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Polymers of Carbonic Acid. 22. Cholesteric Polycarbonates Derived from (*S*)-((2-Methylbutyl)thio)hydroquinone or Isosorbide

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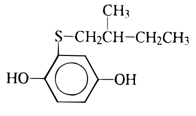
ABSTRACT: (*S*)-((2-Methylbutyl)thio)hydroquinone was prepared from benzoquinone and (*S*)-2-methylbutyl mercaptan. One series of cholesteric copolycarbonates was prepared from this chiral hydroquinone, methylhydroquinone, and 4,4′-dihydroxybiphenyl by interfacial polycondensation with diphosgene. All copolycarbonates were noncrystalline and decomposed upon heating above 250 °C. A Grandjean texture was only observed for one sample. A second series of cholesteric copolycarbonates was prepared from isosorbide, methylhydroquinone, and 4,4′-dihydroxybiphenyl. Four different polycondensation methods were studied and compared in this case. The best results were obtained by polycondensation in pyridine containing organic cosolvents. Two copolycarbonates of isosorbide were obtained which formed a broad cholesteric phase with a Grandjean texture.

Introduction

The carbonate group is certainly less favorable for the stabilization of a liquid-crystalline (LC) order than the ester group, due to its nonlinear structure. Nonetheless it has been demonstrated in previous parts of this series[1,2] and later by other authors[3] that aromatic polycarbonates may form a nematic phase over a broad temperature range, provided they contain a favorable combination of para-linked diphenols, particularly 4,4′-dihydroxybiphenyl (DHB). The aim of the present work was to find out if it is feasible to synthesize cholesteric polycarbonates. Chiral comonomers, regardless of their structure, are less favorable for the LC order of polycarbonates than analogous nonchiral and more symmetrical comonomers. Therefore, the combination of chiral comonomers with carbonate links was a risk for the successful synthesis of thermotropic polycarbonates. However, a successful synthesis of cholesteric polycarbonates capable of forming a Grandjean texture was important as a basis for the synthesis of photosetting or thermosetting cholesteric oligo- and polycarbonates. Such materials are of great interest for their optical properties, because a fixation of the Grandjean texture may yield materials with a selective reflection of circularly polarized light.[4,5]

Two quite different chiral monomers were studied in the present work, namely, a hydroquinone with a chiral substituent (**1**) and isosorbide (**2**). Whereas, the latter monomer is a commercial product, the hydroquinone **1** has hitherto not been described in the literature. The hydroquinone **1** has the advantage that it is a rigid monomer with the OH groups in para position, thus favoring the LC properties of the main chain. Its shortcoming might be a weak influence on the conformation of the main chain, i.e. a weak twisting power. In contrast, isosorbide is known to possess a high twisting power,[6] but it is more flexible, and its OH-groups deviate from a theoretical para axis in two dimensions. However, isosorbide has proven to be an useful building block of cholesteric polyesters, so that in several cases a Grandjean texture has been observed.[7−9]



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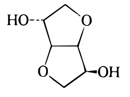

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Experimental Section

Materials. 4,4′-Dihydroxybiphenyl (DHB), methylhydroquinone (MeHQ), benzoquinone, isosorbide, and (*S*)-2-methyl-1-butanol were purchased from Aldrich Co. (Milwaukee, WI) and used without purification. Trichloromethyl chloroformate was purchased from Lancaster Synth. (Karlsruhe, Germany). Pyridine was dried by distillation over freshly powdered CaH_2. CH_2Cl_2 was dried by distillation over P_4O_{10}. isosorbide bischloroformate (mp 44 °C) was a gift of BASF AG. It was prepared from isosorbide, phosgene, and *N*,*N*-dimethylaniline in dry CH_2Cl_2 according to a procedure described in a patent.[10]

(*S*)-2-Methyl-1-mercaptobutane. The tosylate of (*S*)-2-methyl-1-butanol was prepared by means of tosyl chloride and 2 N sodium hydroxide. The crude oily tosylate (n^{20}_{D} 1.5024)[11,12] was reacted with thiourea as usual[13] to yield the product (n^{20}_{D} 1.4483, $[\alpha]^{25}_{D}$ +3.1° in DMSO, $c = 1$ g/dL).

2-[(*S*)-(+)-((2-Methylbutyl)thio)hydroquinone. (*S*)-(+)-2-Methylbuta-1-thiol (0.1 mol) was dissolved in 120 mL of dried CH_3OH. To this solution was added p-benzoquinone (0.1 mol) in CH_3OH (250 ml) and THF (100 ml) dropwise while the reaction temperature was kept at −5 °C, and then the mixture was reacted at room temperature overnight. The whole mixture was filtered and concentrated. The residue was dissolved by 400 mL of ether, washed with water (500 mL) three times, dried with Na_2SO_4, and concentrated again. The obtained solid was recrystallized from toluene/petroleum ether. The final product in the form of a white powder was obtained in a yield of 75%. mp: 71 °C. $[\alpha]^{25} = +24.8°$ ($c = 1$ g/dL). Anal. Calcd: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.25; H, 7.56; S, 15.49.

Isosorbide bis(phenyl carbonate) (6). Isosorbide (28.8 g, 0.2 mol) and pyridine (35 g, 0.44 mol) were dissolved in 250 mL of tetrahydrofuran. To this solution was added phenyl chloroformate (68.9 g, 0.44 mol) dropwise for 1 h while the reaction temperature was kept at 5−10 °C, and the mixture was reacted at room temperature for another 4 h. Then the whole reaction mixture was poured into water. The precipi-

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tated solid was washed with a 5% (by weight) aqueous solution of $NaHCO_3$ and then washed with water several times. The crude product was recrystallized from ethyl acetate: Yield: 76%. mp: 175−176 °C. Anal. Calcd for $C_{20}H_{18}O_8$ (386.36): C, 62.12; H, 4.70. Found: C, 61.91; H, 4.62.

Polycondensations. A. Interfacial Polycondensation. 4,4′-Dihydroxybiphenyl (15 mmol), methylhydroquinone (7.5 mmol), 2-((2(*S*)-2-methylbutyl)thio)hydroquinone (7.5 mmol), diphosgene (16.5 mmol), and 1 drop of triethylamine were dissolved in 100 mL of dried, cold dichloromethane. To this solution was added 80 mL of 1 N sodium hydroxide solution, and both phases were rapidly mixed with an “Ultra Turrax” high-speed stirrer for 10 min and then with a normal mechanical stirrer for 20 min with cooling on ice. When the polymer precipitated from the CH_2Cl_2 solution or when gelation happened, the entire reaction mixture was poured into 1 L of cold methanol. When the polymer was soluble in CH_2Cl_2, the organic phase was separated and poured into 800 mL of methanol and filtered. The isolated polymer was dissolved in CH_2Cl_2 and precipitated again into methanol. Finally the polycarbonate was dried at 80 °C under vacuum. Analogous polycondensations were conducted with free isosorbide instead of the chiral hydroquinone (see Table 3).

B. Melt Polycondensation. Methylhydroquinone (5 mmol), 2-(((*S*)-2-methylbutyl)thio)hydroquinone (5 mmol), 4,4′-biphenyl diphenyl dicarbonate (10 mmol) and zinc acetate (50 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas inlet and outlet tubes. The reaction mixture was heated to 180 °C for 1 h and to 220 °C for 1 h. The evolved phenol was removed with a slow steam of nitrogen. Then the reaction temperature was raised to 240 °C for 1 h and to 260 °C for 1 h under vacuum. The obtained polymer was dissolved (or suspended) in CH_2Cl_2 and precipitated into methanol. Finally the polycarbonate was dried at 80 °C under vacuum.

C. Solution Polycondensation. Diphosgene (16.5 mmol) in 20 mL of dichloromethane was added dropwise into the solution of 4,4′-dihydroxybiphenyl (15 mmol), methylhydroquinone (7.5 mmol), and isosorbide (7.5 mmol) in 30 mL of pyridine. The mixture was reacted at 5−10 °C for 30 min and at room temperature for another 1 h. The mixture was then poured into methanol and filtered. The isolated polymer was dissolved in CH_2Cl_2 and precipitated again into methanol. Finally the polycarbonate was dried at 80 °C under vacuum.

D. Interfacial Polycondensation with Isosorbide Bischloroformate. 4,4′-Dihydroxybiphenyl (15 mmol), methylhydroquinone (7.5 mmol), isosorbide chloroformate (7.5 mmol), and triethylbenzylammonium chloride (50 mg) were dissolved in 100 mL of dried, cold dichloromethane. To this solution was added 80 mL of 1 N sodium hydroxide solution, and both phases were rapidly mixed with an “Ultra Turrax” high-speed stirrer for 10 min with cooling on ice. Then, diphosgene (8.25 mmol) was added and the reaction mixture was poured into 1 L of cold methanol and filtered. The isolated polymer was dissolved in CH_2Cl_2 and precipitated again into methanol. Finally the polycarbonate was dried at 80 °C under vacuum.

E. Solution Polycondensation with Isosorbide Bischloroformate. 4,4′-Dihydroxybiphenyl (10 mmol) was dissolved in 15 mL of dried, cold dichloromethane and 15 ml of pyridine. To this solution was added isosorbide chloroformate (10 mmol) dropwise for 30 min under cooling with ice. The mixture was reacted at room temperature for another 4 h. The entire reaction mixture was poured into 600 mL of cold methanol and filtered. The obtained polymer was dissolved in CH_2Cl_2 and precipitated in methanol again. Finally the polycarbonate was dried at 80 °C under vacuum.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. A solution of 100 mg of polycarbonates in 50 mL of a CH_2Cl_2/TFA mixture (4/1 by volume) was used for all measurements.

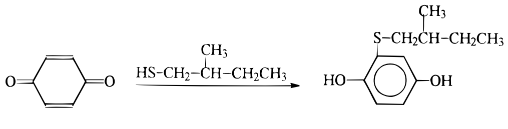
The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating rate or cooling rate of 20 °C/min.

^{13}C NMR spectra were obtained on a Bruker MSL-300 FT-spectrometer in 10 mm o.d. sample tubes. Solutions of 500 mg of polycarbonates in 3 mL of solvent ($CDCl_3$/TFA, 4/1 by volume and containing TMS) were used in all cases. A pulse width of ca. 45° and 32K data points on a 15 000 Hz spectral width along with a relaxation delay of 4 s were used for all measurements.

The optical rotations were measured with a Perkin-Elmer 241 polarimeter at a wavelength of 589 nm in a cuvette of 100 mm length at a concentration of 5 g/L in CH_2Cl_2/TFA (4/1 by volume) at 25 °C.

Results and Discussion

Polycarbonates of 2-(((*S*)-2-methylbutyl)thio)hydroquinone. Although numerous substituted hydroquinones have been described in the literature, hydroquinones bearing a chiral substituent have rarely been described. 2-((*S*)-2-Methylbutoxy)hydroquinone was recently synthesized by Lenz and co-workers[11,12] and successfully used for the preparation of cholesteric polyesters. Unfortunately, the preparation of this chiral hydroquinone is plagued by a low yield and by the need for chromatographic purification. Therefore, attempts were made to synthesize the thio analog **1** in the simplest possible way, namely, by addition of the chiral 2-methylbutyl mercaptan onto 1,4-benzoquinone (eq 1).



(1)

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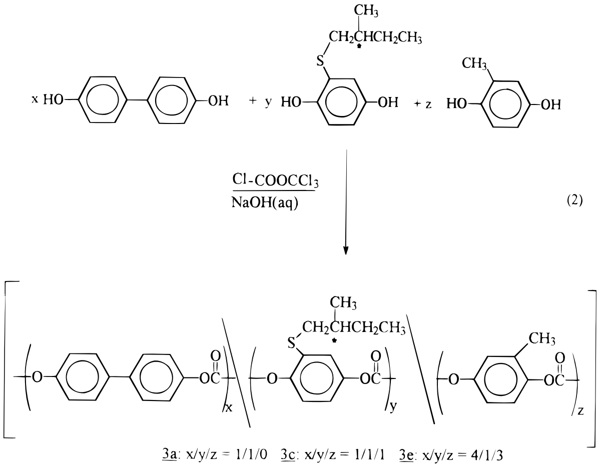
This procedure was indeed successful and the hydroquinone **1** was easy to isolate with satisfactory purity by recrystallization from toluene/ligroin.

It has been demonstrated in previous parts of this series[1,2] that 4,4′-dihydroxybiphenyl (DHB) is important as a mesogenic comonomer for the successful synthesis of liquid-crystalline (LC) copolycarbonates. Therefore, the cholesteric polycarbonates required for the purpose of the present study were designed as copolymers of the chiral hydroquinone **1** and 4,4′-dihydroxybiphenyl. Furthermore, methylhydroquinone (MeHQ) was used as third comonomer to reduce the crystallinity and to improve the solubility. Binary copolycarbonates of DHB and MeHQ have been studied previously[2] and were found to be meltable nematic materials, so the combination of these two diphenols seemed to be promising for the present work. Using the interfacial polycondensation method with “diphosgene” as condensing agent (eq. 2) two chiral binary copolycarbonates (**3a** and **3b**) and four ternary copolycarbonates (**3c−f**) were prepared. In the case of **3d** the synthesis was repeated by a different



(2)

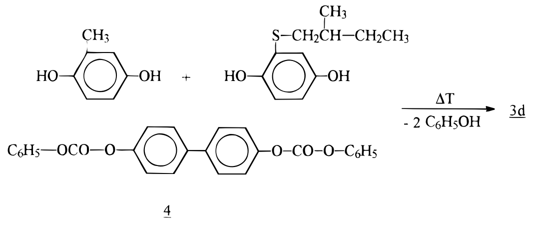
3a: x/y/z = 1/1/0 3c: x/y/z = 1/1/1 3e: x/y/z = 4/1/3
3b: x/y/z = 0/1/1 3d: x/y/z = 2/1/1 3f: x/y/z = 5/1/4

Table 1. Yields and Properties of Copolycarbonates 3a–f

polymer no.	method[a]	yield (%)	η_{inh}[b] (dL/g)	$[\alpha]^{25}$ [c]	elem formula (form. wt)	elem anal.	C	H	S	T_g[e] (°C)
3a	A	91	0.66	–	$(C_{25}H_{22}O_6S)_n$	calcd	66.65	4.92	7.12	–
					(450.52)	found	66.31	4.84	7.15	
3b	A	80	0.12	–	$(C_{20}H_{20}O_4S)_n$	calcd	67.39	5.66	9.00	140
					(356.45)	found	59.82	5.25	8.27	
3c	A	90	0.94	–	$(C_{33}H_{28}O_9S)_n$	calcd	65.99	4.70	5.34	93
					(600.65)	found	64.83	4.76	5.46	
3d	A	90	1.42	−8.5	$(C_{46}H_{36}O_{12}S)_n$	calcd	67.97	4.46	3.95	107
					(812.85)	found	66.58	4.47	4.34	
3d	B	86	insol.	–	$(C_{46}H_{36}O_{12}S)_n$	calcd	67.97	4.46	3.95	92
					(812.85)	found	67.71	4.35	2.95	
3e	A	89	1.23	−6.9	$(C_{88}H_{64}O_{24}S)_n$	calcd	68.74	4.20	2.10	119
					(1537.35)	found	67.85	4.26	2.35	
3f	A	88	1.48	−1.2	$(C_{109}H_{78}O_{30}S)_n$	calcd	68.91	4.14	1.70	115
					(1899.87)	found	68.19	4.18	1.90	

[a] (A) By interfacial polymerization. (B) By melt polymerization. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [c] Measured at 20 °C with $c = 5$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [d] Decomposition occurred. [e] Measured by DSC at a heating rate of 20 °C/min. [f] Observed by polarized microscopy.

method, namely, by thermal polycondensation of **1** and MeHQ with the bisphenylcarbonate of DHB (eq 3).



(3)

However, the polycarbonate obtained in this way proved to be insoluble in all common inert solvents, in contrast to the "interfacial products", and thus, the interfacial method was preferred in all cases. The yields, inherent viscosities, and other properties of the copolycarbonates **3a–f** thus obtained are compiled in Table 1.

Characterization of 3a–f. Prior to any further characterization, the solubilities of the polycarbonates **3a–f** were studied in some detail. All copolycarbonates proved to be soluble in warm dimethylformamide, dimethyl sulfoxide, and $CHCl_3$ (or CH_2Cl_2) containing 20–30 vol% of an acidic cosolvent (e.g. *m*-cresol or trifluoroacetic acid). Furthermore, **3a** and **3c** were soluble in neat chloroform. These good solubilities certainly have two roots. Firstly, they reflect the solubilizing influence of the aliphatic substituents. Secondly, they suggest that the sequences of the copolycarbonates are not far from randomness, in agreement with the ^{13}C NMR spectra discussed below.

The IR spectra of all six polycarbonates display the expected CH stretch vibrations of the aliphatic and aromatic groups in the range of 3000–3300 cm^{-1}. Furthermore, an intensitve "CO band " appeared at 1770 ± 1 cm^{-1}.

The ^1H NMR spectra proved the successful incorporation of both hydroquinones into the polymer chain. However, the quantification of the "aliphatic signals" suggests that the content of MeHQ was somewhat lower than expected from the feed ratio. This result is not surprising, because the anion of MeHQ is the most hydrophilic one of the three comonomers. Its reluctance to react in the organic phase or interface is also reflected in the low molecular weight of the binary copolycarbonate **3b**. The ^{13}C NMR spectra (Figure 1) display numerous signals in the carbonyl region and also numerous peaks of the quaternary (C–O) carbons. The existence of all these splittings and their intensity distribution suggest that the sequences of **3a–f** are indeed close to randomness.

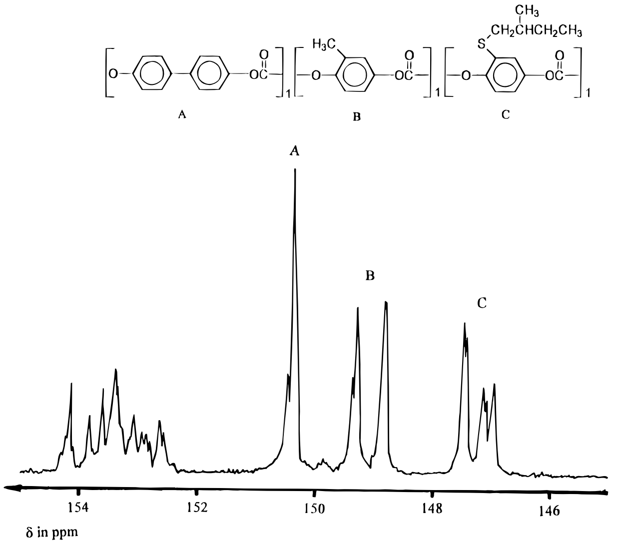


Figure 1. 75.4 MHz ^{13}C NMR spectrum of the copolycarbonate **3c** (in $CDCl_3$/TFA 4:1 by volume): C=O and C–O carbons only.

The DSC measurements revealed that all copolycarbonates **3a–f** were amorphous. Rather low glass transitions (T_g's ~90–120 °C) were found for the ternary copolycarbonates, and a higher T_g was found for **3b** despite its low molecular weight. This higher T_g obviously reflects the absence of the DHB unit, which is capable of undergoing rotational motions around its para axis. Although all these polycarbonates with exception of **3b** form a liquid-crystalline melt, no isotropization endotherm was detectable in the DSC traces because of early thermal degradation. The low thermal stability of**3a–f** is the most negative (and unexpected) property of these polycarbonates. It is clearly related to the chiral monomer **1**. Those polycarbonates rich in **1** begin to degrade slowly above 200 °C and rapidly above 250 °C. In contrast, the copolycarbonates containing isosorbide (**8–10, 11a–c**) show similar rates of thermal degradation only at temperatures above 300 and 350 °C, respectively.

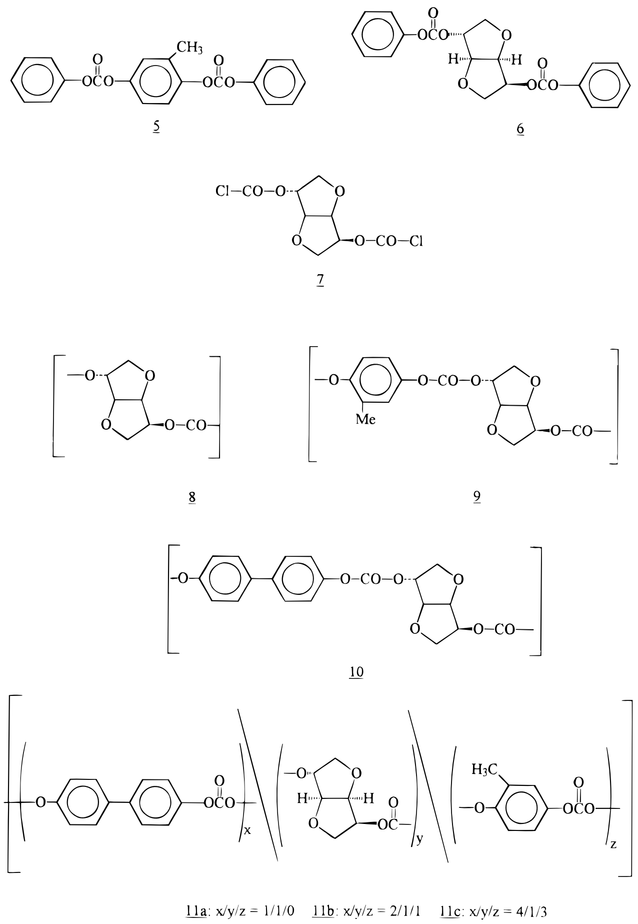
A detailed study of the thermal degradation of **3a–f** was not intended in this work. Yet, due to the low thermostability of **3a–f**, a reversible isotropization could not be realized and it was difficult to define the texture. The most stable polycarbonate of this series proved to

Table 2. Yields and Properties of Copolycarbonates 11a−c

polymer no.	method[a]	yield (%)	η_{inh}[b] (dL/g)	$[\alpha]^{25}_{D}$[c] (deg)	elem formula (formn. wt)	elem anal.	C	H	T_g[e] (°C)	T_f[f] (°C)	T_i[f] (°C)
8	D	71	0.60	+113	$(C_7H_8O_3)_n$	calcd	48.84	4.69	144	250−260	isotropic
					(172.14)	found	48.60	4.71			
9	D	94	0.34	+120	$(C_{15}H_{14}O_8)$	calcd	55.90	4.38	130	220−230	isotropic
					(322.28)	found	55.58	4.21			
10	D	95	0.51	+117	$(C_{20}H_{16}O_8)_n$	calcd	62.50	4.20	160	330−340	isotropic
					(384.35)	found	62.25	4.29			
11a	C	98	0.67	+103	$(C_{20}H_{15}O_8)_n$	calcd	62.67	3.94	149	295−310	isotropic (dec)
					(383.33)	found	62.09	4.05			
11b	A	85	insol.	−	$(C_{41}H_{31}O_{14})_n$	calcd	65.86	4.18	−	260 (dec)	dec without melting
					(747.69)	found	58.23	4.00			
11b	C	98	0.68	+43	$(C_{41}H_{31}O_{14})_n$	calcd	65.86	4.18	121	245	>340[d] (Grandjean)
					(747.69)	found	65.38	4.06			
11b	D	54	insol.	−	$(C_{41}H_{31}O_{14})_n$	calcd	65.86	4.18	−	270−300	biphasic (dec)
					(747.69)	found	65.78	4.18			
11c	C	98	0.86	+28	$C_{83}H_{57}O_{26})$	calcd	67.80	3.91	−	275	>360[d] (Grandjean)
					(1470.35)	found	67.61	4.02			

[a] (A) By interfacial polymerization with free isosorbide. (B) melt polymerization. (C) solution polymerization. (D) interfacial polymerization with isosorbide bischloroformate. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [c] Measured at 25 °C with $c = 5$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [d] Decomposition occurred. [e] Measured by DSC at a heating rate of 20 °C/min. [f] Observed by polarized microscopy.

Chart 1



be **3f**. In this case, the cholesteric melt was rather stable up to 300 °C, and rapid degradation caused irreversible isotropization only at temperatures above 330 °C. Therefore, it was possible to generate a blueish Grandjean texture by shearing the melt at temperatures above 250 °C, where it was mobile enough. This modest success is at least noteworthy as the first example of a cholesteric polycarbonate.

Table 3. Solubilities of the Polycarbonates 8−10 and 11a−c[a]

no.	CH_3Cl	$CHCl_3$/*m*-Cresol (2/1)	CH_2Cl_2/TFA (4/1)	$CHCl_3$/TFA (9/1)	$CHCl_3$/TFA (7/3)	DMF	DMSO
8	−	++	++	++	++	+	+
9	++	++	++	++	++	++	++
10	−	−	++	++	++	−	−
11a(C)	−	−	++	++	++	−	−
11a(D)	−	−	++	++	++	−	−
11b(A)	−	−	−	−	−	−	−
11b(C)	−	−	++	++	++	±	±
11b(D)	−	−	−	−	−	−	−
11c(C)	−	−	++	++	++	−	−

[a] ++ = soluble at room temperature. + = soluble by heating. ± = partially soluble even by heating. − = insoluble.

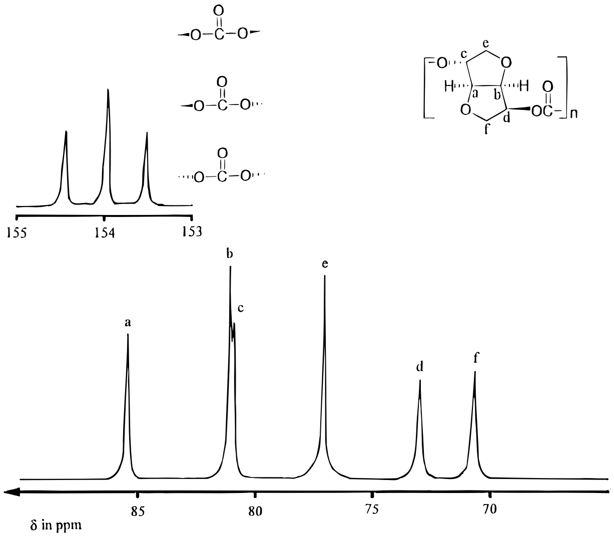


Figure 2. 75.4 MHz ^{13}C NMR spectrum of polycarbonate **8**.

Polycarbonates Based on Isosorbide. The synthesis of cholesteric polycarbonates containing isosorbide as chiral component means that copolycarbonates of an aliphatic diol and diphenols should be synthesized. Most polycarbonates described in literature either exclusively consist of diphenols or of aliphatic diols, and copolycondensations of diols and diphenols have rarely been reported. The authors of this work have not found a pertinent reference. Therefore, four different polycondensation methods were studied and compared in this work, to find out which one will be useful for the synthesis of random copolycarbonates with a random sequence of isosorbide and DHB or MeHQ. For this purpose the monomers **5**−**7** (Chart 1) were needed in addition to **4** and free isosorbide (**2**). Whereas the monomers **4**, **5**,[3] and **7**[10] have been described in litera-

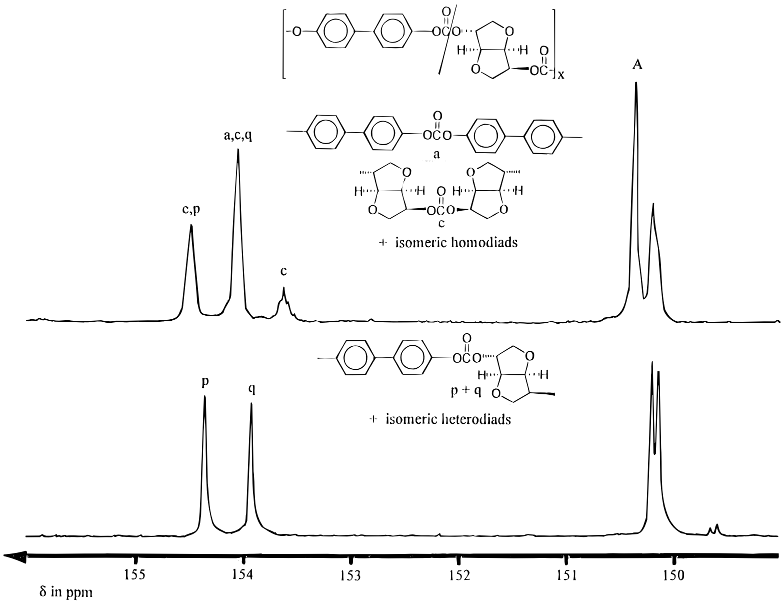


Figure 3. Partial 75.4 MHz ^{13}C NMR spectra of (A) polycarbonate **11a**, (B) polycarbonate **10**.

ture, the monomer **6** was new. It was prepared from isosorbide phenyl chloroformate and pyridine.

On the basis of these monomers the homopolymer **8**, the alternating copolycarbonates **9** and **10**, and the random copolycarbonates **11a**−**c** were prepared. Their yields and properties are summarized in Table 2. The polycarbonate **8** was prepared by polycondensation of the bischloroformate **7** with free isosorbide in an organic solvent mixture containing pyridine as HCl acceptor. The alternating copolymers **9** and **10** were prepared analogously from **7** and MeHQ or DHB. These three polycarbonates were designed to serve as model compounds for a better understanding of the spectroscopic and thermal properties of the copolycarbonates **11a**−**c**.

In the case of **11b**, the following four polycondensation methods were used: (A) interfacial polycondensation using a mixture of **2**, DHB, and MeHQ in combination with diphosgene, (B) polycondensation of DHB, **5**, and **6** in the melt in the presence of zinc acetate as transesterification catalyst, (C) copolycondensation of **2**, DHB, and MeHQ with diphosgene in a water-free organic solvent mixture containing pyridine, and (D) interfacial polycondensation using DHB and MeHQ as nucleophilic monomers and mixtures of the bischloroformate **7** and diphosgene as electrophilic reaction partners.

As demonstrated by the data in Tables 2 and 3, only method C yielded a soluble product. All the products of method B were insoluble in all common solvents, and their elemental analyses were not satisfactory. Therefore, these samples were not listed in Tables 2 and 3. In the case of copolycarbonates **11a** and **11c** only the methods C and D were applied. Again products with a satisfactory solubility were only obtained by method C, which proved to be the only approach suited for the preparation of soluble random copolycarbonates. A more detailed study of the solubilities of polycarbonates **8**−**11** is compiled in Table 3 and does not deserve a detailed comment.

Characterization of Polycarbonates 8−**11.** The IR spectrum of the homopolycarbonate **8** revealed that the "CO band" has a wavenumber of 1749 cm^{-1}, which represents a bathochromic shift of 20 cm^{-1} relative to the aromatic polycarbonates **3a**−**f**. Therefore it was an obvious result that the "CO bands" of the alternating polycarbonates **9** and **10** absorb at 1760 cm^{-1}, a value exactly between those of the aliphatic and fully aromatic polycarbonates.

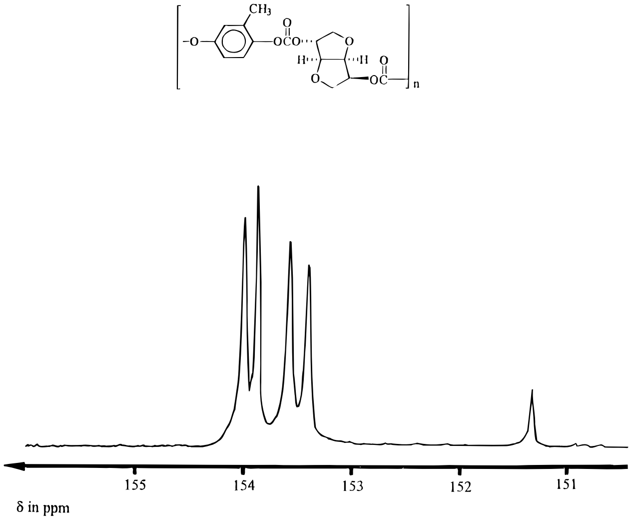


Figure 4. Partial 75.4 MHz ^{13}C NMR spectra of polycarbonate **9**.

The NMR spectroscopic characterization was, of course, restricted to the soluble polycarbonates prepared by method C. The ^{1}H NMR spectrum of **11b** indicates the equimolar incorporation of isosorbide and MeHQ, which is a reasonable result for a polycondensation in an organic reaction medium. More informative are the ^{13}C NMR spectra (Figures 2−4). Three CO signals are detectable in the case of **8** due to the different sterical environment of the OH groups of isosorbide (Figure 2). When the spectrum of copolycarbonate **11a** was compared with that of **10**, the different sequences became evident (Figure 3).

The ^{13}C NMR spectra clearly prove the alternating sequence of **10** and an almost random sequence in the case of **11a**. In the case of polycarbonate **9**, four CO signals can be observed which agree with the expected alternating sequence of both monomers (Figure 4). For a random sequence of **2** and MeHQ, up to 10 CO signals are expected, due to the nonsymmetrical structure of both monomers. In the case of **11b**, numerous signals appear in the "CO region" which were difficult to assign. However, their number and intensities suggest that **11b** possesses a nearly random sequence of all three monomers.

The DSC measurements revealed that all soluble polycarbonates were noncrystalline with glass transitions in the temperature range of 100−150 °C. The glass transition temperatures (T_g's) increase with the higher molar fractions of isosorbide (Table 2). The DSC heating curves did not display an isotropization endotherm of the LC phases because the isotropization of **11b** and **11c** occurred above 330 °C, where thermal degradation affects the phase transitions. Nonetheless, it should be emphasized that the polycarbonates **8**−**11** are considerably more thermostable than **3a**−**f**, so their textures could be studied up to 320 °C.

Optical microscopy with crossed polarizers revealed that the binary copolycarbonates **9** and **10** were completely isotropic. This result is not surprising, because it has been demonstrated for several copolyesters of isosorbide and diphenols that the structure of isosorbide is highly unfavorable for the stabilization of a LC phase.[7,8] Correspondingly, the binary random copolycarbonate **11a** also proved to be isotropic. However, in the case of **11b** and **11c** broad and mobile cholesteric phases were detected. Upon shearing between glass plates, these melts formed blueish Grandjean textures in the reflecting light which were stable for several minutes. This positive results demonstrate that it is possible to synthesize cholesteric polycarbonates by incorporation of isosorbide into nematic copolycarbonates.

Conclusion

The results of this work clearly demonstrate that the chiral hydroquinone **1** is unfavorable for any potential application of cholesteric polycarbonates, because of their low thermal stability. Copolycarbonates containing isosorbide as chiral building block are significantly more thermostable. Despite its unfavorable sterical structure, isosorbide allows the synthesis of cholesteric copolycarbonates with a rather broad cholesteric phase. Several members of isosorbide-containing copolycarbonates formed a blueish Grandjean texture upon shearing of the cholesteric melt. On the basis of this success, several classes of photosetting or thermosetting cholesteric polycarbonates have been prepared which will be described in future parts of this series.

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