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Synthesis and characterization of poly(ester carbonate)s based on bisphenol A and diacid chlorides: a new synthetic approach*

Abbas-Alli G. Shaikh and Swaminathan Sivaram†
Division of Polymer Chemistry, National Chemical Laboratory, Pune 411008, India
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Four new ester carbonate monomers were prepared by reaction of the mono(methylcarbonate) of bisphenol A with dimethyldiphenylsilane, tetraphenylsilane, 2,6-naphthalene and *trans*-1,4-cyclohexane diacid chlorides at 0°C in the presence of an acid acceptor, triethylamine. Monomers were characterized by melting point, ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.), infra-red (i.r.) spectroscopy, mass spectrometry, elemental analysis and thermogravimetric analysis (t.g.a.). Self-polycondensation of monomers in the presence of titanium tetraisopropoxide catalyst resulted in the formation of poly(ester carbonate)s. The structural characterization of polymers was carried out by ^{1}H and ^{13}C n.m.r. and i.r. spectroscopy. Thermal properties were evaluated by differential scanning calorimetry and t.g.a. and crystallinity by X-ray diffraction.

(Keywords: bisphenol A/diacid chlorides; self-polycondensation; poly(ester carbonate)s)

INTRODUCTION

Poly(aryl ester carbonate)s are a class of high-performance engineering polymers that possess a desirable combination of the properties of both poly(aryl carbonate)s and poly(aryl ester)s. Poly(aryl ester carbonate)s based on bisphenol A and tere/iso acids/acid chlorides or dimethyl/diphenyl esters are generally prepared by interfacial phosgenation[1-6] or by melt-phase polycondensation with diphenylcarbonate[7-9]. Very few reports are extant in the literature that describe the preparation of poly(aryl ester carbonate)s based on bisphenol A and dicarboxylic acid moieties other than tere/iso[10-12]. These methods of synthesis involve the use of toxic phosgene and expensive diphenylcarbonate. Therefore, synthetic methods that avoid the use of phosgene or diphenylcarbonate are preferable.

We have earlier reported the synthesis of poly(aryl ester carbonate)s based on bisphenol A and tere/isophthaloyl chlorides using dimethylcarbonate[13]. In continuation of this work, we now report the synthesis of poly(ester carbonate)s derived from bisphenol A, dimethylcarbonate and various diacid chlorides using a two-step reaction sequence. The first step involves the preparation of a new class of ester carbonate monomers, which is followed by self-condensation in the melt phase to poly(ester carbonate)s.

EXPERIMENTAL

Materials

2,6-Naphthalene dicarboxylic acid (Aldrich, USA) was used as received. Dimethylbis(4-carboxylphenyl)silane and diphenylbis(4-carboxylphenyl)silane were prepared according to a literature procedure[14]. 1,4-Cyclohexane dicarboxylic acid (*trans*) was prepared from 1,4-cyclohexanedimethanol (Aldrich, USA) by alkaline $KMnO_4$ oxidation at room temperature. Titanium tetraisopropoxide (Aldrich, USA) was used as received. The mono(methylcarbonate) of bisphenol A was prepared and isolated according to a procedure described elsewhere[13].

Triethylamine (S.D. Fine Chemical, Bombay, India) was refluxed with KOH pellets, distilled under nitrogen and stored over KOH pellets. Dichloromethane was dried by distillation over phosphorus pentoxide and stored over 4 Å molecular sieves. Petroleum ether and benzene solvents were dried with sodium wire.

Measurements

^{1}H n.m.r. spectra of monomers and polymers were recorded on a Varian FT-80A or Bruker 200 MHz instrument, and ^{13}C n.m.r. spectra were recorded on a Bruker 200 MHz n.m.r. spectrometer. I.r. spectra were recorded on a Perkin-Elmer 16PC *FT* i.r. instrument. Mass spectra of monomers were recorded on a Finnigan MAT-1020-B mass spectrometer. Elemental analyses were carried out using a Carlo Erba (Italy) EA 1108 carbon–hydrogen analyser. Melting points were determined in open capillary tubes using a melting-point apparatus (Campbell Electronics, India) and are uncorrected. The inherent viscosity of polymer solutions was determined at 30°C in chloroform and phenol/tetrachloroethane solvents, 0.5% (w/v), using an automated (Schott Gerate AVS 24, Germany) Ubbelohde viscometer. D.s.c. measurements were performed on a

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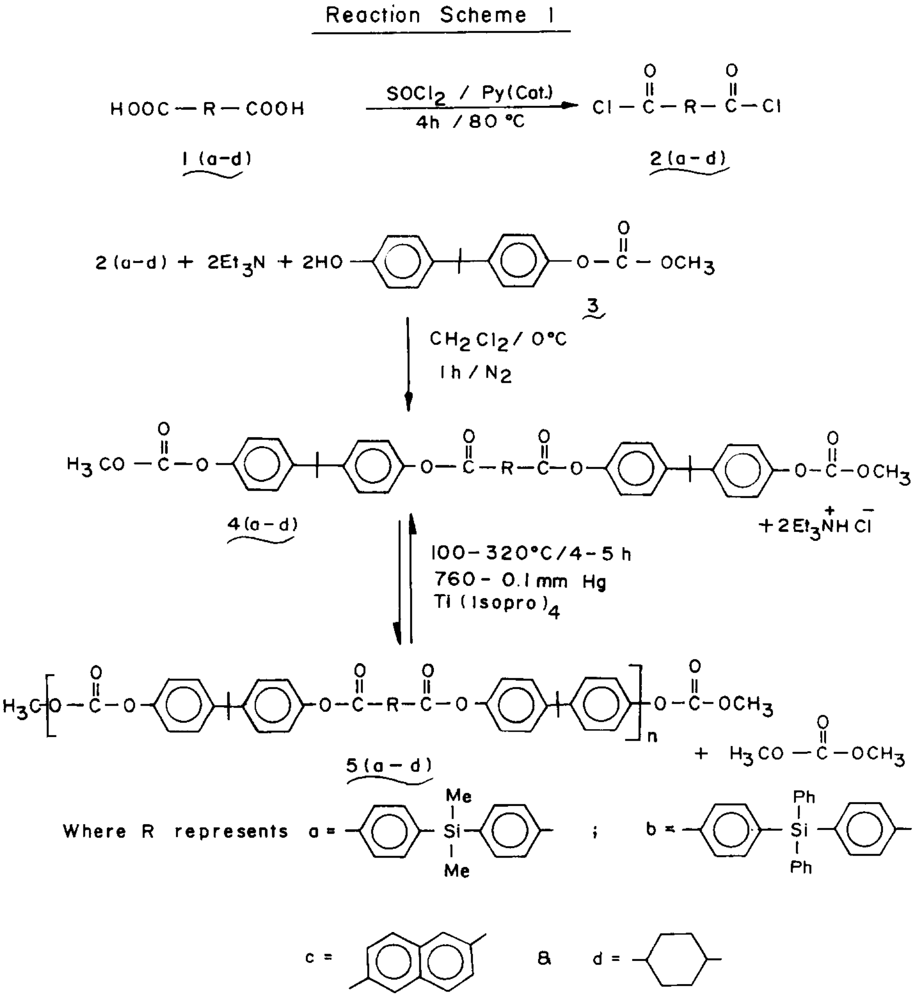
† To whom correspondence should be addressed

Table 1 Characterization of ester carbonate monomers **4a–d**

Monomer	Yield (%)	M.p. (°C)	^{1}H n.m.r. (CDCl$_3$/TMS), δ (ppm)	I.r., Nujol (cm^{-1})	Mass ion peaks (%)	Elemental analysis (%)		
							Calc.	Found
4a	94	64	0.6 (s, 6H), 1.7 (s, 12H), 3.9 (s, 6H), 7–7.4 (m, 16H), 7.6–7.8 (d, 4H, *ortho* to Si), 8.2–8.4 (d, 4H, *ortho* to ester)	1727 (ester) 1216 (C–O) 1763 (carbo) 1266 (C–O) 840 (Si(CH$_3$))	583 (10) 344 (100)	C H	71.77 5.74	71.24 5.75
4b	96	85	1.7 (s, 12H), 3.9 (s, 6H), 7–7.3 (m, 16H), 7–7.6 (m, 10H, Si(Ph)), 7.7–7.8 (d, 4H, *ortho* to Si), 8.2–8.4 (d, 4H, *ortho* to Si(Ph))	1728 (ester) 1216 (C–O) 1764 (carbo) 1266 (C–O) 1430 (Si(Ph)) 1105 700	373 (5) 225 (100)	C H	75.00 5.41	74.79 5.21
4c	95	205–207	1.7 (s, 12H), 3.9 (s, 6H), 7–7.4 (m, 16H), 8–8.4 (dd, 4H), 8.8 (s, 2H)	1730 (ester) 1224 (C–O) 1749 (carbo) 1274 (C–O)	467 (30) 329 (100)	C H	73.40 5.31	73.85 5.64
4d	97	165	1.7 (s, 14H), 2.3 (d, 4H), 2.6 (bs, 2H), 3.9 (s, 6H), 7–7.4 (m, 16H)	1750 (ester) 1216 (C–O) 1765 (carbo) 1266 (C–O)	583 (5) 395	C H	71.18 6.21	71.27 6.25



Scheme 1 The synthetic approach used in this work

Table 2 Polymerization of ester carbonate monomers **4a–d** using 1 mol% Ti(iPrO)$_4$ catalyst

Monomer	Polymerization conditions: temp. (°C)/time (min)/ pressure (mmHg)	Yield[a] (%)	η_{inh}[b] (dl g^{-1})
4a	100–200/30/N$_2$, 200/30/N$_2$, 200/60/0.1, 250/60/0.1 280/60/0.1, 320/30/0.1	86	0.3
4b	same as above	82	0.35
4c	220/60/N$_2$, 220/60/0.1, 280/60/0.1, 320/30/0.1	80	0.49[c]
4d	200/60/N$_2$, 200/60/0/1, 250/60/0.1, 280/60/0.1, 320/30/0.1	82	0.39

[a] Calculated after precipitation from methanol
[b] Determined in chloroform
[c] Determined in phenol/tetrachloroethane (60/40 w/w) solvent mixture

Table 3 ^{1}H n.m.r. study of monomers and polymers

Expected ratio of protons[a]	Observed ratio of protons			
	Monomer	Ratio	Polymer	Ratio
1/1.14/0.85	**4a**	1/1.25/0.89	**5a**	1/1.10/0.80
1/0.88/0.66	**4b**	1/0.88/0.65	**5b**	1/0.72/0.75
1/2.66/2	**4c**	1/2.80/1.80	**5c**	1/2.58/1.78
1/0.72[b]	**4d**	1/0.65	**5d**	1/0.60

[a] Expected ratio of R / bisphenol A (aromatic) / isopropylidene protons in **4a–d** and **5a–d**
[b] See text

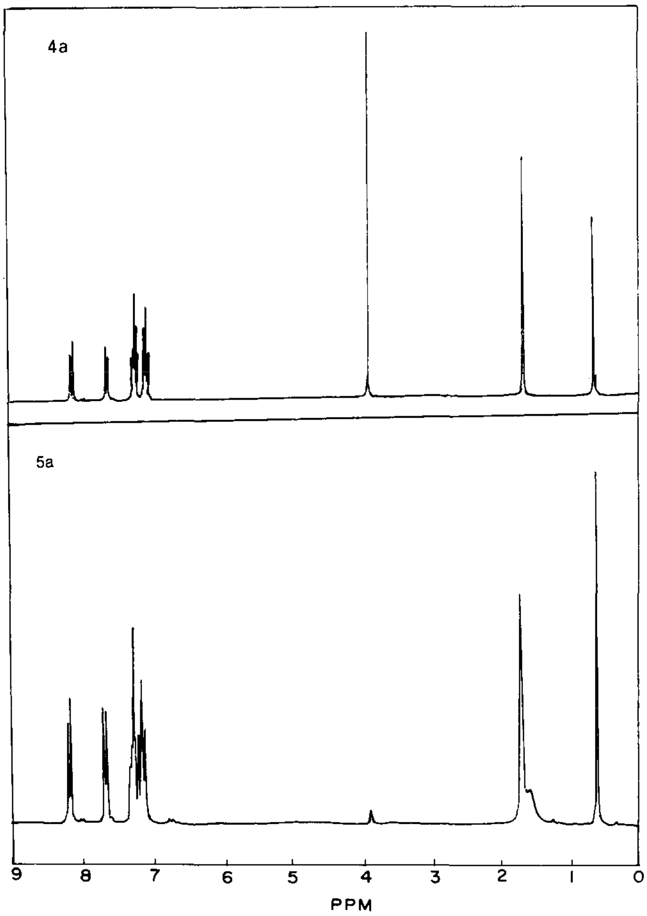


Figure 1 ^{1}H n.m.r. spectra of monomer **4a** and polymer **5a**

Perkin-Elmer DSC-7 in aluminium pans at a heating rate of 20°C min^{-1}. The samples were heated to 250°C twice and cooled to room temperature at a rate of 200°C min^{-1}; finally, the glass transition temperature (T_g) of third runs were recorded. The thermogravimetric analysis was conducted with a Perkin-Elmer TGA-7 at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. The X-ray diffractograms were obtained with a Philips X-ray unit (Philips generator, PW-1730) using Ni-filtered Cu Kα radiation.

Syntheses and polymerizations

Synthesis of diacid chlorides. Dicarboxylic acids **1a–d** were reacted with excess thionyl chloride and refluxed for 4 h at 90°C. Excess thionyl chloride was removed under suction and the resulting diacid chlorides **2a–d** were isolated by crystallization from a suitable solvent.

*Synthesis of ester carbonate monomer **4a**.* To a 50 ml two-necked round-bottomed flask equipped with a nitrogen inlet, guard tube and stirring arrangement, the mono(methylcarbonate) of bisphenol A (**3**) (1 g, 0.0035 mol) and triethylamine (0.35 g, 0.0035 mol) were added in 25 ml dry dichloromethane under nitrogen atmosphere. The flask was placed in an ice–salt mixture. Freshly crystallized and thoroughly dried bis(4-chlorocarbonylphenyl)dimethylsilane (**2a**) (0.59 g, 0.0017 mol) was added at once and the reaction mixture was stirred at 0°C for 1 h. Thin-layer chromatography of the reaction mixture demonstrated that **3** was completely converted to the ester carbonate compound **4a**. The reaction product was washed with distilled water to remove acid chloride salt. Its complete removal was achieved by passing it through a column of silica gel (60–120 mesh) using chloroform as solvent. The yield of **4a** after purification was 1.36 g (94%). All other monomers were prepared in the same manner and characterized by melting point, ^{1}H n.m.r., i.r., mass spectra and elemental analyses; results are shown in *Table 1*. The ^{13}C n.m.r. spectra are shown in *Figure 3*.

*Polymerization of **4a**.* In a typical procedure, monomer **4a** (250 mg, 3×10^{-4} mol) and a solution of titanium tetraisopropoxide (0.74 mg, 3×10^{-6} mol) prepared in 0.38 ml dry benzene were introduced into a glass tube (i.d. 3 cm) under a nitrogen atmosphere, placed in a silicone oil bath and heated to 100°C. The temperature was raised from 100 to 200°C over a period of 30 min and held at 200°C for 30 min. Thereafter the tube was evacuated to 0.1 mmHg and the reaction was allowed to proceed for 60 min each at 200, 250 and 280°C and for 30 min at 320°C. The resulting pale brown polymer was cooled to room temperature and dissolved in chloroform solvent. Polymer **5a** was precipitated in methanol and dried *in vacuo*. The yield of **5a** was 191 mg (86%). It had an inherent viscosity of 0.3 dl g^{-1} at 30°C in chloroform.

All other monomers were polymerized in the same manner with an optimum time–temperature–pressure profile and are shown in *Table 2*.

Table 4 T.g.a. of monomers, and t.g.a. and d.s.c. of polymers

	T.g.a. (°C)					T.g.a. (°C)			D.s.c.
		T_{max}[a]					T_{max}		
Monomer	*IDT*	1	2	3	Polymer	*IDT*	1	2	T_g (°C)
4a	238	269	404	522	**5a**	340	489	–	168
4b	342	363	576	–	**5b**	413	520	626	191
4c	293	310	498	–	**5c**	452	526	–	183
4d	274	324	468	–	**5d**	368	480	–	151

[a] T_{max} = the temperature at which maximum decomposition was observed

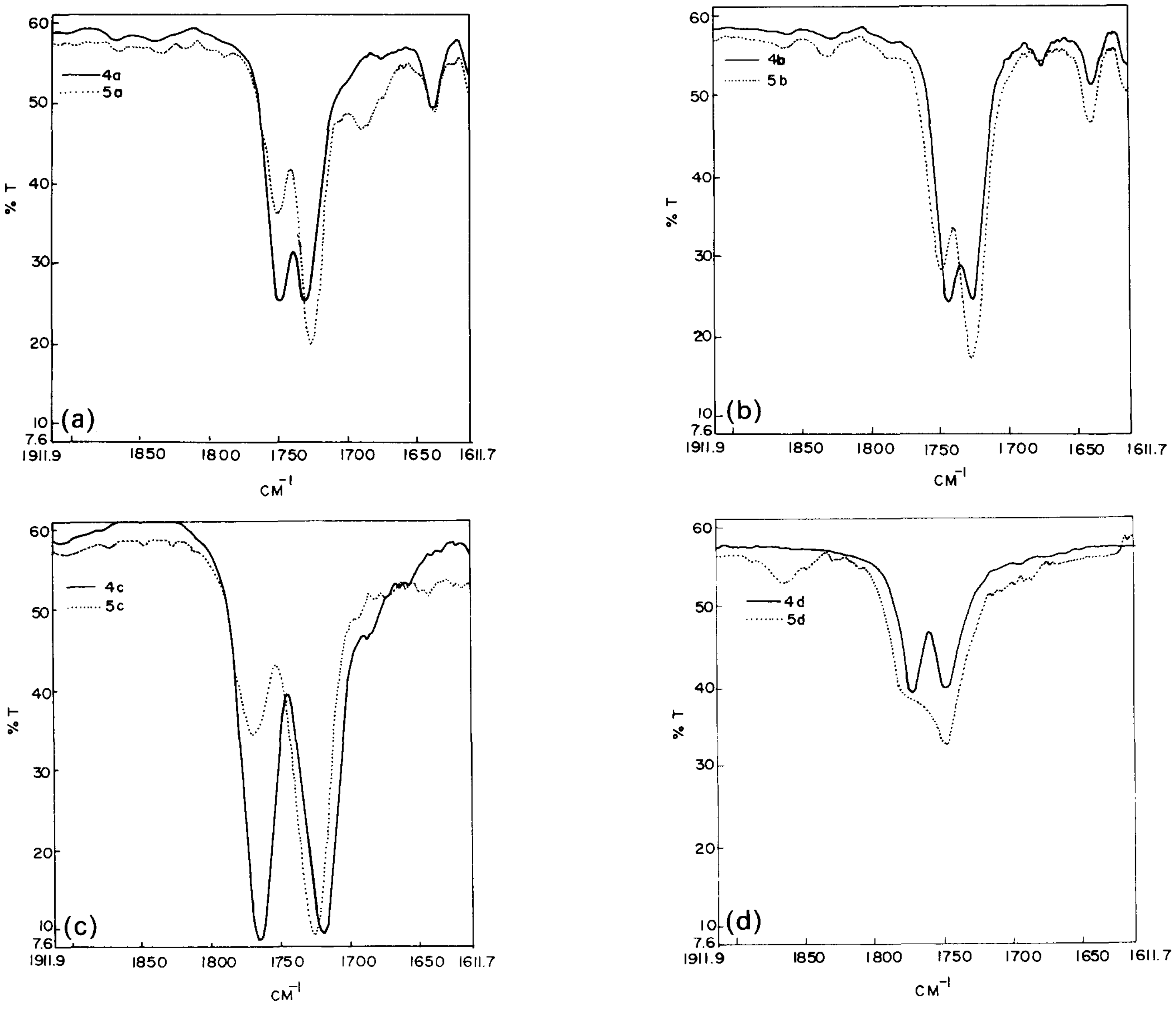


Figure 2 I.r. spectra of monomers **4a–d** and polymers **5a–d**

RESULTS AND DISCUSSION

The synthetic approach used in this study is shown in *Scheme 1*. Dicarboxylic acids **1a–d** were converted to corresponding diacid chlorides **2a–d** by reaction with excess thionyl chloride. Reaction of mono(methylcarbonate) of bisphenol A (**3**) with **2a–d** in dichloromethane at 0°C in the presence of an acid acceptor such as triethylamine gave new ester carbonate monomers **4a–d** in quantitative yield. The ^{1}H n.m.r. spectra of **4a–d** gave a singlet at 3.9 ppm due to the carbomethoxy group (*Table 1*); the i.r. results show two C=O absorptions of equal intensity, due to both ester carbonyl at 1727–1750 cm^{-1} and carbonate carbonyl at 1749–1765 cm^{-1}. A representative ^{1}H n.m.r. spectrum of

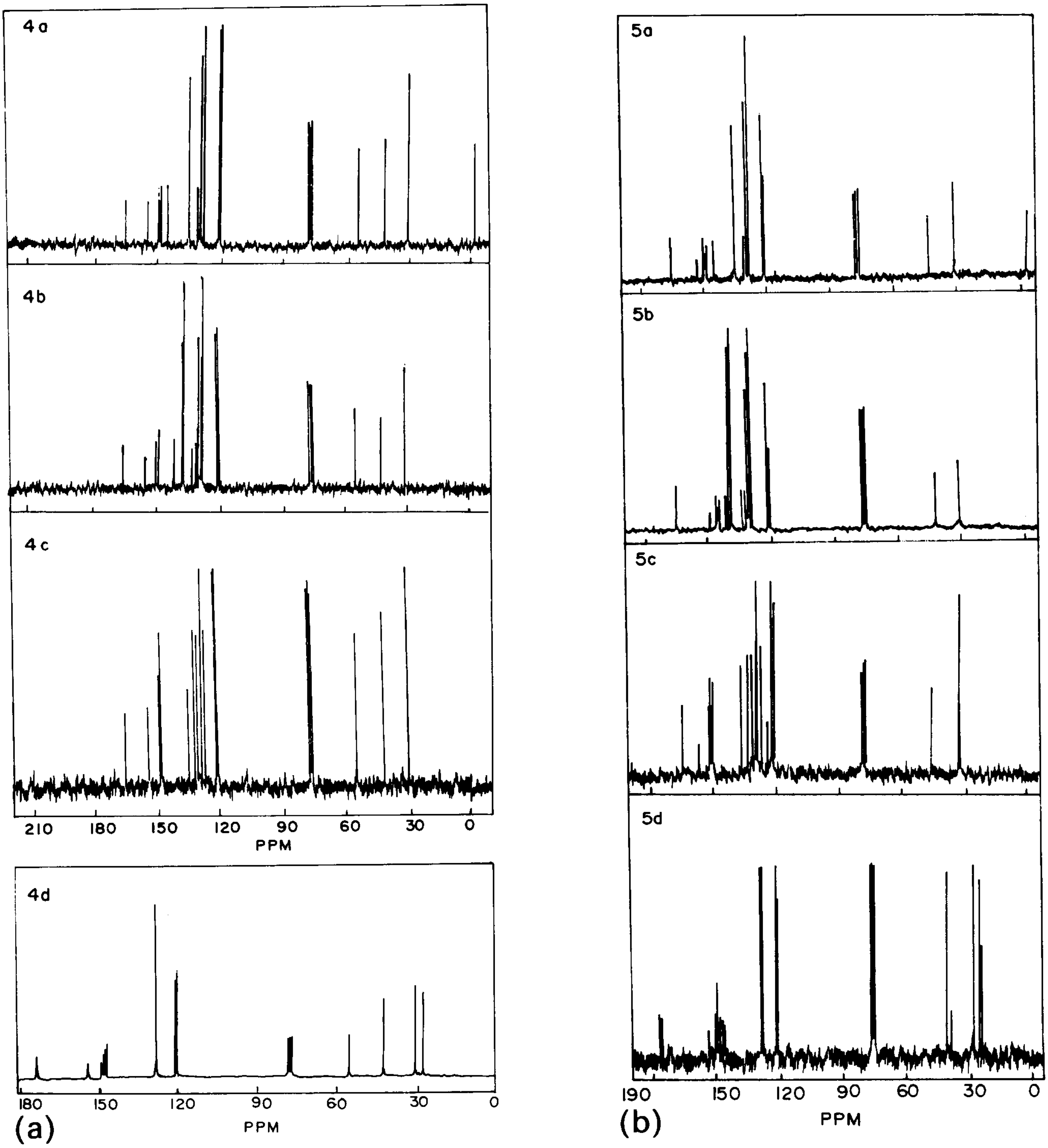


Figure 3 ^{13}C n.m.r. spectra of monomers **4a–d** and polymers **5a–d**

monomer **4a** is shown in *Figure 1*. I.r. spectra of monomers **4a–d** are shown in *Figure 2*. Titanium tetraisopropoxide was chosen as catalyst for polymerization of monomers **4a–d** based on an earlier study. The monomers **4a–d**, by virtue of two methylcarbonate end-groups, underwent smooth self-condensation in the melt, in the presence of titanium tetraisopropoxide as catalyst, in the temperature range of 200–320°C under vacuum (0.1 Torr). The results of self-polycondensation are shown in *Table 2*.

The i.r. spectra of polymers **5a–c** (*Figure 2*) showed a decrease in absorption intensity of the carbonate carbonyl band, indicating that polymerization had occurred via the terminal methoxycarbonate group. The i.r. spectrum of polymer **5d** showed the absence of carbonate band (*Figure 2*). The polymers **5a–c** have an ester and carbonate group occurring in an alternating sequence. The compositions of **4a–d** and **5a–d** were studied by ^{1}H n.m.r., and calculated from the integration of protons of acid chloride moieties (R) to the bisphenol A (aromatic) and isopropylidene protons. In the case of **4d** and **5d**, composition was calculated from the

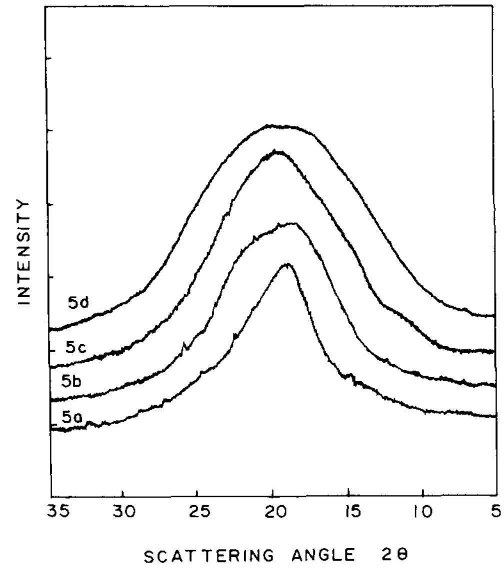


Figure 4 X-ray diffractograms of polymers **5a–d**

integration ratio of R and isopropylidene to aromatic protons. The results obtained are shown in *Table 3*. The expected and observed proton ratios of monomers and polymers were close to each other. This indicates that the repeat structure of polymers **5a–d** is derived from monomers **4a–d**. The only difference in the two n.m.r. spectra was the reduced intensity of the carbomethoxy group at 3.9 ppm. A representative ^{1}H n.m.r. spectrum of polymer **5a** is shown in *Figure 1*.

All monomers and polymers were studied by ^{13}C n.m.r. Monomers **4a–d** showed a peak at 55.01–55.49 ppm due to carbomethoxy group and two peaks of equal intensity at 154.06–154.53 ppm and at 165.04–165.36/173.56 ppm due to carbonate and ester carbonyl groups (*Figure 3*). The ^{13}C n.m.r. spectra of polymers **5a–d** showed the absence of the 55.01–55.49 ppm peak and decrease in the intensity of the carbonate carbonyl peak, indicating that polymerization had occurred via the terminal carbomethoxy group (*Figure 3*).

The alternating sequence of ester to carbonate in poly(aryl ester carbonate)s was studied by ^{13}C n.m.r. and has been reported elsewhere[13]. Polymers **5a–c** showed only a single carbonyl peak due to ester and carbonate group without any splitting, indicating a symmetrical environment. This is possible only if the polymer has a strictly alternating sequence of ester and carbonate groups, in the relative ratio of 2 : 1. Only polymer **5d** showed two ester carbonyl and one carbonate carbonyl peaks (*Figure 3*), indicating the loss of symmetrical environment around the ester carbonyl group.

The thermal properties of poly(ester carbonate)s were evaluated by d.s.c. and t.g.a. T.g.a. of monomers **4a–d** was also recorded and compared with t.g.a. of polymers **5a–d**. The results are shown in *Table 4*. All the monomers undergo stepwise decomposition, indicating that the carbonate and ester groups decompose sequentially. Except for the polymer containing the tetraphenylsilane moiety, all other polymers showed single-step decomposition. All polymers were thermally stable up to 340°C. The glass transition temperatures of the poly(ester carbonate)s varied from 151 to 191°C depending on the type of diacid chloride moiety.

All the polymers synthesized in the present study are amorphous (*Figure 4*) with a broad peak at $2\theta = 16–18°$.

CONCLUSIONS

A new class of ester carbonate monomers were prepared by reaction of mono(methylcarbonate) of bisphenol A with various diacid chlorides at 0°C, using triethylamine as acid acceptor, and were characterized. Self-polycondensation resulted in the formation of poly(ester carbonate)s. The presence or absence of sequential arrangement of ester and carbonate groups in the polymers was shown by ^{13}C n.m.r.

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