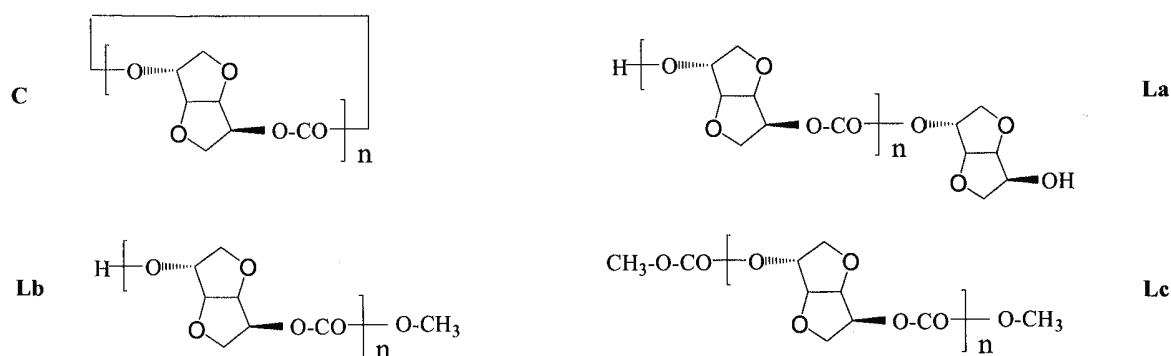


Figure 4. Reaction products of polycondensation of isosorbide and diphsogene in *dioxane*.

dioxane that in the former case only few CH_3OCO -endgroups were formed seemingly due to the decomposition of diphsogene 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 and relative to analogous polycondensations of bisphenol-A. These findings suggested that IHC forms under the given reaction conditions a rather stiff and immobile conformation which hinders cyclization but not chain growth. A conformation which meets these requirements is a helical secondary structure. However, a helix structure is in conflict with several experimental findings. IHC 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.

The assumption that IHC adopts in solution at temperatures $\leq 20^\circ\text{C}$ compact, immobile conformations hindering cyclization, prompted us to synthesize copolycarbonates with isomannide (2) or bisphenol A (3). Incorporation of comonomer into the IHC chain should somehow modify the special conformation and easy cyclization.

2. Copolycarbonates (Copolycarb-1) based on isosorbide and isomannide by means of diphsogene in dioxane

Isomannide was selected, at first, as comonomer, because a copolymer of isomeric repeat units looks like a homopolymer from the point of view of MALDI-TOF mass spectrometry, and thus, facilitates the interpretation of the mass spectra. The three copolycondensations conducted with variation of the excess of diphsogene in dioxane were compiled in Table 1.

All three copolymers contained significant fraction of cyclic polycarbonates. The maximum content of cycles was found for sample No. 2 [+ mol 2% excess of diphsogene] (Figure 5; Table 2).

Table 1. Polycondensation of isosorbide and isomannide by means of diphosgene in dioxane were compiled in Table 1.

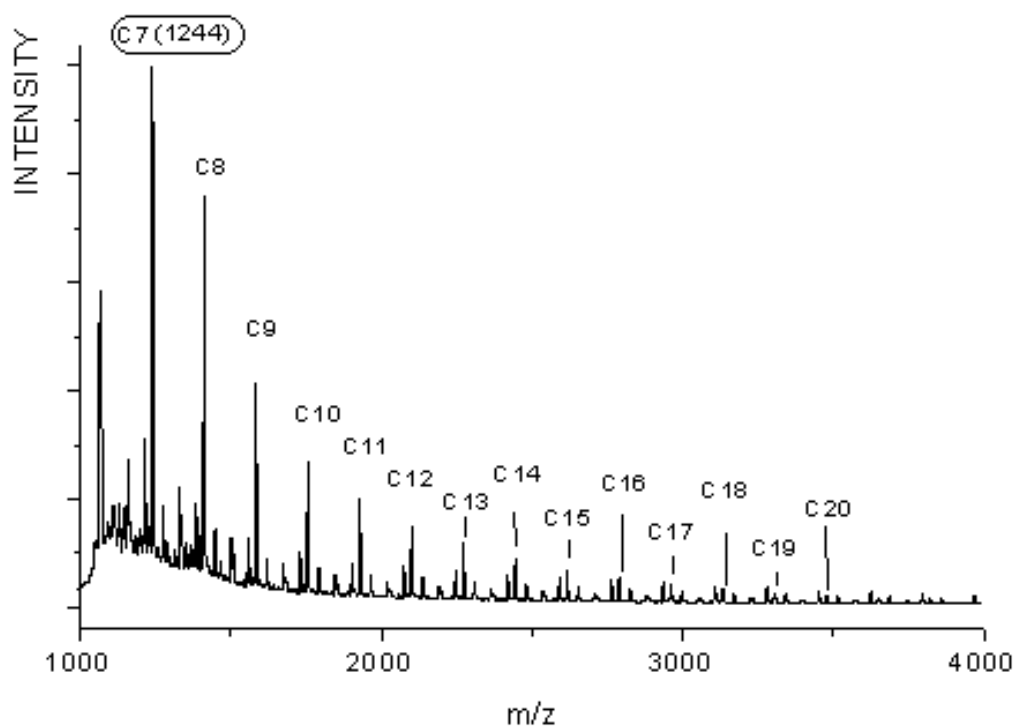
Expt No.	Excess of diphosgene (mol %)	Yields ^{a)} (%)	η_{inh} ^{b)} (dL/g)	Isosorbide/Isomannide ^{c)}	T g ^{d)} (°C)
1	0	89	0.28	1.0/1.03	165
2	2	91	0.24	1.0/1.07	161
3	5	81	0.17	1.0/1.1	103

a) Precipitation into methanol – 2 days in vacuum at 20 °C

b) Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2

c) Molar composition as determined by 1H NMR spectroscopy

d) Measured by DSC at a heating rate of 10 C/min

**Figure 5.** MALDI-TOF mass spectrum of a copolycarbonate prepared from an equimolar mixture of isosorbide and isomannide (No. 2, Table 1).**Table 2.** Masses (Including K⁺) of cyclic copolycarbonates (Copolycarb-1) detectable in the MALDI-TOF mass spectrum.

Pn	7	8	9	10	11	12	13
Cycle Copolycarb-1	1244.12	1416.28	1588.44	1760.6	1932.76	2104.92	2277.08
Pn	14	15	16	17	18	19	20
Cycle Copolycarb-1	2449.24	2621.4	2793.56	2965.72	3137.88	3310.04	3482.2

Its mass spectrum is presented in Figure 5 and illustrates the tremendous difference between these copolycarbonates (Copolycarb-1) and the IHC.

Therefore, these results support the hypothesis that a disturbance of the special conformation of homo IHC improves its segmental mobility in such a way that efficient cyclization can take place in agreement with our theory of kinetically controlled polycondensations.

3. Copolycarbonates (Copolycarb-2) based on isosorbide and bisphenol A by means of diposgene in dioxane

The optimum reaction conditions were now applied to copolycondensation of isosorbide with bisphenol A by means of diposgene (+2 mol% excess) (Table 3).

The chemical structure of the isolated copolycarbonate (Copolycarb-2) was characterized at first by ^1H and ^{13}C NMR spectroscopy.

i) A typical ^1H NMR spectrum is presented in Figure 6. The integration of individual signals of isosorbide and bisphenol A units allowed for the calculation of compositions which agreed largely with the 1:1 feed ratio (Table 3).

ii) The ^{13}C NMR spectra of the CO-signals provided information on the sequences. This spectrum (Figure 7) displays two new signals labeled Y which represent the “crossover steps” from isosorbide to bisphenol A. Due to the fact that one OH-group of isosorbide has an exo-position and the other one an endo-position two different carbonate groups are formed in combination with a symmetrical comonomer. The intensity of these “Y-signals” suggest that, as expected, random sequences were indeed formed.

iii) Finally, MALDI-TOF mass spectrum (m.s.) of copolycarbonate was recorded to elucidate, if and to what extent cyclic oligomers and polymers were formed [16-17].

The extent of cyclization indicates, if the reaction conditions were almost ideal or not, and if the conversions were high or low. This correlation is based

Table 3. Polycondensation of sorbide and bisphenol A by means of diposgene in dioxane at 20°C during 24 hours

Copolycarbonate	Yields ^{a)} (%)	η_{inh} ^{b)} (dL/g)	Isosorbide/ Isomannide ^{c)}	T g ^{d)} (°C)
Copolycarb-2	96	0.72	1.0/1.1	135

a) Precipitation into methanol – 2 days in vacuum at 20 °C

b) Measured at 20 °C with $c = 2 \text{ g/L}$ in CH_2Cl_2

c) Molar composition as determined by ^1H NMR spectroscopy

d) Measured by DSC at a heating rate of 10 C/min

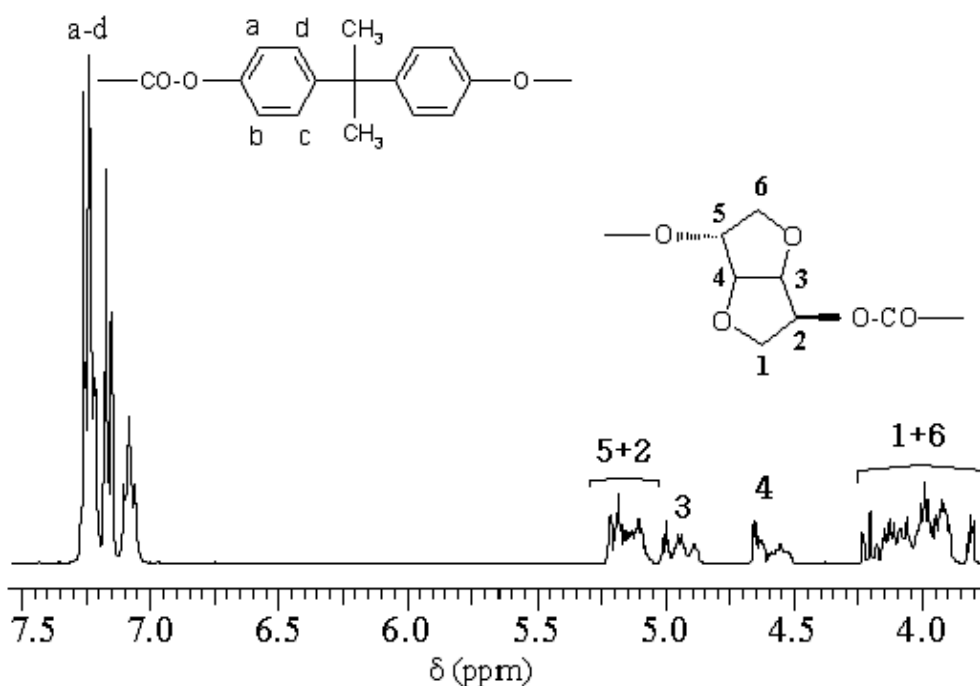


Figure 6. 400 MHz ^1H NMR spectrum of the copolycarbonate based on isosorbide and bisphenol-A (Copolycarb-2).

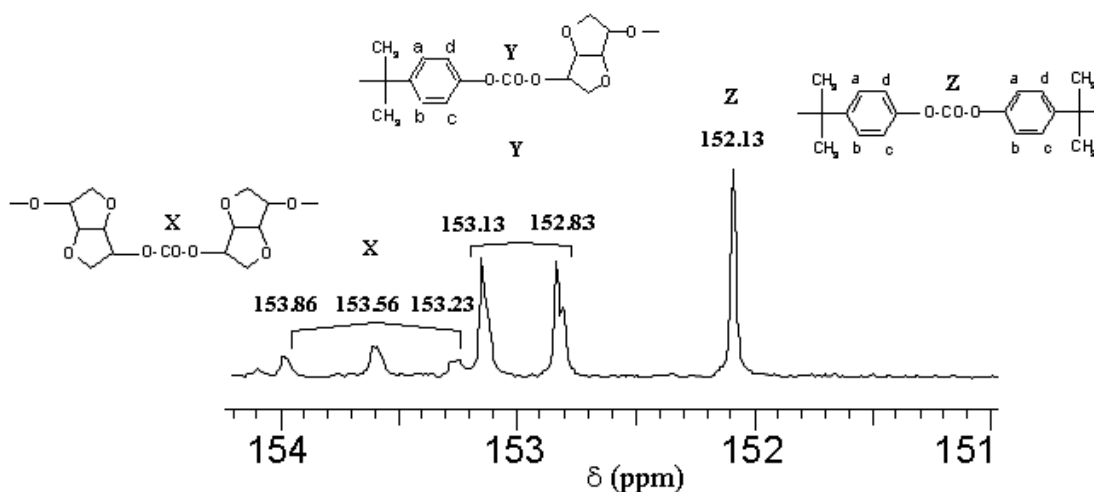


Figure 7. 100.4 MHz ^{13}C NMR spectrum of the CO-signals of random copolycarbonate based on isosorbide and bisphenol-A (Copolycarb-2).

on Kricheldorf's theory of kinetically controlled polycondensation (i.e. absence of any equilibration)¹⁵ which says that cyclization competes with chain growth at any concentration and at any stage of the polycondensation. When side reactions are absent the chain growth is limited by cyclization [15]. Therefore, a high extent of cyclization indicates that side reactions were almost absent, that the conversions were high (e.g. > 99.9%) and that the chain growth was mainly limited by cyclization and can only be improved by higher concentrations of the monomers.

The vast majority of the peaks, of Copolycarb-2, represented cycles consisting of all the numerous combinations of isosorbide and bisphenol A which may be expected from a random copolymerizations.

The assignments of individual peaks are illustrated in Figures 8 and 9, where for example c-[IS₇-BA₃] symbolizes a cycle consisting of seven isosorbide and three bisphenol-A units.

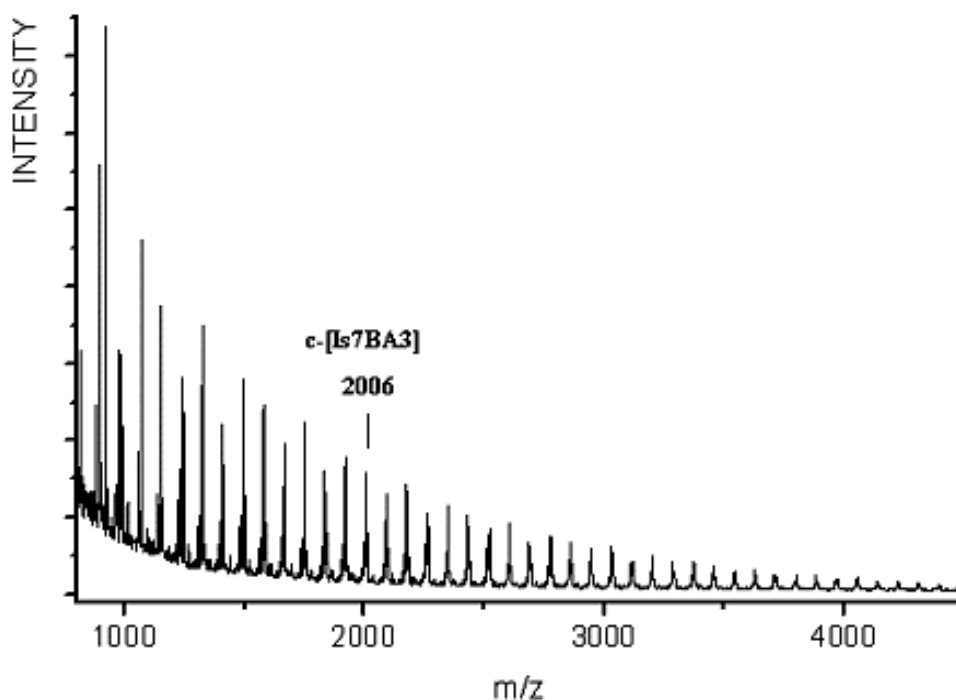


Figure 8. MALDI-TOF mass spectrum of the random copolycarbonate (Copolycarb-2) C means cyclic copolymer c-[IS₇BA₃].

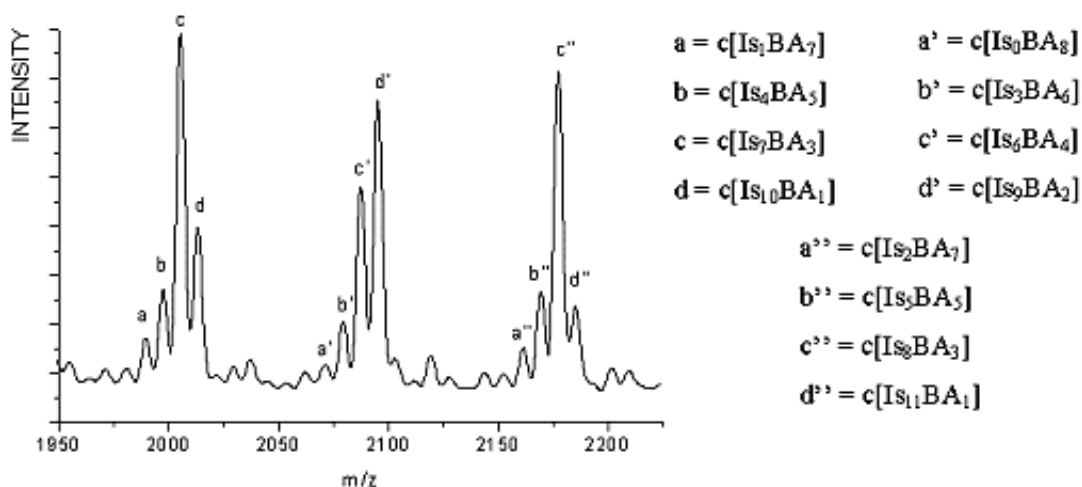


Figure 9. MALDI-TOF mass spectrum (section) of the random copolycarbonate and the assignments of cycles corresponding to the masses listed in Table 4 (IS = isosorbide, BA = bisphenol-A units).

Therefore, these MALDI-TOF mass spectra prove that the conversions were high and the chain growth mainly limited by cyclization.

The molecular weights of the copolycarbonates prepared (based on isosorbide with isomannide or bisphenol A) in this work are comparable or higher than those of standard commercial products. This result also means that the glass transition temperature (T_g s) are representative for the individual classes of novel copolycarbonates (Copolycarb-1 and Copolycarb-2). Remarkable here is the relatively high T_g of 163°C for a completely aliphatic copolycarbonate derived from renewable carbon resources (isosorbide and isomannide).

Conclusions

Pyridine promoted polycondensations of isosorbide and diphosgene below 25°C yielded high molar mass IHC almost free of cyclocarbonates. These findings suggest that IHC adopts below 25°C a compact immobile conformation which hinders cyclization but not chain growth. Copolycondensations of isosorbide with equimolar mixture of isomannide or bisphenol-A by means of diphosgene and pyridine yielded random sequences as evidenced by ^1H and ^{13}C NMR spectroscopy. The MALDI-TOF mass spectra indicated the formation of a high molar fraction of cycles suggesting that high conversions and reaction conditions almost free of side reactions destroying functional groups were achieved. Sufficiently high molecular weights and glass transition temperatures up to 163°C mean that such novel class of copolycarbonates may, in principle, be useful as transparent engineering plastics.

Acknowledgments

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