Polymers of Carbonic Acid. 3. Thermotropic Polycarbonates Derived from 4,4′-Dihydroxybiphenyl and Various Diphenols

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ABSTRACT: Starting from 4,4′-dihydroxybiphenyl and bis(trichloromethyl) carbonate as condensing reagent various copolycarbonates were prepared by the interfacial condensation method. Hydroquinone, methylhydroquinone, chlorohydroquinone, phenylhydroquinone, 4,4′-dihydroxydiphenyl ether, 4,4′-dihydroxybenzophenone, Bisphenol A, 4,4′-dihydroxydiphenyl sulfide, and 4,4′-dihydroxydiphenyl sulfone were used as comonomers. Furthermore, copolycarbonates with an alternating sequence were prepared from 4,4′-dihydroxybiphenyl as models for ^{13}C NMR sequence analyses. The copolycarbonates were characterized by elemental analyses, inherent viscosities, ^{13}C NMR sequence analyses, DSC measurements, microscopy with polarized light, and thermogravimetric analyses. All copolycarbonates are amorphous materials with glass transition temperatures (T_g's) in the range of 90–170 °C. A nematic melt was found for copolycarbonates containing methylhydroquinone, chlorohydroquinone, 4,4′-dihydrodiphenyl ether, and 4,4′-dihydroxybenzophenone. Ternary copolycarbonates consisting of 4,4′-dihydroxybiphenyl, methylhydroquinone, and 4,4′-dihydroxydiphenyl ether or 4,4′-dihydroxybenzophenone are soluble in aprotic organic solvent, and tough films could be cast from their solutions in dichloromethane.

Introduction

In contrast to normal ester groups the carbonate group does not adopt a quasilinear structure at room temperature and thus was considered to not be compatible with the formation of a liquid-crystalline phase. However, in a previous part of this series it was demonstrated for two copolycarbonates derived from 4,4′-dihydroxybiphenyl that fully aromatic polycarbonates may be thermotropic, forming a nematic melt.[1] The present work was aimed at studying structure–property relationships of copolycarbonates derived from 4,4′-dihydroxybiphenyl in more detail.

In this connection it should be mentioned that thermotropic poly(ester carbonates) derived from *tert*-butylhydroquinone and terephthalic acid were reported in the literature.[2,3] Furthermore, several polycarbonates containing aromatic mesogens in combination with aliphatic spacers are known.[4-7] However, fully aromatic polycarbonates (based on 4,4′-dihydroxybiphenyl and methylhydroquinone) have only been described in a quite recent patent.[8] The present work was conducted before the publication of this patent as evidenced by ref 1.

Experimental Section

Materials. 4,4′-Dihydroxybiphenyl, hydroquinone Bisphenol A, 4,4′-dihydroxydiphenyl sulfone, and the silicon-containing diphenols were gifts of Bayer AG (Krefeld-Uerdingen, FRG). 4,4′-Dihydroxydiphenyl sulfide and methyl-, chloro-, and phenylhydroquinone were purchased from Aldrich Co. (St. Louis, MO). 4,4′-Dihydroxybenzophenone was purchased from Lancaster Chemicals (Morecambe, Lancaster, U.K.). All diphenols were recrystallized prior to polycondensation. Bis(trichloromethyl) carbonate was prepared by chlorination of dimethyl carbonate according to the literature.[9] Dichloromethane was dried by distillation over P_4O_{10}.

Polycondensations (Exemplary Procedure). 4,4′-Dihydroxybiphenyl (30 mmol), another diphenol (30 mmol), and bis(trichloromethyl) carbonate (0.25 mmol) were dissolved in 200 mL of dry, cold dichloromethane. This solution was added to 160 mL of precooled 1 N sodium hydroxide, and both phases were rapidly mixed with an "Ultra Turrax" high-speed stirrer for 30 min under cooling with ice. When the polymer precipitated from the CH_2Cl_2 solution, the entire reaction mixture was poured in to 1.5 L of cold methanol. When the polymer was soluble, the organic phase was separated and poured into 1 L of methanol. The precipitated polymer was dried and dissolved in ca. 150 mL of dichloromethane or in a mixture of dichloromethane and trifluoroacetic acid (4:1 by volume). These solutions were filtered or centrifuged and precipitated into 1 L of cold methanol. Finally the copolycarbonates were dried at 60 °C (12 mbar).

Several condensations were repeated, with addition of 4-*tert*-butylphenol as chain stopper (molar ratio diphenols/monophenol of 100:1). In the case of hydroquinone (polycarbonate 1) the synthesis was repeated with addition of 16 g of KNO_3 to the NaOH solution.

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

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

The ^{13}C NMR spectra were obtained on a Bruker MSL-300 FT-spectrometer in 10-mm-o.d. sample tubes. Solutions of 200 mg of polycarbonate in 2 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 15000-Hz spectral width along with a relaxation delay of 4 s were used for all measurements.

The thermogravimetric analyses were conducted with a Perkin-Elmer TGA-2 at a heating rate of 10 °C/min in air.

Results and Discussion

Syntheses. All copolycarbonates of this work were synthesized by the interfacial condensation method in dichloromethane/sodium hydroxide at 0–5 °C. Bis(trichloromethyl) carbonate[9] served as the acylating reagent. This reagent was used in excess (usually 10%) to overcome the hydrolysis of active end groups (e.g., chloroformates). Binary copolycarbonates were in general insoluble in dichloromethane and precipitated in the course of the polycondensation, whereas ternary copolycarbonates remained in solution. Four series of copolycarbonates were prepared (Chart I).

In series 1–4 the substituent of hydroquinone was varied, and in series **2a–d** or **3a,b** the molar ratio of 4,4′-dihydroxybiphenyl and methyl- or chlorohydroquinone was changed. The yields and properties of these copolycar-

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Chart I

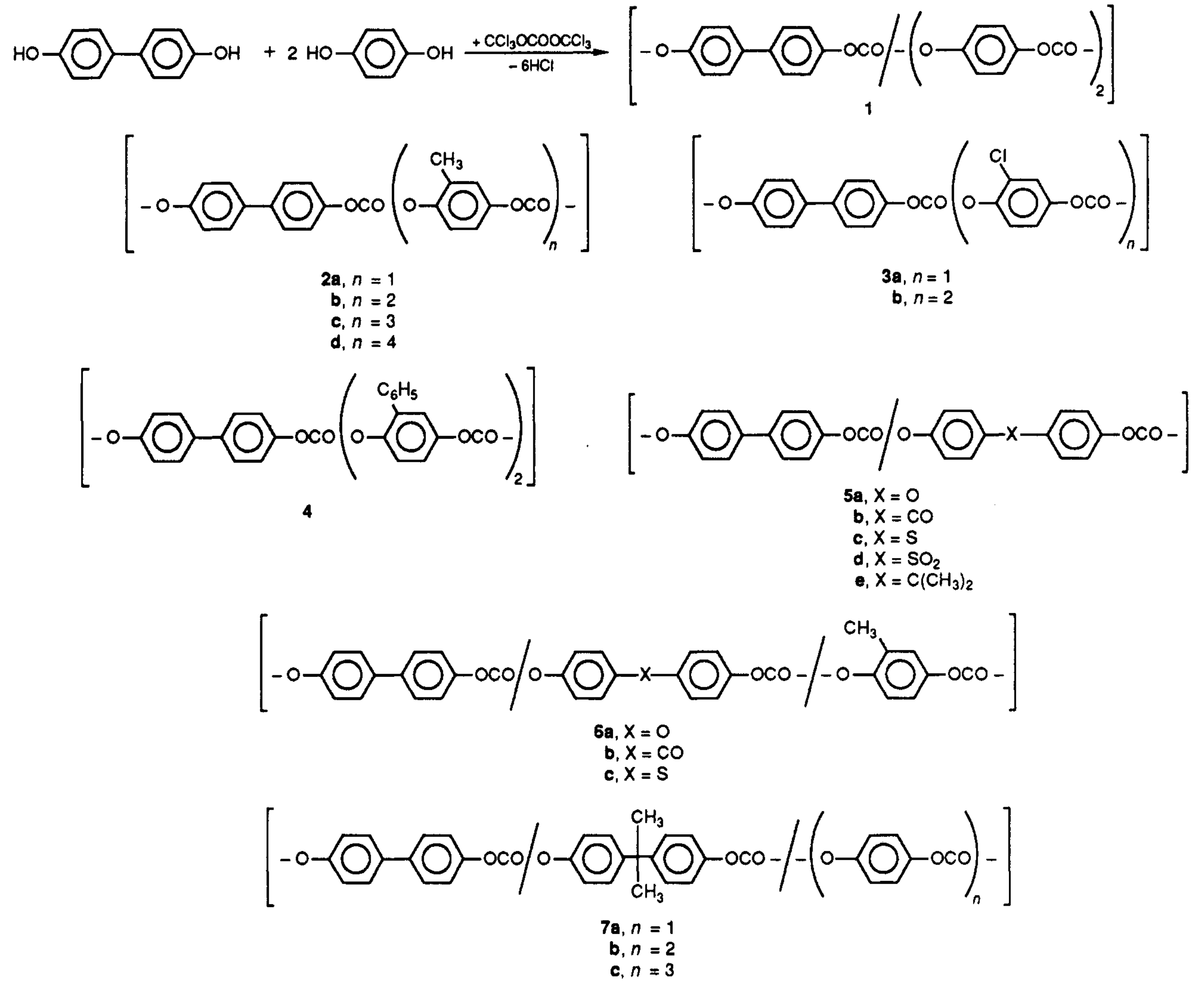


Table I
Yields and Properties of Binary Copolycarbonates Prepared from 4,4′-Dihydroxybiphenyl and Various Hydroquinones

polym formula	feed ratio	method[a]	yield, %	η_{inh},[b] dL/g	elem formula (form wt)	elem anal.			T_g, °C	T_i, °C
							C	H		
1	1:2	A	12[c]	0.10	$C_{27}H_{16}O_9$	calcd	66.96	3.30	95–100[c]	
		B	15[c]	0.09	(484.27)	found	67.20[c]	3.50[c]	100	
2a	1:1	A	46	1.21	$C_{21}H_{14}O_6$	calcd	69.63	3.86	104	370–390
					(362.21)	found	69.40	3.80		
2b	1:2	A	68	0.81	$C_{29}H_{20}O_9$	calcd	67.99	3.90	98	340–360
		B	40	0.25	(512.32)	found	67.66	3.85		
2c	1:3	A	45	0.54	$C_{37}H_{26}O_{12}$	calcd	67.09	3.92	95	300–320
					(662.37)	found	66.88	3.81		
2d	1:4	A	42	0.31	$C_{45}H_{32}O_{15}$	calcd	66.52	3.94	93	
					(812.45)	found	66.30	3.90		
3a	1:1	A	37	0.50	$C_{20}H_{11}ClO_6$	calcd	62.77	2.87	95	400–450
					(382.65)	found	62.98	2.99		
3b	1:2	A	57	0.46	$C_{27}H_{14}ClO_9$	calcd	58.62	2.53		
					(553.17)	found	58.88	2.45	88	300–330
4	1:2	A	71	0.56	$C_{39}H_{24}O_9$	calcd	73.60	3.77		
					(636.39)	found	72.10	3.76	130	

[a] In the case of B *tert*-butylphenol was added as chain stopper. [b] Measured with $c = 2$ g/L at 20 °C in CH_2Cl_2/CF_3CO_2H (4:1 by volume). [c] Fraction soluble in CH_2Cl_2/CF_3CO_2H (4:1 by volume).

bonates are summarized in Table I. Series **5a–e** and the ternary copolycarbonates **6a–c** were designed to study the influence of the bond angle between the aromatic rings of the diphenols on the stability of the mesophase. Yields and properties of these copolycarbonates are listed in Tables II and III.

Because hydroquinone and Bisphenol A are the least expensive diphenols and thus of particular commercial importance, two ternary copolycarbonates (**7a,b**) were prepared from these monomers. All copolycarbonates prepared from unsubstituted hydroquinone and most binary copolycarbonates containing methyl- or chlorohydroquinone were isolated in the form of powders with relatively low inherent viscosities. In contrast, most copolycarbonates prepared from phenylhydroquinone **4** or other diphenols **5a–d** were obtained in the form of fibrous mate-

Table II
Yields and Properties of Binary Copolycarbonates Prepared from 4,4′-Dihydroxybiphenyl and Various Nonlinear Diphenols

polym formula	feed ratio	yield, %	η_{inh},[a] dL/g	elem formula (form wt)	elem anal.	C	H	T_g,[b] °C	T_i,[c] °C
5a	1:1	76	1.38	$C_{26}H_{16}O_7$	calcd	70.93	3.63	110	390–410
				(440.28)	found	70.73	3.59		
5b	1:1	61	0.33	$C_{27}H_{16}O_7$	calcd	71.70	3.54	95	300–330
				(452.27)	found	70.93	3.56		
5c	1:1	57	1.16	$C_{26}H_{16}O_6S$	calcd	68.43	3.51	130	
				(456.35)	found	68.52	3.53		
5d	1:1	45	0.42	$C_{26}H_{16}O_8S$	calcd	63.95	3.28	170	
				(488.32)	found	62.98	3.26		
5e	1:1	59	1.20	$C_{29}H_{16}O_6$	calcd	74.69	4.72	160	
				(466.32)	found	74.43	4.78		

[a] Measured with $c = 2$ g/L at 20 °C in CH_2Cl_2/CF_3CO_2H (4:1 by volume). [b] From DSC measurements with a heating rate of 20 °C/min. [c] Optical microscopy with crossed polarizers at a heating rate of 20 °C/min.

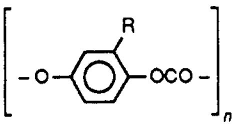
Table III
Yields and Properties of Ternary Copolycarbonates Prepared from 4,4′-Dihydroxybiphenyl, Nonlinear Diphenols, and Hydroquinones

polym formula	feed ratio	method[a]	yield, %	η_{inh},[b] dL/g	elem formula (form wt)	elem anal.	C	H	T_g,[c] °C	T_i,[d] °C
6a	1:1:1	A	30	0.54	$C_{34}H_{22}O_{10}$	calcd	69.17	3.73	90	
	1:1:1	B[a]	66	0.45	(590.34)	found	68.90	3.58	90	300
6b	1:1:1	A	58	0.53	$C_{35}H_{22}O_{10}$	calcd	69.78	3.65	105	290–330
	1:1:1	B[a]	47	0.38	(602.35)	found	69.59	3.64	97	
6c	1:1:1	A	90	0.72	$C_{34}H_{22}O_9S$	calcd	67.34	3.63	112	
					(606.43)	found	66.77	3.60		
7a	1:1:1	A	63	0.63	$C_{35}H_{26}O_9$	calcd	71.20	4.40	140	
					(590.35)	found	71.40	4.48		
7b	2:2:1	A		insol	$C_{56}H_{38}O_{15}$	calcd	70.95	4.00	130	not completely meltable
					(905.56)	found	70.75	3.89		
7c	2:4:1	A		insol	$C_{70}H_{38}O_{15}$	calcd	67.11	6.06	120	not meltable
					(125.27)	found	66.80	6.00		

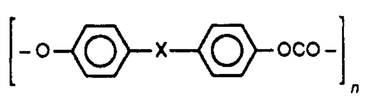
[a] 4-*tert*-Butylphenol was added as chain stopper. [b] Measured with $c = 2$ g/L at 20 °C in CH_2Cl_2/CF_3CO_2H (4:1 by volume). [c] From DSC measurements with a heating rate of 20 °C/min. [d] Optical microscopy with a heating rate of 20 °C/min.

rials, which enabled casting of tough films. Apparently a good solubility of the diphenol or its anions in water (as it is true for hydroquinone) is disadvantageous for high molecular weights. Therefore, the synthesis of 1 was repeated with addition of KNO_3 to the NaOH solution, yet results obtained in this way were not significantly different from those obtained without KNO_3. Difficulties with hydroquinone in interfacial polycondensations are well documented in literature.[10]

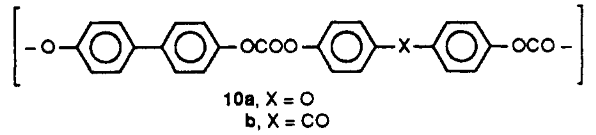
Several homopolycarbonates (**8** and **9**) and alternating copolycarbonates (**10**) were synthesized to enable unambiguous signal assignments in the ^{13}C NMR spectra of the more or less random copolycarbonates (Tables IV and V). The alternating copolycarbonates **10a–e** were synthesized by interfacial polycondensation of the bis(chloroformate) of 4,4′-dihydroxydiphenyl (eq 1). This method does not yield high molecular weights, because hydrolysis competes with polycondensation. Yet for use as spectroscopic models high molecular weights were not required. Because of their low molecular weights polycarbonates **10a–e** were not further characterized and not listed in Tables I–III. Finally several syntheses were repeated with addition of 4-*tert*-butylphenol as chain stopper to generate stable end groups (method B in Tables I–III).



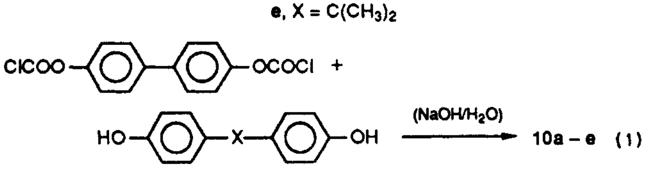
8a, R = CH_3
b, R = Cl
c, R = C_6H_5



9a, X = O
b, X = CO
c, X = S
d, X = SO_2



10a, X = O
b, X = CO
c, X = S
d, X = SO_2
e, X = $C(CH_3)_2$



NMR Spectroscopic Characterization. For a correct interpretation of structure–property relationships of copolymers it is important to have at least some basic information on composition and sequence of the different monomer units. This is, of course, also true for the copolycarbonates of this work because the interfacial cocondensation of two or three different diphenols does not necessarily result in copolycarbonates with the composition of the feed ratio and with a random sequence. Different acidities of the OH groups and different solubilities of the diphenol anions in water and dichloromethane, respectively, may cause deviations. Unfortunately, the homopolycarbonates of hydroquinone or 4,4′-dihydroxybiphenyl and copolycarbonates **7b** and **7c** are insoluble in nondestructive NMR solvents. All other polycarbonates of this work were soluble in 3:1 (by volume) mixtures of $CDCl_3$ and trifluoroacetic acid, so that all NMR measurements were conducted in this solvent system.

The ^1H NMR spectra revealed that the incorporation

Table IV
^{13}C NMR Chemical Shifts, δ (Carbonyl Groups Only), of Various Copolycarbonates Measured in $CDCl_3/CF_3CO_2H$[a]

	chemical shifts, δ (ppm relative to internal TMS[b])					
copolycarbonates of 4,4′-dihydroxybiphenyl and	x	y	z	a	b	c
4,4′-dihydroxydiphenyl ether (**5a**)	154.76	154.92	155.09			
4,4′-dihydroxybenzophenone (**5b**)	154.60	155.29	155.15			
4,4-dihydroxydiphenyl sulfide (**5c**)	154.96	154.36	154.03			
4,4′-dihydroxydiphenyl sulfone (**5d**)	154.56	155.21	155.44			
Bisphenol A (**5e**)	154.77	155.00	155.19			
methylhydroquinone (**2b**)	154.67	154.13	154.34	153.65	153.78	153.99
chlorohydroquinone (**3b**)	154.70	153.15	153.54	151.74	152.00	152.39
phenylhydroquinone (**4**)	154.76	153.88	154.21	152.97	153.65	153.38

[a] 3:1 by volume. [b] The assignments are illustrated in Figures 2 and 3.

Table V
^{13}C NMR Chemical Shifts, δ, of Various Homopolycarbonates Measured in $CDCl_3/CF_3CO_2H$[a]

	chemical shift, δ (ppm, relative to internal TMS)				
			further carbons[b]		
polycarbonate of	C=O[b]	C—O[b]			
4,4′-dihydroxydiphenyl ether	155.02	155.94 146.62	122.79	120.43	
4,4′-dihydroxybenzophenone	155.13	152.14	135.14	133.10	121.79
4,4′-dihydroxyphenyl sulfide	154.01	150.45	134.82	133.00	122.30
4,4′-dihydroxydiphenyl sulfone	155.23	151.21	138.60	130.22	123.04
Bisphenol A	155.07	149.71	149.05	128.68	120.76
			43.15	31.00	
methylhydroquinone (**8b**)	154.03				
	153.82	149.36	132.77	124.23	123.00
	153.70	147.97	120.15		16.00
phenylhydroquinone[b] (**8c**)	153.52				
	153.25	149.50	136.80	135.70	129.30
	152.65	146.20	123.60	121.20	

[a] 3:1 by volume. [b] All signals are multiplets.

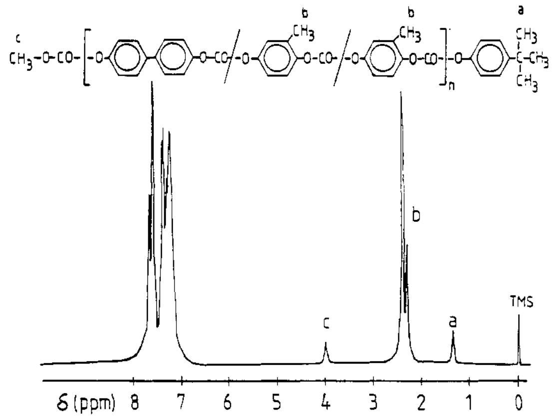


Figure 1. 100-MHz ^{1}H NMR spectrum of copolycarbonate **2b** prepared by interfacial condensation in the presence of 4-*tert*-butylphenol (measured in $CDCl_3/CF_3CO_2H$ 3:1 by volume).

of methylhydroquinone into copolycarbonates **2a–d** is slightly lower than expected from the feed ratio. Obviously the lower solubility of the anion in dichloromethane compared with that of 4,4′-dihydroxybiphenyl is responsible for this result. The same results are expected for the copolyesters of hydroquinone (1) and chlorohydroquinones **3a** and **3b**, yet in these cases ^{1}H NMR spectra were not measurable or a reliable evaluation of the signal patterns was not feasible. The ^{1}H NMR spectra also indicate that the incorporation of 4-*tert*-butylphenol, which is easily detectable by a sharp singlet at 1.33 ppm (Figure 1), is higher than the feed ratio. Correspondingly both yields and viscosities of samples prepared with chain stopper were lower than those synthesized without (Tables I–III). Furthermore, the ^{1}H NMR spectra revealed that all polycarbonates precipitated into methanol contain methyl carbonate end groups (Figure 1). Obviously the chloroformate end groups resulting from the excess of triphosgene were not completely hydrolyzed during the interfacial condensation.

The ^{13}C NMR spectra of all copolycarbonates revealed that the carbonyl signals are sensitive to sequence effects, i.e., to diads. The simple signal patterns were found for the copolycarbonates **5a–e**. All three possible diads are well resolved and exhibit signal intensities that agree with random sequence. As demonstrated by parts A–C of Figure 2, the structure of the signal patterns may vary with the nature of the diphenols. The signal assignments are based on comparisons with spectra of homopolycarbonates **9a–e** and alternating copolyesters **10a–e**. In contrast to the random copolymers **5a–e**, the ^{13}C NMR spectra of the alternating copolymers **10a–e** only exhibit one CO signal. This CO signal agreed in all cases with the strongest peak of the triplet patterns of **5a–e** (signal y in Figure 2 and Table IV), and, thus, the ^{13}C NMR data of **10a–e** are not separately listed in Tables IV or V. In order to check the influence of different relaxation times on the signal intensities of the CO signal patterns, most samples were measured with two different relaxation delays (4 and 10 s). As expected, slightly higher intensities were found for the longer delay time, yet the intensity ratios of different diads did not change.

When methyl-, chloro-, and phenylhydroquinone are used as components of copolycarbonates, more complex CO signal patterns are obtained. The nonsymmetrically placed substituents of these diphenols cause a constitutional sequence isomerism. Thus, the copolycarbonates **2a–d**, **3a,b**, and **4** may possess sequences with six different diads, and as shown in Figure 3 all six diads could be resolved. The signal assignments are based on comparisons with low molecular weight model compounds derived from cresols, chlorophenols, or phenylphenols. Yet a detailed discussion of synthesis and characterization of these model compounds is beyond the scope of

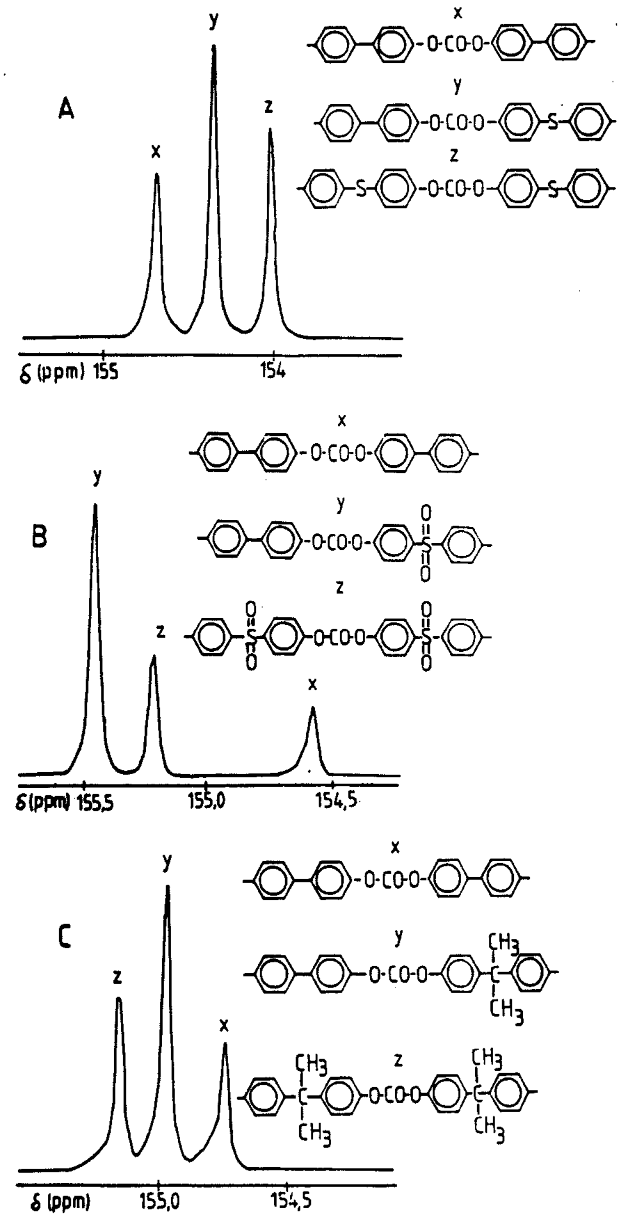


Figure 2. 75.4-MHz ^{13}C NMR spectra of three binary copolycarbonates measured in $CDCl_3/CF_3CO_2H$ (3:1 by volume): (A) **5c**; (B) **5d**; (C) **5e**.

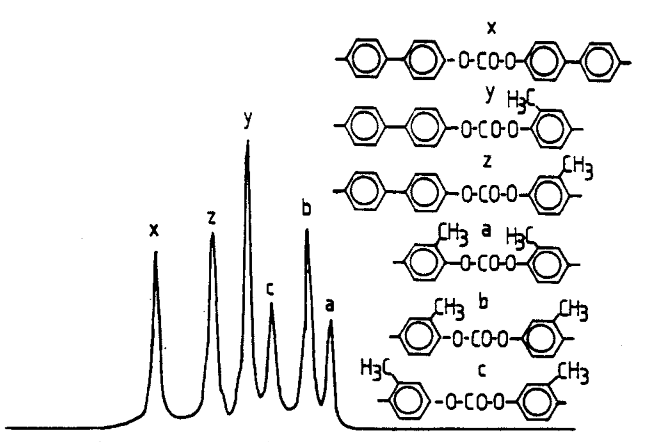


Figure 3. 75.4-MHz ^{13}C NMR spectrum of copolycarbonate **2b** measured in $CDCl_3/CF_3CO_2H$ (3:1 by volume).

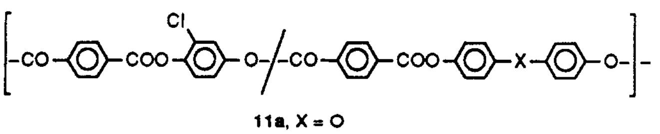
this work and will be published separately. Anyway, the ^{13}C NMR spectra of these copolycarbonates confirm the formation of random sequences and a lower rate of incorporation for chloro- or methylhydroquinone (Figure 3).

Thermal Properties. All copolycarbonates were subjected to DSC measurements with a heating or cooling rate of 20 °C/min. The DSC traces of all random copolycarbonates have in common that a glass transition step is detectable, whereas endotherms or exotherms are completely lacking. Thus, the DSC measurements indicate an amorphous character of these samples, which was confirmed by WAXS powder patterns. Furthermore, the DSC traces do not give any clear-cut information on the existence of mesophases. The reason for this negative result was revealed by optical microscopy. Those polycarbonates forming a nematic melt possess a broad temperature range of isotropization. The isotropization of most copolycarbonates occurs over a range of ca. 20 °C, yet in some cases (e.g., **2c**), this range may be as broad as 50 °C. Obviously chemical heterogeneity and broad block length distributions are responsible for this effect.

In the case of copolycarbonate **1**, the crude material (intensively washed with methanol and water yet not reprecipitated) and the soluble fraction (see Table I) showed quite different properties. The crude material did not melt up to ca. 400 °C, where darkening and degradation prevented further characterization. The soluble fraction formed an isotropic melt above the glass transiton temperature, T_g. Regardless of end groups, homogeneous melts with the typical threaded schlieren texture of a nematic phase were observed for the copolycarbonates of methylhydroquinone (**2a–c**). The stability of the nematic phase decreases with increasing molar fraction of methylhydroquinone and has almost completely vanished in the case of **2d**. Again a nematic melt was found for both copolycarbonates of chlorohydroquinone (**3a,b**), whereas the copolymer of phenylhydroquinone **4** only forms an isotropic melt. Thus, these results demonstrate that the substituent of the hydroquinone unit has an enormous influence on the properties of copolycarbonates **1–4**.

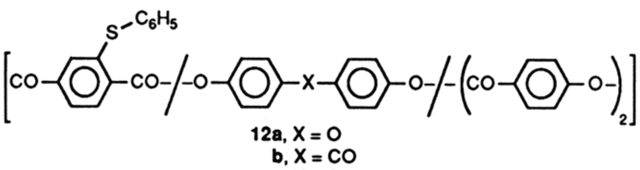
In series **5a–e** nematic phases were observed for the copolycarbonate of 4,4′-dihydroxybenzophenone (**5b**) and for **5a**, as described previously.[1] All other members of series **5** only form isotropic phases. The properties of series **6a–c** parallel those of **5a–c**. The copolycarbonates **5a,b** and **6a,b** form a nematic melt; **5c–e** and **6c** do not. These results underline that the thermotropic character of the copolycarbonates strongly depends on the structure of the diphenols combined with 4,4′-dihydroxybiphenyl. Of particular interest in this connection is the role the bond angle of X plays in series **5a–e** and **6a–c**.

Lenz and Jin[11] have studied the same parameter in the copolyesters **11**. They stated (without mentioning

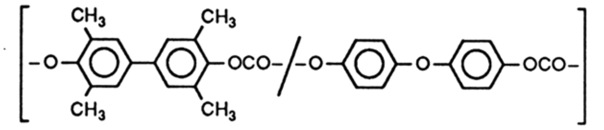


11a, X = O
b, X = CO
c, X = S
d, X = SO_2
e, X = $C(CH_3)_2$

the origin of their information) that the angles of X agree with each other within the range of 5°. Therefore, they attributed the unfavorable influence of S, SO_2, and $C(CH_3)_2$ groups on the stability of mesophases to their steric demands (i.e., the space-filling character) relative to the ether oxygen in **12a**. However, the X-ray analyses of low molecular model compounds indicate that S, SO_2, and $C(CH_3)_2$ groups linking aromatic rings adopt bond angles in the range of 100–110° whereas 121 and 123° angles



12a, X = O
b, X = CO
c, X = S
d, X = SO_2
e, X = $C(CH_3)_2$



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were found for 4,4′-disubstituted benzophenones and diphenyl ethers, respectively.[12–14] Thus, it is obvious that the properties of the copolycarbonates **5a–e** and **6a–c** depend mainly on the bond angles. Only nonlinear diphenols with bond angles >120 °C allow the stabilization of a nematic phase in copolycarbonates **5a–e** or **6a–c**. This result perfectly agrees with studies of the copolyesters **12a–e**. Only copolyesters **12a** and **12b** form a nematic melt.[15]

The role of the 4,4′-dioxybiphenyl unit as mesogenic group is underlined by two comparisons. First, in series **2a–d** the stability of the nematic phase decreases with an increasing molar fraction of methylhydroquinone. Second, a copolycarbonate prepared from 4,4′-dihydroxytetramethyldiphenyl and 4,4′-dihydroxydiphenyl ether (**13**) exclusively formed an isotropic melt. Obviously the lower *L*/*D* ratio of the tetramethylbiphenyl unit suffices to destabilize the mesophase. Another interesting observation concerns the role of OH end groups. When the copolycarbonates **6a** and **6b** were synthesized without chain stoppers (like all copolycarbonates of this work) the viscous melt if annealed above T_g slowly solidified upon further heating. Birefringence was observed, yet it was not clear whether it was stress induced or the result of a nematic phase. In contrast, the samples prepared with *tert*-butylphenol end groups displayed texture of nematic phase and with formation of birefringent droplets (Figure 4). Because of this observation several syntheses were repeated with addition of 4-*tert*-butylphenol to check the reproducibility of properties (method B in Tables I–III).

Finally the thermostability of several copolycarbonates was determined to find out if the isotropization is affected by thermal degradation. The short-time thermostabilities were measured by thermogravimetric analyses conducted at a heating rate of 10 °C/min in air. The data listed in Table VI show that all polycarbonates begin to degrade around or below 350 °C, possibly influenced by the oxidative instability of the unblocked OH end groups. Thus these data and the microscopic observation suggest that mainly in the case of copolycarbonates containing hydroquinones the reversibility of isotropization is indeed affected by thermal degradation.

Conclusion

Owing to the additional oxygen, the carbonate group possesses one bond angle more than ester groups and is thus less prone to adopt the linear conformation required for the stabilization of a mesophase. The lack of a mesophase in the case of polycarbonate **4** and the existence of a nematic phase in the case of phenylhydroquinone terephthalate may serve as experimental evidence for this hypothesis. The formation of nematic phases up to temperatures around 350 °C in the case of polycarbonates **2a,b**, **3a,b**, and **5a,b** indicates, on the other hand, that the carbonate group is much more compatible with the steric requirements of a nematic order than previously expected on the basis of a bond angle in the range of 120–130° (bond angles of oxygens: ca. 120 °C in esters and 123 °C in aromatic ethers). Possibly vibrations widening the bond angle at higher temperatures (so-called dynamic bond angle) may contribute to a favorable conformation in the nematic melt, as recently discussed for polyesters of nonlinear diphenols.[15] Anyway, the present results clearly demonstrate that carbonate groups are well compatible with the mesogenic character of aromatic main-chain polymers.

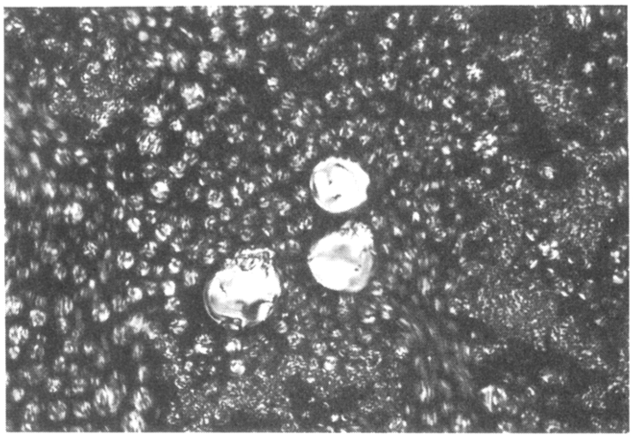

Figure 4. Micrograph taken with crossed polarizers (original magnification ca. ×320 (the micrograph as printed is 60% of the original)): nematic droplets of copolycarbonate **5a** at 290 °C.

Table VI
Thermogravimetric Analyses of Copolycarbonates Conducted with a Heating Rate of 10 °C/min in Air

polym formula	η_{inh}, dL/g	temp with following wt loss 1%	5%	10%	20%	50%
2a	1.21	220	323	348	375	420
2b	0.81		377	404	431	460
3b	0.46		356	395	455	536
4	0.56		295	407	425	473
5a	1.38	236	394	415	442	475
5b	1.16	347	417	427	445	490
6a	0.72		364	370	392	421

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Registry No. 1 (copolymer), 126190-35-0; **2** (copolymer), 123585-70-6; **3** (copolymer), 126190-36-1; **4** (copolymer), 126190-37-2; **5a** (copolymer), 123585-71-7; **5b** (copolymer), 126190-

38-3; **5c** (copolymer), 126190-39-4; **5d** (copolymer), 126190-40-7; **5e** (copolymer), 123585-72-8; **6a** (copolymer), 126190-41-8; **6b** (copolymer), 126190-42-9; **6c** (copolymer), 126190-43-0; **7** (copolymer), 126190-44-1; **8a** (homopolymer), 126190-45-2; **8** (SRU), 126326-98-5; **8b** (copolymer), 126216-14-6; **8b** (SRU), 126326-97-4; **8c** (copolymer), 85023-39-8; **8c** (SRU), 85086-67-5; **9a** (copolymer), 30527-04-9; **9a** (SRU), 32129-53-6; **9b** (copolymer), 126190-46-3; **9b** (SRU), 94289-16-4; **9c** (copolymer), 29832-45-9; **9c** (SRU), 28930-32-7; **9d** (copolymer), 30231-71-1; **9d** (SRU), 28930-33-8; **10a** (copolymer), 126190-47-4; **10a** (SRU), 126190-52-1; **10b** (copolymer), 126190-48-5; **10b** (SRU), 126190-53-2; **10c** (copolymer), 126190-49-6; **10c** (SRU), 126190-54-3; **10d** (copolymer), 126190-50-9; **10d** (SRU), 126190-55-4; **10e** (copolymer), 126190-51-0; **10e** (SRU), 28932-67-4.

Synthesis of 2-(2-Hydroxyphenyl)-2*H*-benzotriazole Monomers and Studies of the Surface Photostabilization of the Related Copolymers

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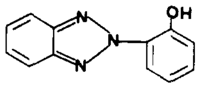
ABSTRACT: An improved three-step process for the synthesis of 2-(vinylhydroxyphenyl)-2*H*-benzotriazole derivatives is discussed. In addition, some studies of the surface photooxidation of styrene/vinylbenzotriazole copolymers were carried out. The results indicate that the 2-(vinylhydroxyphenyl)-2*H*-benzotriazole derivatives, whether used as an additive or introduced into the polymer chain, are unsuitable as a photostabilizer for the surface of polystyrene while the bulk of polystyrene is protected when very low concentrations of the derivatives are used.

Introduction

For most commercial polymers (acrylics, cellulosics, polyesters, polystyrene, poly(vinyl chloride), etc.), some type of photostabilization is required in order to protect such materials against the effect of UV irradiation. For example, after a few weeks of exposure to sunlight, polypropylene deteriorates severely and unsaturated polyesters yellow.

Several types of heat and light stabilizers can be employed:[1-16] (a) UV screeners; (b) UV absorbers; (c) excited-state quenchers; (d) free radical scavengers and/or hydroperoxide decomposers. The choice of satisfactory photostabilizers for light exposure depends upon the end use to which the polymer is put. Generally, a combination of different additives is necessary to obtain a synergistic effect.

2-(2-Hydroxyphenyl)-2*H*-benzotriazoles have been indicated as powerful ultraviolet-absorbing molecules, and a number of compounds with this basic structure have been synthesized and used as UV absorbers.[2-4,17-19]



When the surface to volume ratio is high, as in films, coatings, and fibers, such additives, because of their low molecular weights, may exhibit low compatibility and can also be lost by exudation, volatilization, or leaching during fabrication or end use. In recent years, a significant effort has been made to prepare stabilizers with better compatibility and higher molecular weight by introducing long alkyl chains into the additive molecule[2] or by synthesizing the appropriate monomer and copolymerizing it into the polymer backbone.[20-30]

Methods have been reported in the literature for the synthesis of such monomers; the most important structures are shown in Table I. These monomers have been then introduced by random copolymerization or by grafting. Styrene, acrylates, and butadiene derivatives of (vinylhydroxyphenyl)-2*H*-benzotriazoles have been obtained in this way.

It has not yet been demonstrated whether the presence of a photostabilizing moiety in the surface (outermost 50 Å) is capable of inhibiting surface photooxidation. In fact, ESCA studies on the surface photooxidation of commercial polymers such as polystyrene indicate that the extent and nature of the degradation are not typical of the bulk material and thus conventional photostabilizing substances may not be effective. In addition, the photostability of the appropriate stabilizer in the surface regions, where the partial pressures of oxygen and the photon flux are higher than those in the bulk material, may differ from that of the bulk material.

Polyesters containing low percentages of (hydroxyphenyl)-2*H*-benzotriazole in the chain have been studied by ESCA in earlier work.[31] Initially, the ESCA analysis showed that the amount of nitrogen (arising from the UV stabilizer) on the surface layer was similar to that found by elemental nitrogen analysis of the bulk poly-

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