1092. *Polyesters Containing Carbohydrate Residues.*

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Polyphenyl esters have been synthesised by interfacial polycondensation of 4,4′-isopropylidenediphenol with di-*O*-methylenehexaroyl dichlorides. Inherent viscosities are less than those of polyesters prepared from aromatic acid dichlorides. Application of the acid dichloride–glycol reaction in an anhydrous melt to the preparation of carbohydrate polyesters has been briefly studied.

The high polymer-melt temperatures of some of the methylenedioxypolyamides prepared by interfacial polycondensation [1] suggested that the di-*O*-methylenehexaroyl dichlorides might form useful polyphenyl esters with bisphenols. Eareckson [2] showed that polyphenyl esters of high molecular weight can be prepared by mixing an aqueous solution of the sodium salt of the bisphenol containing a dispersing agent with a solution of the diacid chloride in a water-immiscible organic solvent. The formation of polyphenyl esters, however, differs from polyamidation in several respects. It is considered [3-5] that the latter is initiated when the diamine comes into contact with the acid dichloride in the organic phase, so that polyamides are formed essentially in the organic solvent where the acid chloride is protected from hydrolysis. In polyesterification the interfacial reaction is different owing to the poor solubility of the diphenoxide, which is the reactive species, in the organic phase. Morgan and Kwolek [3,4] believe that, although the polyester film is formed initially in the organic phase, subsequent film growth occurs from the aqueous phase at the interface. Consequently, the less readily hydrolysed aromatic acid chlorides, such as terephthaloyl and isophthaloyl dichloride, give polyphenyl esters with much higher molecular weights than do the easily hydrolysable aliphatic acid chlorides, *e.g.*, adipoyl and sebacoyl dichloride.[2] We now report the synthesis of polyphenyl esters from substituted carbohydrate acid dichlorides.

The polyesters were prepared by the stirred interfacial polycondensation reaction [2] of 4,4′-isopropylidenediphenol, $CMe_2(C_6H_4{\cdot}OH\text{-}p)_2$, with 2,3:4,5-di-*O*-methylene-galactaroyl, 2,4:3,5-di-*O*-methylene-D-glucaroyl, and -L-idaroyl dichloride,[1] and some of their properties are given in Tables 1 and 2. Copolymer (AC) was synthesised from equal parts of dimethylene-galactaroyl and -idaroyl dichloride.

In general, inherent viscosities were higher than those [2] (*ca.* 0·1) for polyesters prepared from simple aliphatic acid chlorides (adipoyl and sebacoyl dichloride) but lower than those (1·6—1·9) of the polymers from terephthaloyl and isophthaloyl dichloride. Although dimethylenegalactaroyl dichloride gave polymer (A2) with the highest viscosity, results with this acid chloride were difficult to reproduce, and frequently condensations carried out under apparently the same conditions gave wide variations in yield and viscosity (compare A3 and A4). This can probably be attributed to the relatively rapid hydrolysis of the acid chloride, which is influenced by factors such as rate of addition of acid chloride solution, rate of stirring, etc.,[4] that are difficult to reproduce. Although choice of organic solvent for condensation was important in determining the final viscosity of polyesters obtained from aromatic acid chlorides,[2] it was less significant here, and again this is probably because the hydrolysis of the acid chloride is the main factor limiting viscosity. Other variables were also studied. When emulsifying agent was omitted, polymer (A5) of low viscosity was obtained. Reduction in reaction temperature from 20° to 0° increased the yield with

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[1] Bird, Black, Dewar, and Hare, *J.*, 1963, 1208.

[2] Eareckson, *J. Polymer Sci.*, 1959, **40**, 399.

[3] Morgan and Kwolek, *J. Polymer Sci.*, 1959, **40**, 299.

[4] Morgan and Kwolek, *J. Polymer Sci.*, 1962, **62**, 33.

[5] Frunze, Kurashev, and Kozlov, *Russ. Chem. Rev.*, 1961, **30**, 252.

all organic solvents but had an adverse effect on viscosity. The use of an excess of alkali decreased both yield and viscosity

Dimethyleneglucaroyl dichloride gave polyester with a negative rotation and low viscosity. Condensation with dimethyleneidaroyl dichloride was the most reproducible, and yields of 65—75% and viscosities of 0·30—0·37 were consistently obtained; methylene chloride was the best organic solvent. Copolymer (AC) containing both galactaric and idaric acid residues had a specific rotation that was slightly more than half that of the idaric acid homopolymer. Polymer-melt temperatures were highest for the idaric acid polyester and lowest for the galactaric acid polyester, the copolymer and glucaric acid homopolymer having intermediate values.

TABLE 1.

Properties of polyphenyl esters.

4,4′-Isopropylidenediphenyl ester		Organic solvent (ml.)	Pre-cipitant	Yield (%)	Found * (%) C	Found * (%) H	$\eta_{\text{inh.}}$	$[\alpha]_D$	Polymer-melt temp.
Di-*O*-methylenegalactarate	(A1)	C_6H_6 (40)	EtOH	61·7	64·7	5·0	0·39	0·0	116—124°
	(A2)	C_6H_6 (25)	EtOH	54·8	64·4	5·6	0·52	0·0	—
	(A3)	CCl_4 (15)	Me_2·CO	64·4	64·8	5·35	0·37	0·0	123—133
	(A4)	CCl_4 (15)	Me_2·CO	90·7	64·7	5·5	0·43	0·0	110—120
	(A5)	CCl_4 (15)	None †	70·0	63·9	5·5	0·13	0·0	123—128
	(A6)	$CHCl_3$ (25)	EtOH	59·0	64·5	5·6	0·35	0·0	—
Di-*O*-methylene-D-glucarate	(B1)	CH_2Cl_2 (25)	EtOH	38·0	64·7	5·6	0·20	−70°	234—238
	(B2)	$CHCl_3$ (25)	EtOH	72·3	64·1	5·55	0·16	−62	230—235
Di-*O*-methylene-L-idarate	(C1)	CH_2Cl_2 (25)	Me_2·CO	68·1	64·2	5·2	0·37	+113	290—300 decomp.
	(C2)	$CHCl_3$ (60)	Me_2·CO	74·3	63·7	5·2	0·30	+113	—
Copolymer (AC)		CH_2Cl_2 (25)	EtOH	64·6	63·8	5·2	0·41	+64	213—220

* $[C_{23}H_{22}O_8]_n$ requires C, 64·8; H, 5·2%. † Detergent omitted.

TABLE 2.

Solubilities of polyphenyl esters in the solvent specified [soluble cold (++), soluble hot (+), insoluble (—)].

Polyester	$CHCl_3$	EtOAc	Pyridine	H·CO_2H	H·CO·NMe_2	Me_2SO	*m*-Cresol	*o*-Chlorophenol
(A)	++	+	++	—	++	++	++	++
(B)	++	—	++	—	++	++	++	++
(C)	—	—	—	—	++	++	++	++
(AC)	—	—	++	—	++	++	++	++

TABLE 3.

Properties of polyalkyl esters.

Polyester	Yield (%)	Found (%) C	Found (%) H	Formula of unit	Required (%) C	Required (%) H	$\eta_{\text{inh.}}$	$[\alpha]_D$	Polymer-melt temp.
Poly(tetramethylene di-*O*-methylenegalactarate)...	98·9	50·0	5·8	$C_{12}H_{16}O_8$	50·0	5·6	0·16	0·0	130—140°
Poly(decamethylene di-*O*-methylene-L-idarate) ...	96·5	57·8	7·5	$C_{18}H_{28}O_8$	58·1	7·6	0·20	+95°	195—199

Interfacial polycondensation cannot be used for the synthesis of linear polyesters by reaction of aliphatic glycols with acid dichlorides, for the condensation is too slow, relative to competing hydrolysis of the acid chloride, for the formation of high polymers.[3] We have, however, applied the acid dichloride–glycol reaction in an anhydrous melt [6] to the preparation of poly(tetramethylene di-*O*-methylenegalactarate) from 2,3:4,5-di-*O*-methylenegalactaroyl dichloride and butane-1,4-diol. With this glycol and 2,4:3,5-di-*O*-methylene-L-idaroyl dichloride, the intermediate polyester of low molecular weight (see Experimental

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[6] Flory and Leutner, U.S.P. 2,589,688/1952.

section) failed to melt without decomposition, so that further polymerisation in the melt was not possible. With decane-1,10-diol, however, the intermediate polyester melted at 197°, and further polycondensation of the melt at 210—220° gave optically active poly(decamethylene di-*O*-methylene-L-idarate) as a brown glass. Some of the properties of these two polymers are given in Table 3.

Only low viscosities were obtained, owing to slight decomposition of the carbohydrate residues at the high temperature required for melt polycondensation. Polymer-melt temperatures, however, were much higher than those of simple aliphatic polyesters; for example, poly(tetramethylene sebacate) melts at 60—65°.

EXPERIMENTAL

The di-*O*-methylenehexaroyl dichlorides were prepared as previously described.[1]

Materials.—Shell Chemical Co.'s 4,4′-isopropylidenediphenol (bisphenol A) was recrystallised three times from 1 : 1 v/v acetic acid–water, then having m. p. 158° (Found: C, 79·1; H, 6·9. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·1%). Butane-1,4-diol was purified by the procedure of Evans, Mighton, and Flory,[7] and decane-1,10-diol was recrystallised twice from dry ethylene dichloride, then having m. p. 72·5—74°. 1,2-Dimethoxyethane was redistilled twice from sodium, the fraction boiling at 85·5° being collected. Methylene chloride was stored over calcium chloride for several months and redistilled before use. Benzene was redistilled from phosphoric oxide. Chloroform was freed from ethanol by washing with water, dried ($CaCl_2$), stored over calcium chloride and potassium carbonate, and redistilled before use.[8]

General Methods.—Specific rotations were measured at 20° in a 2-dm. tube in 2 : 3 w/w tetrachloroethane–phenol. Polymer-melt temperatures were measured on a Kofler hot-stage. Inherent viscosity $[\eta_{\text{inh.}} = \ln(\eta_{\text{soln.}}/\eta_{\text{solv.}})/c]$ was determined [8] in 2 : 3 tetrachloroethane–phenol at 25° at a concentration (*c*) of 0·5 g. of polymer per 100 ml.; results are expressed in dl./g.

General Procedure for the Preparation of Polyphenyl Esters by Interfacial Polycondensation.—The stirred interfacial polycondensation reaction of Eareckson [2] was used. A solution of bisphenol A (228 mg., 1 mmole), sodium hydroxide (2 mmoles), and sodium lauryl sulphate (50 mg.) in water (30 ml.) was mixed in a high-speed macerator, a solution of the acid dichloride (271 mg., 1 mmole) in the appropriate organic solvent (15—60 ml.; see Table 1) was added rapidly, and the emulsion was stirred for 5 min. at 20°. The mixture was poured into acetone or ethanol (100 ml.) to coagulate the polymer, which was washed with water, ethanol, and ether, and dried over phosphoric oxide at 20°/0·5 mm. The idaric polyesters (C1 and C2 in Table 1) and the copolymer (AC) were pure at this stage, but the galactaric acid and glucaric acid polymers (A1—A6, B1 and B2) were purified by dissolution in dimethylformamide and reprecipitation in dilute sodium chloride solution.

Products are described in Tables 1 and 2.

Poly(tetramethylene di-O-*methylenegalactarate).*—Di-*O*-methylenegalactaroyl dichloride [1] (1·526 g., 5·64 mmoles) was added to butane-1,4-diol (508 mg., 5·64 mmoles); a vigorous reaction occurred with evolution of hydrogen chloride. Dimethoxyethane (10 ml.) was then added to dissolve any unchanged glycol or acid chloride, the mixture refluxed for 30 min., and the solvent removed under reduced pressure. The white solid was cautiously heated in a nitrogen atmosphere until it melted (120—130°), the temperature was raised to 150° for 1 hr. with nitrogen bubbling through the melt, and finally the molten polymer was heated at 200—210° for 2 hr. Fibres could be drawn from the cooling melt. The hard glass was dissolved in chloroform (25 ml.) and reprecipitated with light petroleum (b. p. 40—60°), to give *poly(tetramethylene di*-O-*methylenegalactarate)* as a light brown powder (1·607 g., 98·9%).

Poly(decamethylene di-O-*methylene*-L-*idarate).*—Di-*O*-methylene-L-idaroyl dichloride [1] (815 mg., 3 mmoles) was added to decane-1,10-diol (524 mg., 3 mmoles), followed by sufficient dimethoxyethane (2 ml.) to wet the bulky acid chloride; no hydrogen chloride was evolved in the cold. The mixture was refluxed for 2 hr. with a slow nitrogen stream directed on to the surface to remove hydrogen chloride, and dimethoxyethane was removed to give the intermediate polyester, the weight (1·18 g.) of which indicated a loss of hydrogen chloride equivalent

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[7] Evans, Mighton, and Flory, *J. Amer. Chem. Soc.*, 1950, **72**, 2018.

[8] Sorenson and Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publ., Inc., New York, 1961, p. 41.

to 72·8% reaction. The white solid was cautiously heated in a nitrogen atmosphere until it melted (197—210°), and the temperature maintained at 210—220° for 90 min. with nitrogen bubbling through the melt; the melt viscosity reached a maximum after 1 hr. The *polyester* cooled to a hard brown glass (1·082 g., 96·5%). When the reaction was carried out in boiling triethylene glycol dimethyl ether $Me\cdot[O\cdot CH_2\cdot CH_2]_3\cdot OMe$ (b. p. 216°), there was less darkening of the product but viscosity was not increased.

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