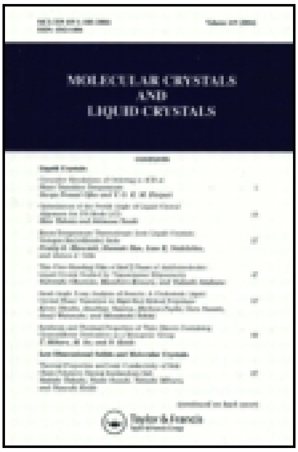

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Synthesis and Characterization of Novel Side-Chain Liquid Crystalline Polycarbonates

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SYNTHESIS AND CHARACTERIZATION OF NOVEL SIDE-CHAIN LIQUID CRYSTALLINE POLYCARBONATES

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Abstract Side-chain liquid crystalline (SCLC) polycarbonates were prepared by copolymerization of carbon dioxide with epoxides, carrying a nitrostilbene mesogenic group and spacers of different lengths. The polymerization, carried out in an autoclave at high carbon dioxide pressure, was catalyzed by an organozinc catalyst. The number average molecular weight of the polymers, as determined by GPC, was in the range of 4,300 to 38,000. The polydispersity of the polymers ranged from 5.9 to 80. ^{1}H NMR and ^{13}C NMR studies revealed that the obtained polymers contain carbonate linkages (67-94%) as well as ether linkages in their backbone. Liquid-crystalline properties of the polymers were investigated by DSC, X-Ray diffraction and polarized optical microscopy.

INTRODUCTION

In recent years side-chain liquid crystalline polymers (LCPs) with a variety of mesogenic groups, spacers and polymer backbones have been prepared. Polymer backbones of different flexibilities that have been investigated include polysiloxanes, poly(meth)acrylates, polyethers, poly(vinyl ethers) and polyurethanes. Up to now no side-chain LCPs have been reported with a polycarbonate backbone.

Aromatic and aliphatic polycarbonates are generally prepared from diols and phosgene. Another method to prepare aliphatic polycarbonates, starting from carbon dioxide and epoxides, using organozinc catalysts, has first been published by Inoue and coworkers[1]. In this way the use of the highly toxic phosgene or its derivatives can be avoided. In most cases simple epoxy monomers, such as propylene oxide and 1,2-epoxycyclohexane[2], were copolymerized with CO_2. In only one case a monomer with a cholesteryl group, a potential mesogenic group, was used, but no liquid crystalline properties were reported[3].

The present paper deals with the synthesis and characterization of side-chain liquid crystalline polycarbonates, prepared by copolymerization of carbon dioxide and mesogenic epoxides. The aim of this work is to study the copolymerization reaction and the structure-property relationships of the resulting side-chain liquid crystalline polycarbonates as a function of spacer length and copolymer composition. Also the ternary copolymerization of a mesogenic epoxide, a non-mesogenic epoxide and carbon dioxide is described.

EXPERIMENTAL SECTION

Synthesis of monomers and intermediates

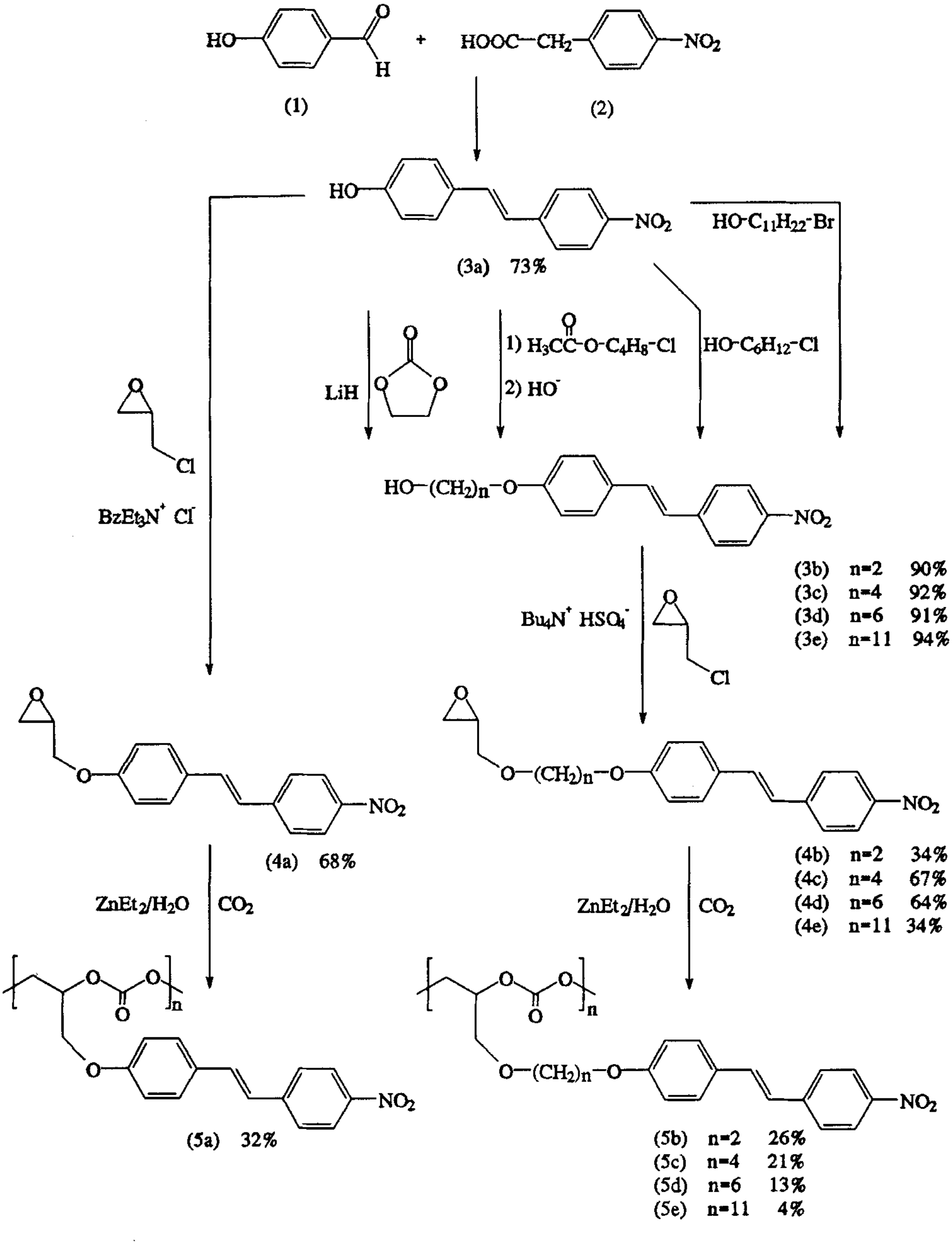
The preparation of the monomers and polymers is outlined in *Scheme 1*. All chemicals for monomer synthesis were used as received, without further purification. Dioxane was dried extensively by refluxing in the presence of sodium and benzophenone, prior to distillation under nitrogen. 1,2-Epoxyoctane was distilled from calcium hydride in a nitrogen atmosphere at reduced pressure. The purity of all products was checked by HPLC and TLC; the structures were confirmed by ^{1}H NMR.

(E)-4-hydroxy-4'-nitrostilbene **(3a)**: The mesogenic group was prepared from 4-hydroxybenzaldehyde **(1)** and 4-nitrophenylacetic acid **(2)**, by the method of Wreesman and Erdhuisen[4]. Yield 73.3%, m.p. 206-209° C.

4-(2-hydroxyethoxy)-4'-nitrostilbene **(3b)**: 48.24 g of **3a** and 19.38 g of ethylene carbonate were dissolved in 50 ml of hot DMF under nitrogen. 40 mg of lithiumhydride was added and the mixture was refluxed for 2 h. When the CO_2 evolution ceased the mixture was cooled to 85° C and poured out into 400 ml of 1N HCl. The precipitate was washed with water and dried in vacuo at 50° C to yield 56.8 g (99.5%) of crude product, which was recrystallized from a mixture of 750 ml of ethanol and 150 ml of ethyl acetate. The crystals were dried in vacuo at 50° C to yield 51.5 g (90.2%) of pure product. Nematic liquid crystal: m.p. 139.0-141.0° C, T_i 144.6° C.

4-(4-hydroxybutoxy)-4'-nitrostilbene **(3c)**: 60.31 g of **3a**, 49.8 g of K_2CO_3, 4.98 g of KI and 54.2 g of 4-chlorobutyl acetate were dissolved in 400 ml of DMF and the mixture was refluxed for a few min. until the dark solution became yellow. The reaction mixture was allowed to cool to 90° C and was precipitated in 1.2 l of 2N HCl. The yellow ppt. was filtrated, washed with water and dried in vacuo at 80° C. Yield 88.1 g (99.2%) of crude 4-(4'-nitro-4-stilbenyloxy)butyl acetate.

80 g of the acetate was dissolved in 250 ml of hot dioxane. At 75° C first 250 ml of ethanol was added and then a 20% aqueous solution of 14.0 g of NaOH. The hydrolysis was instantaneous and after 1 min. the reaction mixture was neutralized with 2.5 ml of conc. HCl and poured out in 1.5 l of water. The yellow ppt. was filtrated, washed with water and dried in vacuo at 80° C to yield 70.3 g (99.7%) of crude



Scheme 1

product, which was recrystallized from acetone. The crystals were dried in vacuo at 50°C. Yield: 65.1 g (92.4%) of yellow needles. Nematic liquid crystal: m.p. 131.5-133.5°C, T_i 150°C.

4-(6-hydroxyhexyloxy)-4'-nitrostilbene (**3d**) was prepared by the method of Wreesman and Erdhuisen[4], starting from **3a** and 6-chlorohexanol. Yield 90.7%, m.p. 154.8-157.6°C.

4-(11-hydroxyundecyloxy)-4'-nitrostilbene (**3e**) was prepared similarly from **3a** and 11-bromoundecanol. Yield 94.3%, enantiotropic L.C.: K 100.3 S_c 115.3 N 120.2°C I.

4-(2,3-epoxypropoxy)-4'-nitrostilbene (**4a**): Synthesis of this monomer was based on the method of Cser[5]. 24.3g of **3a** and 0.228g of benzyltriethylammonium chloride were dissolved in 200 ml of epichlorohydrin at 70°C. With vigorous stirring a 20% aqueous solution of 4.0 g of NaOH was slowly added. After 2.5 h. 0.911g (4 mmol) of benzyltriethylammonium chloride was added and the temperature was raised to 80°C in order to increase the conversion. After 20 min. the reaction was complete. The epichlorohydrin layer was washed with water while hot, dried with $MgSO_4$, filtrated and cooled to room temperature. The yellow crystals were recrystallized twice, from acetonitrile and dioxane respectively. The product was dried in vacuo at 50°C to yield 20.3 g (68.3%) of a monotropic nematic liquid crystal: m.p. 146.5-148.4°C, I-N transition 127°C.

4-[2-(2,3-epoxypropoxy)ethoxy]-4'-nitrostilbene (**4b**): preparation of this monomer and other aliphatic glycidyl ethers (**4c-e**) was based on the method of Mouzin and coworkers[5]. 28.53 g of **3b** and 3.395 g of tetrabutylammonium hydrogen sulfate were dissolved in 250 ml of epichlorohydrin at 60°C. The solution was cooled to 40°C and a 50% aqueous solution of 80 g of NaOH was slowly added in 15 min. with vigorous stirring. The temperature was raised to 55°C and after a total reaction time of 45 min. the reaction was terminated. The organic layer was separated and washed successively with water, 1N HCl and again with water until neutral. The solvent was evaporated and the solid residue was dissolved in 150 ml of acetonitrile and refluxed for 1 h. in the presence of 2.5 g of activated carbon. After a hot filtration the solution was allowed to crystallize at room temperature. The yellow crystals were recrystallized twice from respectively acetonitrile and a 1:1 mixture of acetone and ethanol. The crystals were dried in vacuo at 50°C to yield 11.7 g (34.3%) of pure product: m.p. 106.2-108.8°C.

Epoxides with longer spacers (**4c-e**) were prepared similarly. Monomer **4c** was also purified by recrystallization, **4d** and **4e** were purified by column chromatography.

Preparation of the polymerization catalyst

The diethylzinc/water (1:0.9) catalyst was prepared under nitrogen in a thoroughly dried three-necked flask with a vacuum/nitrogen inlet, a magnetic stirring bar and a dropping funnel with septum inlet. A small amount of diethylzinc was transferred via a double-tipped needle from the container into the dropping funnel of known weight. Thus, for example 1.23 g (10 mmol) of diethylzinc was transferred. With a hypodermic syringe 10 ml of dry dioxane was added to the diethylzinc in the funnel and this solution was transferred into the reaction flask. 10 ml of dioxane and 162 μl (9 mmol) of water were mixed together in the dropping funnel and slowly added in about 5 min. to the stirred diethylzinc solution, which was cooled by an ice bath. The catalyst solution was allowed to react at room temperature for another 25 min. The clear and colorless catalyst solution (0.5 M with respect to diethylzinc) was used immediately after preparation.

Polymerization procedure

All polymerizations were carried out by basically the same procedure as reported in literature[3]. When necessary (e.g. because of solubility problems) reaction conditions were modified.

Copolymerization of mesogenic epoxide **4a** *with* CO_2*:* 7.433 g of **4a** was transferred into a 250 ml autoclave with a magnetic stirrer. In a carbon dioxide atmosphere 10 ml (20 mol% with respect to the epoxide) of catalyst solution and 20 ml of dioxane were added with a hypodermic syringe. The autoclave was flushed twice with CO_2 to remove traces of air. The pressure was increased to 60 atm. and the temperature was raised to 70° C. After stirring the reaction mixture for 72 h. the reaction mixture was dissolved in 100 ml of hot DMF. 0.83 ml of conc. HCl was added to the turbid solution in order to dissolve the catalyst. The polymer was precipitated in 200 ml of methanol. The ppt. was dissolved in 100 ml of DMF and the same procedure was repeated. The polymer was dissolved in 50 ml of dioxane and precipitated with 25 ml of methanol twice. The final ppt. was freeze-dried from dioxane and further dried in vacuo at 50° C. Yield 2.73 g (32.0%) of polymer.

The polymerization procedure was similar for the other epoxides. Purification was similar for polymers **4b** and **4c**, but **4d** and **4e** were dissolved in $CHCl_3$ and washed with diluted HCl to remove the catalyst.

Ternary copolymerization of **4d**, *epoxyoctane (mole ratio 1:2) and* CO_2*:* 4,97 g of **4d**, 3.206 g of 1,2-epoxyoctane and 15 ml of catalyst solution (20 mol% with respect to the total amount of epoxide) were transferred into the autoclave. After flushing the autoclave with CO_2, polymerization was carried out at 60 atm. and 70° C for 72 h. The turbid viscous reaction mixture was diluted with 200 ml of chloroform and stirred for 15 min. with 50 ml of 1N HCl. The organic layer was washed twice with water and poured into 500 ml of methanol. The ppt. was dissolved in 150 ml of DMF and after a warm filtration at 50° C precipitated in 500 ml of methanol. The ppt. was dissolved in 150 ml of chloroform, precipitated in 500 ml of methanol and freeze dried from dioxane to yield 3.88 g (39.5%) of copolymer.

Similarly, polymers were prepared with a 2:1, 1:1 and 0:1 feed ratio of mesogenic epoxide **4d** and 1,2-epoxyoctane.

RESULTS AND DISCUSSION

Synthesis of monomers and intermediates

As described in the experimental part most of the products were obtained in high yields. The purity of the compounds was generally high, which could be accomplished by one or more recrystallizations. Only monomers **4d** and **4e** had to be purified by column chromatography. Monomers **4a** and **4c** are monotropic nematic LC; intermediates **3b**, **3c** and **3e** are enantiotropic LC; all other compounds are crystalline.

Polymerization reactions

The results of the copolymerization reactions of CO_2 and mesogenic epoxides **4a-e** are displayed in Table I. A series of copolymerizations of CO_2, **4d** and non-mesogenic 1,2-epoxyoctane was also carried out in order to gain more insight in the polymerization reaction. These results are shown in Table II.

TABLE I Copolymers of CO_2 and mesogenic epoxides **4a-e**.

Polymer	Spacer n	Yield (%)	$M_n \times 10^{-3}$ (g/mol)[a]	$M_w \times 10^{-4}$ (g/mol)	M_w/M_n (-)	carbonate content[b] (mol%)
5a	0	32.0	35.1	145.0	41.4	76.4
5b	2	26.4	15.2	55.5	36.5	77.8
5c	4	20.5	38.7	49.5	12.8	75.5
5d[c]	6	12.7	4.3	16.9	39.2	66.6
5e	11	3.7	14.8	122.0	82.9	67.7

[a] Molecular weight data obtained by GPC in NMP at 70°C using a refractive index detector calibrated with polystyrene standards.
[b] Chemical composition determined by ^1H NMR.
[c] Polymerization time 139 h. instead of 72 h.

Polymer structure

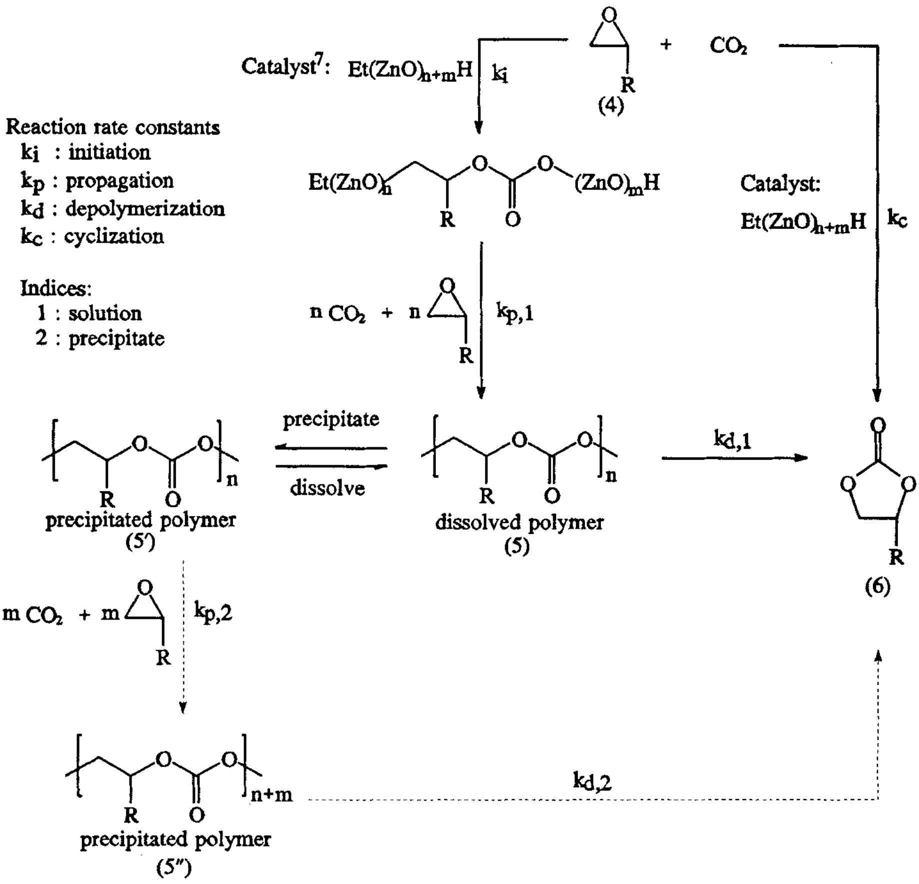
The resulting polymers are not completely alternating, i.e. besides carbonate linkages they also contain some ether linkages, due to homopolymerization of some epoxide molecules. The carbonate content is calculated from the peak at 5 ppm of the methine proton in the ^1H NMR spectrum. This peak appears as a single peak with a relative intensity of 1 in a polycarbonate homopolymer or < 1 in a poly(ether-carbonate). If the ether linkages are randomly distributed in the chain, the methine peak shows a small 'satellite' peak at 4.9 ppm, indicating that the linkage next to the methylene group is an ether. In all polymers described in this paper this 'satellite' peak is present, indicating a more or less random distribution of ether linkages in the polymers. The peak (at approx. 4 ppm) of the methine proton next to an ether linkage can not be distinguished since it is overlapped by several other peaks.

Polymerization process

As can be seen from Table I the polymer yield strongly decreases with increasing spacer length. It was observed that the monomers with a relatively long spacer (6 and 11) gave a turbid viscous solution after polymerization and that the monomers with short spacers (0, 2 and 4) precipitated from the reaction mixture, yielding a sticky or solid lump of dioxane-insoluble matter. The heterogeneity of the reaction system is an important reason for the high polydispersity of all polymers. Assuming that polymerization only occurs in solution and not in the precipitated state, it should be expected that the polymer yield and the molecular weight would be highest for the well-soluble polymers. However, the opposite result was obtained.

An explanation is presented in *Scheme 2*. This scheme shows a survey of all important reactions and processes during polymerization. The reaction mechanism is too complex to perform actual kinetic studies to verify the scheme and determine all possible rate constants, but the scheme contains enough information to explain the polymerization results. Relatively slow or unlikely reactions are indicated with a dashed arrow. Initiation and propagation proceed via insertion of CO_2 and epoxide in the catalyst molecule. Termination occurs by rearrangement of the active site of the catalyst or by reaction with a protic compound or another reactive molecule, such as oxygen[7]. The theory that initiation and propagation proceeds via insertion of the monomers in the catalyst molecule is supported by our own observations: when a $ZnEt_2$/resorcinol catalyst is used, one of the end groups of the polymer was identified by ^1H NMR as a resorcinol group[8].

It was found by NMR and IR analysis of the reaction mixture that the conversion of epoxide is almost complete. It was also found that, beside the polymer, a five-membered cyclic carbonate **(6)** is practically the only product formed. In those cases where the polymer yield is very low, almost all the epoxy monomer was converted into this cyclic side-product. There are at least two mechanisms responsible for the formation of **(6)**: direct formation from epoxide and CO_2 and depolymerization of the polycarbonate. Evidence for the depolymerization of polycarbonates by similar catalysts was recently found for poly(propylene carbonate)[9]. It is not clear to what extent either of the two reactions contributes to the final amount of cyclic carbonate. It is



Scheme 2

possible to polymerize cyclic carbonates with different ring sizes[10-14]. However, five-membered cyclic carbonates are thermodynamically rather stable and produce only low molecular weight polymers with low carbonate contents. It is therefore assumed that under the present conditions the formation of cyclic carbonate is irreversible.

During polymerization, at a critical molecular weight, the polymer precipitates. This depends on the spacer length and it was found that the tendency to precipitate is higher for short spacers. From the fact that the poorly-soluble polymers nevertheless reach a high molecular weight we conclude that the propagation proceeds after precipitation but at a lower rate: $k_{p,2} < k_{p,1}$. We conclude that precipitation of the polymer must have a similar, but much stronger effect on the depolymerization. The depolymerization rate decreases to a very low value: $k_{d,2} << k_{d,1}$. Comparing the propagation and depolymerization reactions, we conclude that the dissolved polymers are subject to a relatively rapid depolymerization, whereas the precipitated polymer remains almost unchanged. This explains completely, considering the fact that the epoxide conversion is almost complete, the (initially unexpected) low yield of the well-soluble polymers.

Ternary copolymerization

The results of the ternary copolymerizations are displayed in Table II. All the isolated ternary copolymers are readily soluble in dioxane. In these experiments the amount of mesogenic epoxide was constant and the amount of epoxyoctane was varied. The amount of catalyst was always 20 mol% of the sum of both epoxides.

TABLE II Ternary copolymers of CO_2, **4d** and 1,2-epoxyoctane.

feed ratio (mol% **4d**)	product ratio[a] (mol% **4d**)	Yield (%)	$M_n \times 10^{-3}$ (g/mol)[b]	$M_w \times 10^{-4}$ (g/mol)	M_w/M_n (-)	carbonate content[a] (mol%)
100[c]	100.0	12.7	4.3 (4.6)	16.9 (5.6)	39.2 (14.1)	66.6
67	80.5	16.7	14.6 (11.6)	8.5 (5.6)	6.4 (5.8)	74.9
50	62.0	18.4	15.0 (11.2)	23.0 (15.2)	15.3 (13.6)	84.2
33	35.8	39.5	21.8 (29.3)	70.6 (67.5)	32.4 (23.0)	93.5
0[d]	0.0	15.6	(121.1)	(109.0)	(9.0)	93.2

[a] Chemical composition determined by ^1H NMR.

[b] Molecular weight data obtained by GPC in NMP at 70°C using a refractive index detector calibrated with polystyrene standards. Values between parentheses measured in THF at 35°C.

[c] Polymerization time 139 h. [d] Polymerization time 24 h.

It was found that the highest yield was obtained in the experiment in which the largest amount of epoxyoctane was added. Two important parameters determine the final polymer yield:

- The propagation rate strongly depends on the total monomer concentration and thus on the amount of epoxyoctane.
- The depolymerization rate however, depends more on the number of polymer chains, which is relatively low if the molecular weight is high.

We now conclude that extra epoxyoctane obviously contributes to a higher yield. In the first place it increases the polymerization rate and as a result the molecular weight increases. In the second place, since there are relatively few chain ends then, the depolymerization is relatively slow. Both effects lead to a higher yield and a higher molecular weight, which is completely in agreement with our results.

From ^1H NMR measurements it was found that the mesogen-content in the polymers is slightly higher than in the feed mixture. This is probably due to some fractionation of the polymer during isolation and purification. From ^1H NMR data it can not be distinguished whether a random copolymer or perhaps a (multi)block copolymer with mesogenic and non-mesogenic blocks is formed. The results show that the overall carbonate content strongly increases with increasing amount of epoxyoctane. Up to 95% of the groups adjacent to the methine proton of an epoxyoctane unit is a carbonate and only 60-70% of the groups adjacent to the methine proton in the mesogenic unit is a carbonate. No straightforward answer can be given to the question why apparently carbon dioxide preferentially occupies a position next to an epoxyoctane unit and not a mesogenic unit. Like in the binary copolymers, the ether linkages are more or less randomly distributed.

Liquid crystalline properties

All of the obtained binary copolymers are liquid crystalline and also some of the ternary copolymers show liquid crystallinity. The results of the mesophase characterization are displayed in Table III. DSC and polarized optical microscopy were used to determine the phase transitions and the LC phases. X-ray data were mainly used to confirm the mesophases; details are not given here.

TABLE III Thermal behavior of the LC polycarbonates.

Spacer n	CC[a] (%)	Phase transitions[b] and temperatures(°C) (Enthalpy J/g)
0		G 109 K 174 (1.3) N 235 (3.4) I[c]
2		G 64 S_A 125 (2.3) I
4		G 47 S_A 157 (2.8) I
6	100	K(+G) 22 K 57 (10) S_B 77 (1.1) S_A 146 (3.0) I
	80.5	K(+G) 23 K 52 (12.5) S_x 137 (1.8) I
	62.0	K+G 16 K 51 (5.0) S_x 138 (0.4) I
	35.8	G 12 I
	0.0	G -23 I
11		K(+G) 21 K 58 (9.4) S_x 160 (5.7) I

[a] CC=copolymer composition, mol% of mesogenic units in the 1,2-epoxyoctane/**4d**/CO_2 ternary copolymer.

[b] Data from the second heating run. K(+G)=(semi)crystalline, G=glass, S=smectic, N=nematic, I=isotropic.

[c] Sample decomposes below the clearing temperature.

In general, determination of the mesophases by polarized optical microscopy was difficult. Only polymer **5d** forms bâtonnettes on cooling from the isotropic melt and a S_A fan-shaped texture on further cooling. Polymer **5a** shows a colorful, sometimes Schlieren-like texture. Other polymers do not develop typical textures; often fine grains or a somewhat marble-like texture is formed. The phase transitions, measured by DSC, can be remarkably sharp, but because of the high polydispersity the melt viscosity of the samples is so high that the development of texture is extremely slow. Moreover the high molecular weight chains already phase-separate while the low molecular weight chains are still isotropic. For this reason it is better to study liquid crystalline behavior on monodisperse polymers, for example prepared by living polymerization. Since a high polydispersity is inherent to the present polymerization reaction the only way to obtain monodisperse polymers is by fractionation. This will be subject of further studies.

It can be seen from Table III that no clear relation can be found between phase transition temperatures and the spacer length. This is probably due to the variations in molecular weight and to the broad molecular weight distribution of the different polymers. Furthermore the polymers differ somewhat in chemical composition: from 67 mol% to 78 mol% carbonate units in the chain.

However, there is a clear relation between the glass transition temperature and the spacer length. A sharp rise in the T_g is observed as the spacer length decreases. The maximum T_g is about 110°C for polymer **5a**, in which there is no extra spacer between the mesogenic group and the former glycidyl group. It is evident that the bulky side groups cause severe hindrance of the main chain motion. The decreasing T_g at increasing spacer length is not only caused by the decoupling of the stiff side-chains and the flexible polymer backbone, but also by an additional plasticizing effect of the spacers. Because of the effective decoupling of the ordered side groups from the amorphous main chain there is an increasing tendency towards side-chain crystallization for the polymers with long spacers.

Polymer **5d** exhibits both a S_A phase and a S_B phase, the latter being formed only after annealing for a few hours just above the melting point. The melting point appears only after annealing just above the T_g. For polymer **5e** the tendency to crystallize is so high that the T_g can hardly be detected. The glass transition can only be observed after rapid quenching of the polymer to a temperature below the T_g. It is immediately followed by an exothermic so-called 'cold crystallization' and a normal melting peak.

In the ternary copolymers a drop in the T_g is observed as the content of epoxyoctane increases, due to the plasticizing effect of the hexyl side-chains. The clearing enthalpy shows a strong decrease until the liquid crystalline phase completely disappears at 64% of epoxyoctane units. The clearing point slightly decreases but there is a remarkable peak broadening with respect to the binary copolymers.

CONCLUSIONS

Copolymerization of carbon dioxide and mesogenic epoxides proved to be an interesting new method for preparation of side-chain liquid crystalline polycarbonates. Moderately high molecular weight polymers with a rather broad molecular weight distribution are achieved. The polymerization mechanism is complex and cyclization and depolymerization reactions lead to the formation of a 5-membered cyclic carbonate as the main side-product. The mesophases could be characterized by DSC, polarized optical microscopy and X-ray diffraction, but no clear relation between phase transition temperatures and spacer length has been found. For accurate phase behavior studies monodisperse samples should be prepared by fractionation of the polydisperse polymers.

An interesting feature of the present polymerization is that polymers can be prepared with a rather high T_g, about 110°C. These could be interesting for NLO applications or for optical data storage, provided that the mesophase is nematic and can easily be aligned.

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