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POLYARYLATES

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I. INTRODUCTION

Polyarylates are hetero-chain polyesters of dihydric phenols. Polymers of this type were first described in 1898 by Einhorn[1], who studied the reaction between phosgene and catechol, resorcinol, and quinol. A cyclic monomeric carbonate was obtained with catechol and polymeric products with resorcinol and quinol. Bischoff and Hedenström[2], in 1902, described the formation of polyarylates of oxalic acid by the reaction of diphenyl oxalate with quinol and resorcinol.

Until recent times little or no work on polyarylates was reported in the literature, but in the last decade a number of articles have appeared concerning this class of polymers. Particular attention was paid to the study of polyarylates after Schnell[3] had reported the results of his studies on polyesters of dihydric phenols of various structures with carbonic acid, which possessed a number of technically valuable properties. Since then articles devoted to a study of these types of polyarylates have been published regularly[4-28].

Data concerning other polyarylates have become available[29-72], the most interesting concern the polyesters of dihydric phenols and aromatic dicarboxylic acids[31-40,46,47,48,51-54,70,71] and some mixed polyesters of dihydric phenols[33-35,54,72]. These polyesters also have the following useful properties: high softening point, good dielectric properties, resistance to attack by chemical reagents, the ability to produce stable films, etc. There is, therefore, every reason to expect that these polymers will be extensively used in the future.

II. METHODS OF PREPARATION OF POLYARYLATES

1. Transesterification Reactions

(a) The preparation of polyarylates from dihydric phenol diacetates and dicarboxylic acids. Wallsgrove and Reeder[30], and Levine and Temin[48] describe the preparation of polyarylates by the reaction of dihydric phenol diacetates with dicarboxylic acids:

$$CH_3COOArOCOCH_3 + HOOCRCOOH \rightarrow \rightarrow CH_3COOH + (-OArOCORO-)_n.$$

For example, Levine and Temin obtained by this method the polyesters of 2,2-bis(4-hydroxyphenyl)propane with adipic, 3-methyladipic, and sebacic acids, and of p,p'-dihydroxydiphenyl with adipic acid, as well as other polyarylates.

To prepare polyarylates by this method, the polycondensation is carried out in the fused state in the presence of a

catalyst, for example metallic magnesium, at high temperatures in a current of an inert gas, the mixture being heated *in vacuo* at a certain stage of the reaction.

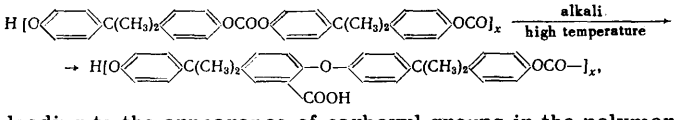
This method is not entirely satisfactory because it cannot be used successfully for the preparation of high-softening-point polyarylates. Moreover, the polyarylates produced frequently become highly coloured during the reaction.

(b) Synthesis of polyarylates by the reaction of dicarboxylic esters with dihydric phenols:

$$R'OCORCOOR' + HOArOH \rightarrow ROH + (-OArOCORCO-)_n.$$

This method has been used for the preparation of polycarbonates[3,20,21,25]. Diphenyl carbonate is usually used as the starting material. The polycondensation is conducted in the molten state at 150°–300° in an oxygen-free atmosphere. Polyesterification is accelerated by the use of a vacuum and by stirring[3]. Thompson and Goldbaum[21] showed that an excess of diphenyl carbonate was desirable during the initial stages of its reaction with 2,2-bis-(4-hydroxyphenyl)propane (dian or bisphenol A). This allowed a more rapid and complete conversion of the bisphenol A, desirable because this phenol may decompose at temperatures above 180°.

The polyesterification reaction is markedly accelerated in the presence of a catalyst. Schnell[3] showed that acidic catalysts (boric acid, toluene-*p*-sulphonic acid, zinc chloride) were only slightly effective. Basic catalysts such as the alkali and alkaline-earth metals, their oxides and hydroxides, amines, zinc oxide, lead oxide, etc., significantly increased the rate of polycondensation. Large quantities of strongly basic catalysts could, however, cause side reactions, leading to the formation of branched and cross-linked structures, under the conditions used for the polycondensation. Schnell[3] postulated that this was due to the following rearrangement:



leading to the appearance of carboxyl groups in the polymer chain, as possible centres for branching and cross-linking.

Transesterification can be used to produce polyarylates on an industrial scale. The high viscosity of the melt during the production of polycarbonates precludes the preparation of polymers with very high molecular weights by this method. It is difficult to obtain polycarbonates of molecular weight greater than 50 000.[3]

2. Reaction of Dicarboxylic Acid Chlorides with Dihydric Phenols

(a) Preparation of polyarylates by the polycondensation of dicarboxylic acid chlorides with dihydric phenols at high temperatures has been described in a number of papers[31-35,39,41-45,49,56-69]:

$$ClCORCOCl + HOArOH \rightarrow HCl + (-OArOCORCO-)_n.$$

Korshak and Vinogradova synthesised several polyarylates by heating dicarboxylic acid chlorides with dihydric phenols, initially in a stream of nitrogen and then at a reduced pressure (~1–2 mm Hg). They obtained polyesters of terephthalic and isophthalic acids with 2,2'-dihydroxydiphenyl[31], and of sebacic acid with resorcinol and bisphenol A [35], and other polyarylates.

Several workers have used the method of polycondensation in the melt to prepare phosphorus-containing polyarylates using phosphorus oxychloride and the dichlorides of phosphorus-containing acids (phosphinic, phosphinous, thiophosphinic, and phosphoroamidic) with dihydric phenols[41-45,56-66].

In general the production of these polyarylates is accomplished with equimolar quantities of the starting materials, at high temperatures, with good mixing of the reaction mixture, and usually in the presence of a catalyst (*e.g.* heavy-metal halides). A current of inert gas is maintained during the reaction to ensure the rapid removal of the hydrogen chloride produced and to exclude air from the system. In the last stage of the reaction the temperature is increased (sometimes up to 250°–300°) and the pressure reduced[57].

Piiroya[44] studied the kinetics and mechanism of the polycondensation in the melt of resorcinol and phenoxyphosphoryl dichloride at 110°, 150°, and 200°, with reaction times from 8 h to 25 h and with equimolar and other ratios of the starting materials. Piiroya's studies showed that the yield of polyester and its molecular weight varied linearly with the reaction temperature. Any alteration from the equimolar ratio of the starting materials caused significant reduction in the molecular weight of the polymer. The production of polyester during the first hour of the experiment was very rapid but later slowed down considerably. The molecular weight and yield of polyester at 150° reached a maximum after 20 h and could not be increased, although some of the starting materials remained unconverted. The author concluded that the retardation of the reaction rate was caused by the high viscosity of the reaction mixture.

With the aim of increasing the rate of reaction between resorcinol and phenoxyphosphoryl dichloride, Raudsepp and Piiroya[45] studied the catalytic effect of calcium chloride and aluminium chloride on the polycondensation. The use of calcium chloride permitted the reaction to be carried out at much lower temperatures. Thus, at 110°, the molecular weight of the polyester reached 1350 after only 8 h, and the polyester of maximum molecular weight (~2300) was obtained at 150°. In the presence of aluminium chloride, polyester of molecular weight up to 2500 was obtained with complete conversion of the initial materials. The authors concluded that the molecular weight of the polyesters in these systems ceased to increase because of the high viscosity of the reaction medium.

These authors[45] subjected the polyesters of molecular weight ~2500, obtained by polycondensation in the melt at 150° in the presence of aluminium chloride, to further polycondensation in chlorobenzene. They were thus able to obtain polymers of molecular weight ~5000. Even higher increases in the molecular weight of the polyester (up to 7500) were achieved by the addition of pyridine to the chlorobenzene to combine with the hydrogen chloride evolved during the reaction.

Synthesis from dicarboxylic acid chlorides and dihydric phenols in the molten state has only limited application and cannot be used for the production of high softening-point polyarylates such as those from terephthalic acid and quinol, resorcinol, bisphenol A and some other phenols. Because of the high softening point of these polyesters the

reaction mass solidifies soon after the start of the reaction and cannot be remelted without decomposition. Consequently, the reaction stops during its very early stages. The above disadvantages can be avoided by carrying out the polycondensation in solution.

Korshak and Vinogradova[31,32-35] have described the preparation of a number of homogeneous and mixed polyarylates by heating dicarboxylic acid chlorides with dihydric phenols in a high-boiling solvent at high temperatures. They also studied[32] the kinetics and mechanism of this reaction in solution in Dowtherm A using as examples isophthaloyl chloride and terephthaloyl chloride with bisphenol A between 150° and 210°, terephthaloyl chloride with 2,2′-dihydroxydiphenyl, resorcinol, and quinol at 170°, and sebacic acid chloride with bisphenol A at 150°.

It was shown that the reaction proceeds by a bimolecular mechanism. Rate constants and extent of reaction are shown in Table 1. These authors also found that the rate constants for the reaction of bisphenol A with isophthaloyl and terephthaloyl chloride varied according to the Arrhenius equation (*cf.* Fig. 1). By applying the method of least squares to the experimental data from these two reactions, Arrhenius equations of the following form are obtained: $K = 7.13 - 4963/T$ and $K = 5.81 - 4308/T$ respectively. From the above equations, the activation energy for the isophthaloyl chloride–bisphenol A reaction is 19 700 cal with a frequency factor of 0.646×10^6. The corresponding values for the terephthaloyl chloride–bisphenol A reaction are 22 700 cal and 0.135×10^8. The higher value of the frequency factor for the latter reaction was explained by the authors as due to a steric effect. The reactive groups in isophthaloyl chloride present greater obstacles to the approach of a second molecule than in the case of the *para*-substituted compound.

Comparison of the rate constants of the various reactions, shown in Table 1, permits certain conclusions concerning the influence of the structure of the starting materials on the reaction rates[32]. It was shown that isophthaloyl chloride reacts with bisphenol A at a higher rate than terephthaloyl chloride. Replacement of an aromatic by an aliphatic acid chloride markedly increases the reaction rate. Thus, at 150° the reaction of sebacic acid chloride with bisphenol A proceeds at a rate about 60 times greater than that with isophthaloyl chloride and 115 times greater than that with terephthaloyl chloride.

The reaction rate also depends on the structure of the dihydric phenol. The reaction rates of the various phenols studied, with terephthaloyl chloride at 170°, varies in the following manner: quinol > resorcinol > 2,2′-dihydroxydiphenyl > bisphenol A.

The authors[32] also found that the extent of reaction, in a given time, increased with the temperature and concentration of reactants. The variation of the composition of the reaction mixture and the change in reduced viscosity of the polyester in cresol during the reaction of isophthaloyl chloride with bisphenol A at 220° are shown in Fig. 2. It can be seen that the reduced viscosity of the polyester in cresol continuously increases as the reaction proceeds, *i.e.* the molecular weight increases. Since the quantity of polymer changes only slightly after the third hour and the quantity of the low-molecular fraction is very small at this time, it follows that increase in polymer chain length must involve mainly polymer molecules.

TABLE 1. Rate constants and extent of reaction between dicarboxylic acid chlorides and dihydric phenol.

Reactants	Reaction temp., °C	Rate constant, 10^6 litre × × mole^{-1} × × sec^{-1}	Extent of reaction after 7 h
HO–C(CH$_3$)$_2$–OH+ (I) + isophthaloyl chloride	150	5.72	0.17
	170	10.70	0.26
	180	17.99	0.38
	200	50.30	0.63
	210	92.00	0.72
(I) + terephthaloyl chloride (II)	150	2.99	0.09
	170	6.56	0.17
	180	14.30	0.33
	190	30.40	0.46
	210	79.60	0.64
(I) + sebacoyl chloride	150	34.40	—
2,2′-Dihydroxydiphenyl + (II)	170	6.90	0.16
Resorcinol + (II)	170	7.06	0.19
Quinol + (II)	170	11.70	0.27

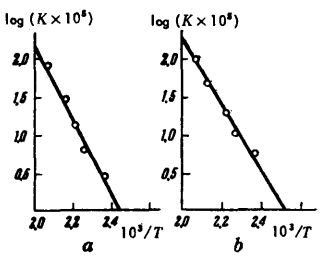


Fig. 1. Temperature variation of the rate constant for the reaction of bisphenol A with *a*) terephthaloyl chloride and *b*) isophthaloyl chloride.

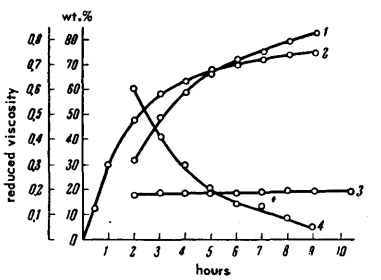


Fig. 2. Kinetics of the polycondensation of isophthaloyl chloride with bisphenol A at 220°: 1) quantity of hydrogen chloride liberated during the reaction; 2) quantity of polyester present in the reaction mixture; 3) quantity of reactants and low-molecular polyesters in the reaction mixture; 4) inherent viscosity of the polyester.

A detailed study of the influence of the various factors on the polycondensation of terephthaloyl chloride and bisphenol A was described by Korshak and coworkers[39]. They studied the effect of a number of solvents, the ratios of starting materials, the temperature, and reaction time on the reduced viscosity of the polyester and its yield.

The results obtained (Table 2) show that polyarylates with the greatest reduced viscosity were obtained in solution in ditolylmethane with an initial reactant concentration 0.6 M. The polymers prepared in Dowtherm A and tetralin were discoloured and difficult to extract, whereas those produced in ditolylmethane were pale yellow and easily extracted.

A study of the effect of temperature (220° and 240°) and reaction time on the reduced viscosity of the polyarylate in ditolylmethane solution showed that the best results were obtained at 220°. The authors[39] established that polyarylates with the highest molecular weight were obtained when an equimolar mixture of reactants was used. The variation of the reduced viscosity of the polyester with the initial reactant ratio is shown in Fig. 3. Yamaguchi, Takayanagi, and Kuriyama[49] describe the production of poly(quinol adipate) by heating adipoyl chloride with quinol in nitrobenzene in an inert atmosphere.

It was found[43,69], during a study of the influence of various factors on the reaction of methylphosphinic acid dichloride with quinol in Dowtherm A between 140° and 170°, that the extent of reaction increased with increase in the temperature and concentration of reactants (*cf.* Fig. 4). An especially marked increase was observed during the first hour, when the reaction is mainly between the monomers. Determination of the composition of the reaction mixture and of the reduced viscosity during the course of the reaction showed that the molecular weight of the polyester increases with time. In view of the relative quantities of free monomers and polymer in the reaction mixture, the authors concluded that after 4–5 h the growth of the polymer chains was largely due to reaction between polymer molecules. The reaction of methylphosphinic acid dichloride with quinol was found to be of second order. At 150° the reaction rate constant was 0.00033; at 160°, 0.000444; at 170°, 0.000557 litre mole^{-1} sec^{-1}. The authors[43] established that the variation of the rate constant with temperature was in accordance with the Arrhenius equation. The activation energy is 10 470 ± 700 cal mole^{-1}.

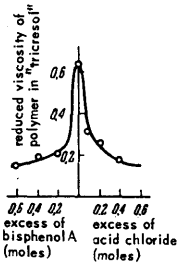


Fig. 3. Variation of the reduced viscosity of the polyarylate in cresol in relation to the initial ratio of reactants.

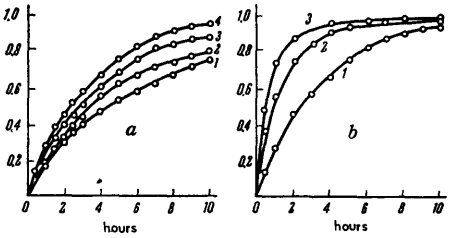


Fig. 4. The degree of completion (ordinate) of the reaction between methylphosphinic dichloride and quinol in nitrobenzene solution:
a) at different reaction temperatures: 1) 140°; 2) 150°; 3) 160°; 4) 170°;
b) with different initial concentrations of reactants (170°), M: 1) 0.1; 2) 0.3; 3) 0.5.

TABLE 2. Dependence of the reduced viscosity in "tricresol" and the yield of terephthalic acid-bisphenol A polyarylates on the solvent and the concentration of the reactants.

Concentration of reactants, M	Reduced viscosity in tricresol			Yield, %		
	polycondensation in					
	ditolylmethane*	Dowtherm A	tetralin**	ditolylmethane	Dowtherm A	tetralin
0.05	0.30	0.25	0.15	44.0	70.0	—
0.10	0.40	0.33	0.20	57.0	70.0	15.2
0.20	0.42	0.35	0.22	67.0	76.5	48.0
0.30	0.40	0.29	0.26	67.0	81.5	70.0
0.40	0.49	0.43	0.30	71.0	76.0	73.0
0.60	0.62 (0.89)	0.42	0.28	76.0	81.0	43.5
0.80	0.60	0.47	0.36	73.5	75.0	46.0
1.00	0.54 (0.60)	0.50	0.30	81.0	77.0	58.0

* The polycondensations were carried out in a stream of nitrogen with a gradual increase in temperature from 100° to 220° over a period of 3 h, and then at 220° for 10 h.

** The temperature was gradually increased during the polycondensation (under nitrogen) from 100° to 195° over 2.5 h and maintained at 195° for 10 h.

The synthesis of phosphorus-containing polyarylates from phosphorus oxychloride and the dichlorides of phosphonic acids with dihydric phenols by polycondensation in solution has also been described in a number of other papers[57,61,67,68].

(b) Preparation of polyarylates by polycondensation at phase boundaries. This type of polycondensation was first used for the preparation of

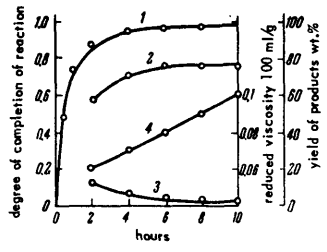


Fig. 5. Kinetics of the reaction between methylphosphinic dichloride and quinol in nitrobenzene of 170° (concentration 0.5 M): 1) degree of completion of the reaction; 2) overall yield of polyesters; 3) quantity of low-molecular compounds; 4) reduced viscosity of the polyester.

polyarylates as long ago as 1898 by Einhorn[1]. The application and detailed study of this method of preparing polymers began only during recent years[3,20,21,35-37,46,47,51-54].

In principle "interfacial" polyesterification involves the reaction of dicarboxylic acid chlorides and dihydric phenols at the boundaries of two phases. The acid chloride dissolved in an organic solvent is caused to react with a solution of the phenol in aqueous alkali. The reactions are carried out at atmospheric pressure at low, sometimes even at room, temperature at a very rapid rate (minutes).

The advantages of this method are readily apparent in comparison with the high-temperature reaction which is carried out in solution or in the melt in a current of inert gas, sometimes over a period of many hours, and which requires the application of a vacuum during the last stages of the reaction in the melt. The advantages of polycondensation at phase boundaries permit the use of this method for the production of polymers from thermally unstable reactants and also from substances which contain reactive groups (for example, double bonds) which could react under the usual conditions of homogeneous polycondensations. Recent literature data show that the interfacial method gives polyarylates with very much higher molecular weights (up to 275 000 [47]) than those produced by high-temperature polycondensation.

Data concerning interfacial polyesterification and its mechanism are very scarce[36-38,52-54]. Morgan[53] suggested that polyesterifications of this type apparently involve nucleophilic attack of the phenoxide ion on the dicarboxylic acid chloride. The reaction of a dihydric phenol with an acid chloride proceeds very slowly at room temperature unless the phenol is ionised.

Because the interaction takes place at phase boundaries, the area of boundary surface should have a significant effect on the polycondensation process, the amount of contact between the reactants depending on the surface area. The boundary surface in two immiscible liquids can be varied by the use of emulsifying agents and by agitating of the reaction mixture.

Korshak, Vinogradova, and Lebedeva[36] studied the interfacial reaction of isophthaloyl chloride with bisphenol A and found that the yield of polyarylate was strongly dependent on the rate of agitation. An increase in the agitation rate from 500 r.p.m. to 1500–1700 r.p.m. led to an increase in the yield from 46% to 93%.

The presence in the reaction mixture of an emulsifying agent, its nature, and concentration, also had a marked influence on the reduced (inherent) viscosity and yield of the polyarylate. The influence of emulsifying agents, such as sodium stearate, "Mersolate" (sodium salts of aliphatic sulphonic acids), "Novost'" (sulphonated higher alcohols), "OP-20" (mono- and di-alkylphenyl ethers of polyethylene glycol), "Trilon B" (the disodium salt of ethylene diamine tetra-acetic acid), "Nekal" (mixed sodium salts of mono-, di-, and tri-s-butylnaphthalenesulphonic acids), on the interfacial polyesterification of isophthaloyl chloride and bisphenol A has been investigated. The best results were obtained when Mersolate and Nekal were used as emulsifying agents. Thus, the reduced viscosity of the polyarylate in cresol obtained in the presence of Nekal approached 1.44, and with Mersolate 1.54, while in the absence of an emulsifying agent it was only 1.02 after the same time and under similar conditions. The use of Mersolate and Nekal clearly leads to a product of high molecular weight.

The relation between the concentration of emulsifying agent and the reduced viscosity and yield of polyarylate was studied. The results showed that the optimum concentrations of Mersolate and Nekal were 1 wt.% and 1–2 wt.% respectively.

Eareckson[54] also investigated the influence of a series of emulsifying agents on the reduced viscosity of solutions of the mixed polyarylate prepared from bisphenol A and a 1 : 1 (mole ratio) mixture of isophthaloyl and terephthaloyl chlorides. The emulsifiers studied were: "Triton X-100", a non-ionic polyoxyethylene detergent, "MP 189" (the sodium salt of a sulphonated kerosene fraction), and "Duponol ME" (mainly sodium lauryl sulphate). The results in Table 3 show that Duponol ME was the best emulsifying agent.

TABLE 3. The influence of various emulsifying agents on the viscosity of the mixed polyarylate of bisphenol A with isophthalic and terephthalic acids (composition 1:0.5:0.5).

Solvent	Emulsifying agent	η_{inh}	Yield, %
Trichloroethylene	MP 189	0.74	92
»	Triton X–100	0.74	92
»	Duponol ME	1.45	92
Toluene	MP 189	0.92	92
»	Triton X–100	0.88	92
»	Duponol ME	1.46	95
o-Dichlorobenzene	MP 189	0.45	92
»	Triton X–100	0.64	—
»	Duponol ME	1.00	89

Note: $\eta_{inh} = ln\ \eta_{rel}/c$ determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°.

The influence of the rate and sequence of adding the reactants on the reduced viscosity of the polyarylate was also examined[36]. It was found that under similar experimental conditions the highest reduced viscosity was obtained by the addition of a solution of isophthaloyl chloride (in *p*-xylene) to an alkaline solution of bisphenol A. Moreover, the time taken to add the reactants was found to have an effect: the best results were obtained by mixing over a period of 9–18 min. The yield of polyester (85–94%) was not significantly affected by the rate of addition of the reactants nor by the sequence of addition.

The initial concentration of reactants has a marked influence on the molecular weight of the polyester produced. Korshak, Vinogradova, and Lebedeva[36] presented data concerning the relation between the yield and the reduced viscosity of the polyarylate from bisphenol A–isophthaloyl chloride and the concentration of the equimolar mixture of reactants. It can be seen from Fig. 6. that the reduced viscosity of the polyester passes through a maximum obtained when the concentration of the starting materials is 0.10 M. Lower and higher initial concentrations were found to yield polyesters of lower reduced viscosities. The reduced viscosity was not further affected by concentrations greater than 0.3 M. Variation in the initial reactant concentrations had little influence on the yield of polyester (78–91%).

The dependence of the reduced viscosity and yield of polyester on the nature of the solvent was studied (Table 4). A large variety of compounds were used as solvents: aliphatic hydrocarbons (n-heptane), aromatic hydrocarbons (benzene, toluene, and xylenes), chlorinated aliphatic hydrocarbons (chloroform, carbon tetrachloride, dichloroethane, and *sym*-tetrachloroethane), chlorinated aromatic hydrocarbons (chlorobenzene) and also tetralin, diethyl ether, and petroleum ether.

The reduced viscosity of the polyester produced was found to depend strongly on the nature of the solvent. In the absence of an emulsifier the highest reduced viscosities of the polyester were obtained when aromatic hydrocarbons were used as solvents for isophthaloyl chloride, the best results being obtained with xylenes. The reduced viscosity of the polyester prepared in the isomeric xylenes increased in the following manner: *p*-xylene > *m*-xylene > *o*-xylene.

Emulsifying agents widen the range of solvents which can be used for interfacial polyesterification reactions[38]. Data are also given in Table 4 concerning the yield and reduced viscosity of polyesters prepared by the interfacial polyesterification of isophthaloyl chloride in various solvents in the presence of Nekal.

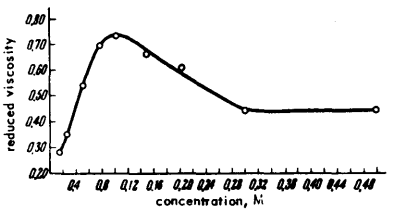


Fig. 6. Variation of the reduced viscosity of polyester in cresol with the concentration of reactants.

TABLE 4. The influence of the solvent on the reduced viscosity and yield of the polyarylate.

Solvent for the isophthaloyl chloride	Experiments with emulsifying agent (Nekal*)		Experiments without emulsifying agent	
	reduced viscosity of polyester in cresol	yield, %	reduced viscosity of polyester in cresol	yield, %
p-Xylene	1.46	80	1.02	88
Tetralin	0.64	80	0.28	86
n-Pentane	0.94	84	0.30	quantitative
Carbon tetrachloride	1.12	83	0.40	»
Chloroform	0.44	77	0.12	»
Dichloroethane	0.72	80	0.16	80
Tetrachloroethylene	1.02	82	—	—
Trichloroethylene	0.96	80	—	—
Chlorobenzene	0.72	80	0.20	83
Diethyl ether	0.58	87	0.33	77
Petroleum ether (b.p. 70°–72°)	—	—	0.22	91
Tetrachloroethane	—	—	0.10	17
Benzene	—	—	0.25	91
Toluene	—	—	0.26	84
m-Xylene	—	—	0.60	88
o-Xylene	—	—	0.45	80

* A 1.5% solution of Nekal in the aqueous phase was used.

In every case the use of an emulsifier increased the reduced viscosity of the polyarylate in cresol 2–3 times, compared with the reduced viscosity of polyarylates prepared in the absence of emulsifiers. Thus, polyesters of high reduced viscosity were prepared in n-heptane, carbon tetrachloride, tetrachloroethane, and trichloroethane solutions, as well as in *p*-xylene.

Eareckson[54] studied the influence of the nature of the solvent on the reduced viscosity of the mixed polyarylate of bisphenol A with isophthalic and terephthalic acids, of composition 1 : 0.5 : 0.5. His results are set out in Table 5. The author concluded that the proper choice of solvent was very important since it determined the molecular weight of the polymer. Thus, solvents which dissolved the polymer favoured the formation of polymers of higher molecular weight.

The polyester of highest molecular weight was obtained in chlorinated hydrocarbons in which the mixed polyarylate was readily soluble. According to Eareckson[54] these solvents have the capacity to swell the polymer films at the phase-boundaries through which the acid chloride migrates and reacts with the phenoxide ions in the aqueous phase. If the polymer becomes completely insoluble in the organic phase, hard polymer films prevent the migration of the acid chloride molecules and seriously limit the yield and molecular weight of the polymer.

The effect of temperature on the interfacial polycondensation of isophthaloyl chloride with bisphenol A was studied[36] at 20°, 30°, 50°, 60°, and 70°. It was shown (Fig. 7) that the reduced viscosity was lowered from 0.74 to 0.16 as the temperature was increased from 20° to 70°. The yield of polyarylate was also reduced to 70–75% from 88% at 20°.

TABLE 5. Effect of solvent on the reduced (inherent) viscosity of the mixed polyarylate.

Solvent for the acid chloride	Yield of polyester, %	η_{inh}
Chloroform	89	2.31
1,1,2;Trichloroethane	95	1.73
Dichloroethylene	92	1.59
Trichloroethylene	94	2.02
o-Dichlorobenzene	89	1.00
o-Nitrotoluene	87	0.86
Toluene	95	1.62
Xylene	92	1.15
Cyclohexane	94	1.38

Note. η_{inh} was determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°, $\eta_{inh} = ln\,\eta_{rel}/c$.

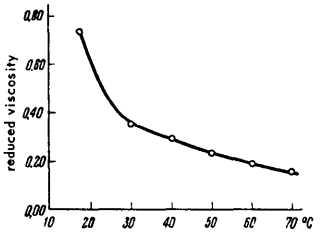


Fig. 7. Relationship between the reduced viscosity of polyester in cresol and the reaction temperature.

The following competing reactions are possible during polyesterifications at phase-boundaries when one of the phases is aqueous:

$$ClCOC_6H_4COCl + NaOC_6H_4C(CH_3)_2C_6H_4ONa \rightarrow \rightarrow NaCl + Cl[-COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-]_xNa; \quad (1)$$

$$ClCOC_6H_4COCl + H_2O \rightarrow \begin{matrix} \rightarrow HOCOC_6H_4COOH + HCl \\ \searrow ClCOC_6H_4COOH + HCl \end{matrix}; \quad (2)$$

$$NaOC_6H_4C(CH_3)_2C_6H_4ONa + HCl(HOCOR-\ldots) \rightarrow \begin{matrix} \rightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + NaCl(NaOCOR-\ldots); \\ \searrow NaOC_6H_4C(CH_3)_2C_6H_4OH + NaCl \end{matrix} \quad (3)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + H_2O \rightarrow \rightarrow HO[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + HCl; \quad (4)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + HCl(HOCOR-\ldots) \rightarrow Cl[COC_6H_4COOC_6H_4C.(CH_3)_2C_6H_4O]_xH + NaCl(NaOCOR-\ldots). \quad (5)$$

The first leads to the synthesis of polymer. The remainder [(2)–(5)] prevent polymer formation either by converting the reactants or the growing chains to unreactive compounds, *i.e.* chain termination takes place. Since polymers were obtained in good yields in most of the cases studied, the authors conclude that the first type of reaction predominates and proceeds at a much higher rate than the others.

The reduction in yield and molecular weight of the polyester with increased temperature may be explained by the increased role of these latter reactions, the rate of which increases at higher temperatures. The removal of the reactive groups from the reactants leads, on the one hand, to a reduction in the yield of polymer and, on the other hand, to a change in the reactant ratio which eventually leads to chain termination (*i.e.* causes a reduction in the molecular weight of the polyester). These reactions may also affect the functional groups of the growing chains and likewise cause chain termination.

In many classical homogeneous polycondensations it was found[73,74] that the initial ratio of the reactants had a considerable bearing on the molecular weight of the polymer. Attempts have also been made[37] to determine the influence of the reactant ratio on the molecular weight and yield of the polyester prepared by the interfacial method.

The relationship between the reduced viscosity of the polyarylate, prepared from isophthaloyl chloride and bisphenol A, and the reactant ratio is shown in Fig. 8. In all experiments the concentration of sodium hydroxide used was equivalent to the diol (*i.e.* the molar ratio of diol to sodium hydroxide was 1 : 2).

It can be seen from Fig. 8 that the polyarylate prepared from equimolar quantities of reactants possessed the highest reduced viscosity (*i.e.* the highest molecular weight). An increased concentration of isophthaloyl chloride (to the left of the maximum) or of the dihydric phenol (to the right of the maximum) caused a reduction of the reduced viscosity of the polyarylate. An excess of bisphenol A has the greater effect. When an 80% excess of isophthaloyl chloride was used, a polyester with a reduced viscosity more than half that of the product made with an equimolar ratio was obtained (0.46 and 0.74 respectively).

The authors compared the variation of the molecular weight of the polyesters prepared with an excess of the acid component in the above example and in the polycondensation of ethylene glycol with adipic acid[73,74] in the melt. They noted that in both cases the molecular weight fell as the excess of the acid compound was increased, but in the latter case an 80% excess of adipic acid led to an approximately sixfold reduction in the molecular weight of the polyester.

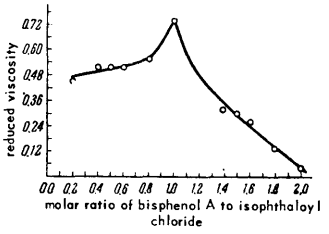


Fig. 8. Variation of the reduced viscosity of polyester in cresol with the reactant ratio.

It may be concluded from the above data that the ratio of the reactants has a significant effect on the molecular weight of the polyester produced by both interfacial polycondensation and those in the melt, although the mechanism of the action of the component in excess is different.

The possible competing reactions during polyesterification at phase boundaries, when one of the phases is aqueous, have already been indicated. One reaction leads to the synthesis of polyester while the others are chain breakers. In the presence of excess isophthaloyl chloride the following reactions, which would prevent the growth of polyester chains, are possible:

$$ClCOC_6H_4COCl + H_2O(NaOH) \rightarrow \rightarrow HOCOC_6H_4COOH + HCl(NaCl); \quad (1)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + H_2O(NaOH) \rightarrow HO[COC_6H_4COOC_6H_4C.(CH_3)_2C_6H_4O]_xNa + HCl(NaCl); \quad (2)$$

$$NaOC_6H_4C(CH_3)_2C_6H_4ONa + HCl(HOCOR-...) \rightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + NaCl(NaOCOR-...); \quad (3)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + HCl(HOCOR-...) \rightarrow Cl[COC_6H_4COOC_6H_4C.(CH_3)_2C_6H_4O]_xH + NaCl(NaOCOR-...); \quad (4)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + ClCOC_6H_4COCl \rightarrow Cl[COC_6H_4COOC_6H_4C.(CH_3)_2C_6H_4O]_xCOC_6H_4COCl + NaCl. \quad (5)$$

Since the authors obtained polymers in good yields in each experiment of this series, it clearly follows that the extent of reactions (1) and (3) was small, although some of the isophthaloyl chloride must be hydrolysed. The fact that the polyester made with an excess of isophthaloyl chloride has a much greater reduced viscosity than that produced from an excess of bisphenol A was explained on the grounds that partial hydrolysis of the acid chloride does in fact compensate for and reduce the excess of this component.

The role of the excess component during polycondensation in the melt is twofold. Under certain conditions and at a definite stage of the reaction, it may act as a chain breaker. This would explain why the polymers obtained had similar terminal groups. On the other hand, the excess component could cause the destruction of polymer chains (notably those of the greatest length) which would also contribute to a reduction in the molecular weight.

During polyesterification at the boundary between two phases the destructive reaction is clearly not possible. The reduced molecular weight of the polymer must, therefore, arise from the prevention of chain growth. This clearly also explains why an excess of the acid component has less effect (in reducing the molecular weight of the polyester) in interfacial polyesterification than it has during polycondensation in the melt or in homogeneous solutions at high temperature.

As has been indicated above, the growth of the molecular weight of the polyester may be stopped not only by hydrolysis reactions which act as chain breakers but also by the conversion of the phenoxide group to a hydroxy group by hydrogen chloride [reactions (3) and (4) above] produced by the hydrolysis of the acid chloride. Korshak and coworkers carried out a series of reactions in which the amount of sodium hydroxide used was sufficient to neutralise completely the isophthaloyl chloride (*i.e.* in the molar ratio 4 : 1) in order to eliminate the influence of hydrogen chloride during a study of the effect of the reactant ratio on the polycondensation process. The results of these experiments (Fig. 9) indicated that the polymer of maximum reduced viscosity was obtained when the molar ratio bisphenol A : : isophthaloyl chloride was 1.7 rather than equimolar (*cf.* Figs. 8 and 9). This shift of the maximum to the region where a relatively high excess of the phenol was used must be associated with an increase in the role played by the acid chloride hydrolysis reactions because large quantities of free alkali are present in the reaction mixture.

The authors conclude that the results obtained in interfacial polyesterification depend on the quantity of sodium hydroxide in the aqueous phase. The alkali is necessary both to produce the phenoxide and to combine with the hydrogen chloride liberated during the polyesterification process. In view of this, Korshak *et al.*[37] carried out a series of experiments in which the bisphenol A : isophthaloyl chloride ratio and the other experimental conditions were kept constant and the quantity of alkali in the aqueous phase was varied. The results (Fig. 10) show that the polymer of greatest reduced viscosity was obtained when the alkali used was only slightly in excess (0.2–0.3 mole) of that required for the conversion of the dihydric phenol to the phenoxide. Higher concentrations of sodium hydroxide clearly led to an increase in the hydrolysis of both isophthaloyl chloride and the terminal acyl chloride groups of the growing chains. This prevented chain growth and caused a fall in the polymer yield and a marked lowering of its reduced viscosity.

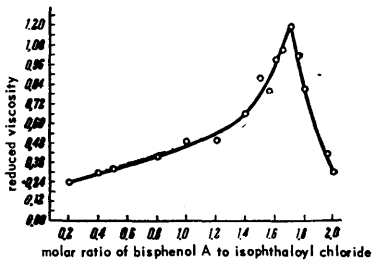


Fig. 9. Variation of the reduced viscosity of polyester in cresol with the reactant ratio.

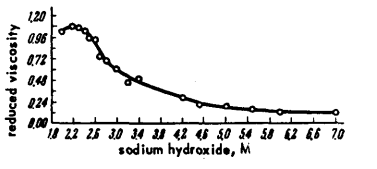


Fig. 10. Variation of the reduced viscosity of polyester in cresol, in relation to sodium hydroxide concentration.

Eareckson[54] found that the base used to combine with the hydrogen chloride also has an effect on interfacial polyesterification. The best results were obtained with sodium hydroxide. Potassium hydroxide gave poorer results and the yield was greatly reduced when pyridine was employed. It is obvious from the above results that the reaction cannot be accomplished successfully merely by ensuring the presence of a substance in the reaction mixture which can combine with acid. The presence of phenoxide ions in the system appears to be a necessary condition for the production of high-molecular polyarylates[54].

The structure of the reactants also has a marked effect on the reaction. Thus, dihydric phenols which contain electronegative substituents (*e.g.* sulphonic acid and carbonyl groups) do not enter into polycondensation reactions as readily as unsubstituted dihydric phenols or those with electropositive substituents[54].

Electronegative groups, which increase the acidity of the phenol, lower the reactivity of phenoxide ion which, according to Morgan[52,53] and Eareckson[54], is the active species in interfacial polyesterification. Eareckson[54] explained the much lower molecular weights of the polyarylates obtained from 4,4′-dihydroxybenzophenone, 2,4-dihydroxybenzophenone, 4,4′-dihydroxydiphenylsulphone and 2,4-dihydroxybenzaldehyde (Table 6) as due to the electronegative substituents in the dihydric phenol.

The addition of monofunctional substances to the reactants in interfacial polyesterification was also studied[37]. Substances of a chemical nature similar to that of the reactants (benzoyl chloride and phenol) were used as additives. The addition of either benzoyl chloride or phenol caused a significant lowering of the reduced viscosity (*i.e.* the molecular weight) of the polyarylate (Figs. 11 and 12). Small quantities of either benzoyl chloride or phenol are the most effective.

The additive reacts with either the reactant or the growing polymer chain and blocks their reactive end groups and consequently their ability to enter into further reactions.

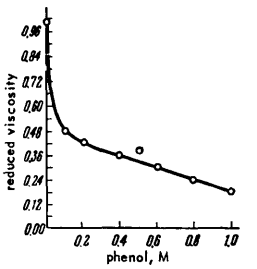


Fig. 11. Variation of the reduced viscosity of polyester in cresol, in relation to phenol concentration.

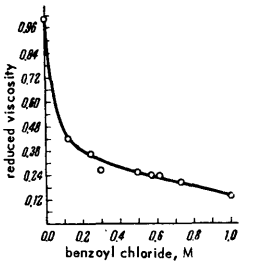


Fig. 12. Variation of the reduced viscosity of polyester in cresol, in relation to benzoyl chloride concentration.

TABLE 6. Effect of dihydric phenol structure on the reduced (inherent) viscosity of the polyarylate

Dihydric phenol	Acid chloride	η_{inh}
4,4′-Dihydroxybenzophenone	sebacoyl	0.01
2,4-Dihydroxybenzophenone	isophthaloyl : terephthaloyl (50 : 50)	0.38
	ditto	1.38
4,4′-Dihydroxydiphenylpropane	isophthaloyl	0.41
4,4′-Dihydroxydiphenyl sulphone	»	1.86
4,4′-Dihydroxydiphenyl sulphone	isophthaloyl : terephthaloyl (50 : 50)	0.54
2,4-Dihydroxydiphenylbenzaldehyde	ditto	0.20
Resorcinol	»	1.01

Note. η_{inh} was determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°, $\eta_{inh} = ln\,\eta_{rel}/c$.

These reactions may be described by the following equations:

$$NaOC_6H_4C(CH_3)_2C_6H_4ONa + C_6H_5COCl \rightarrow \rightarrow C_6H_5COOC_6H_4C(CH_3)_2C_6H_4OCOC_6H_5 + NaCl; \quad (1)$$

$$\ldots - COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4ONa + C_6H_5COCl \rightarrow \rightarrow \ldots - COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4OCOC_6H_5 + NaCl; \quad (2)$$

$$ClCOC_6H_4COCl + C_6H_5ONa \rightarrow \rightarrow C_6H_5OCOC_6H_5COOC_6H_5 + NaCl; \quad (3)$$

$$\ldots - COC_6H_4C(CH_3)_2C_6H_4OCOC_6H_4COCl + C_6H_5ONa \rightarrow \rightarrow \ldots - OC_6H_4C(CH_3)_2C_6H_4OCOC_6H_4COOC_6H_5 + NaCl. \quad (4)$$

A number of compounds have been suggested as catalysts for polyesterification at phase boundaries, *e.g.* quaternary ammonium bases[3,20,21,46,47,53], sulphonium compounds[47], tertiary amines and their salts[20,53].

(b) Preparation of polycarbonates by the polycondensation of phosgene and dihydric phenols in pyridine or in the presence of

pyridine. The polycondensation of phosgene with dihydric phenols, *e.g.* bisphenol A, proceeds according to the equation

$$x\mathrm{HOC_6H_4C(CH_3)_2C_6H_4OH} + x\mathrm{COCl_2} \rightarrow \rightarrow [-\mathrm{OC_6H_4C(CH_3)_2C_6H_4OCO}-]_x + 2x\mathrm{HCl}.$$

The reaction is usually carried out by passing phosgene into a solution of the dihydric phenol in pyridine. Pyridine is used (a) to combine with the liberated hydrochloric acid, (b) as a solvent, and (c) because it apparently catalyses the reaction[21]. When the volume of phosgene admitted reaches the stoichiometric quantity, the reaction mixture suddenly becomes very viscous. The polymer is precipitated from the reaction mixture with methanol, isopropanol, or other similar substances.

Phosgene may also be polycondensed with a dihydric phenol in benzene, toluene, chlorobenzene, dioxan, methylene chloride, trichloroethylene, and other solvents by the addition of a stoichiometric or larger quantity of pyridine (based on the available hydrogen chloride) to these solvents.

The molecular weight of polycarbonates prepared by this method may be varied by changing the reaction temperature, the concentration of dihydric phenol, the rate of addition of phosgene, etc.[21] This method for the production of polycarbonates is economically less attractive than other syntheses because of the consumption of pyridine.

3. Preparation of Polyarylates from Diketenes and Dihydric Phenols

In 1959 Korshak, Rogozhin, and Volkov[55] suggested a new method for the synthesis of polyesters based on the known reaction of glycols and dihydric phenols with carbon suboxide. The authors obtained polyarylates of malonic acid by the reaction of carbon suboxide with quinol and bisphenol A:

$$x\mathrm{HOArOH} + x\mathrm{O{=}C{=}C{=}C{=}O} \rightarrow \rightarrow x\mathrm{O{=}C{=}CH{-}COOArOH} \rightarrow [-\mathrm{OCCH_2COOArO}-]_x.$$

The polymerisations were carried out in chloroform in sealed tubes. The reaction temperature was increased from -50° to +10° over a period of 24 h, and continued for a period of 5–10 days at room temperature.

Analogous reactions might be anticipated with other bis-ketenes.

III. PROPERTIES OF POLYARYLATES

1. Chemical Properties

The chemical properties of polyarylates have been described in a number of papers [3,17,19-21,26,40,47,54,69]. Schnell[3,20], Rémond[19], Hechelhammer and Peilstöcker[26], and others have reported data concerning the chemical properties of polycarbonates. Stability to water, aqueous solutions of neutral salts, concentrated mineral acids (including nitric and hydrofluoric acids), aqueous organic acids, oxidising agents (even in acid media), solutions of weak alkalis (such as sodium carbonate and bicarbonate), higher alcohols, aliphatic and alicyclic hydrocarbons, oils, fats, grape, orange, and tomato juices, and tincture of iodine is a characteristic property of polycarbonates[3,17,19,20,21,26].

Polycarbonates possess limited stability to the action of strong alkalis, such as sodium and potassium hydroxides, which slowly corrode the sample surface, while its molecular weight and other physical properties remain substantially unaltered[3]. The thickness of a bisphenol A polycarbonate film was reduced from 110μ by 24, 29, and 46μ after treatment with 5, 10, and 20% solutions of sodium hydroxide respectively for a period of 13 weeks[3]. The polycarbonate of 2,2-di(4-hydroxy-3,5-dichlorophenyl)propane was significantly more resistant to hydrolysis. The properties of this polymer were unaltered after contact with a 20% solution of sodium hydroxide for 13 weeks at room temperature. Polycarbonates are not stable to ammonia and amines[17,19,26].

Schnell[3] established that the colour and mechanical properties of bisphenol A polycarbonate films were unaltered after 72 h irradiation with ultra-violet light. The properties of a similar polycarbonate film were also found to be essentially unchanged after storage in air at 150° for 26 weeks, or 8 weeks at 170°. Data concerning the stability of polycarbonate films to atmospheric oxygen at various temperatures are presented in Table 7.[20]

The physical properties of the polyarylates from bisphenol A and terephthalic acid were described in a paper by Korshak *et al.*[40] They showed that these polyarylates were stable to ethanol, chloroform, dioxan, carbon tetrachloride, methylene chloride, dimethylformamide, ethyl methyl ketone, benzene, chlorobenzene, *p*-xylene, tetrachloroethane, tetrachloroethylene, tetrahydrofuran, and n-heptane. Partial solubility was achieved in some of the above solvents after heating for 3 h at the boiling point (if this was less than 100°) or at 100°; this treatment did not significantly lower the reduced viscosity of the polymers in cresol.

The stability of polyarylates to the action of *m*-cresol at different temperatures was also studied (Figs. 13–15). From Figs. 13 and 14 it can be seen that the viscosity of the solutions of polyarylates, produced from bisphenol A and isophthaloyl chloride by either interfacial polyesterification (Fig. 14) or by the high-temperature polyesterification in homogeneous solution, decreased with increasing temperatures and heating periods. The polyarylate prepared by the interfacial technique was, however, more prone to

TABLE 7. Stability of polycarbonate films to the action of atmospheric oxygen[20].

Bisphenol	Thickness of film, μ	Temp., °C	Duration of treatment, weeks	Tensile strength, kg cm^{-2}	Elongation at rupture, %
Bisphenol A	45	140	0	663	54
			4	664	8
			8	749	7
			12	684	8
	50	150	0	868	105
			14	695	15
			26	705	12
	80	160	0	774	148
			8	647	58
			12	635	14
1,1-di-(4-Hydroxyphenyl)-cyclohexane	65	170	0	814	56
			4	769	8
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	60	190	0	1023	7
			4	1006	10
			8	1007	9

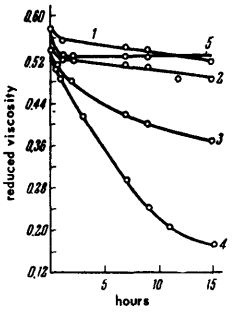


Fig. 13. Decomposition of the bisphenol A-isophthaloyl chloride polyarylate, prepared by homogeneous polycondensation in cresol:
1) 105°; 2) 140°; 3) 164°; 4) 183°, in an atmosphere of nitrogen;
5) 105° in air.

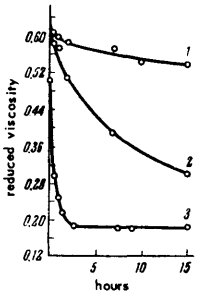


Fig. 14. Decomposition of the bisphenol A-isophthaloyl chloride polyarylate, prepared by interfacial polycondensation of *m*-cresol in an atmosphere of nitrogen:
1) 85°; 2) 105°; 3) 183°.

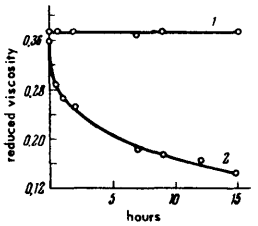


Fig. 15. Decomposition of the bisphenol A-terephthaloyl chloride polyarylate, prepared by homogeneous polycondensation in *m*-cresol in an atmosphere of nitrogen:
1) 105°; 2) 183°.

depolymerisation than that made by homogeneous (equilibrium) polycondensation. Thus, the reduced viscosity of the polyarylate made by the latter method was reduced from 0.56 to 0.48 after heating for 15 h at 105° in *m*-cresol, whereas the reduced viscosity of the polyarylate made by the heterogeneous procedure was approximately halved (0.64 to 0.30) by a similar treatment. Evidently this is a reflection of the different molecular-weight distribution in the polyarylates made by the equilibrium and non-equilibrium polycondensations. There is every reason to believe that there is a wider distribution of molecular weights in polyarylates made by the heterogeneous method. If this is so, the polymer must contain some molecules of very high molecular weight which are most prone to decomposition.

The stability of the polyarylate to cresol also depends on its chemical structure. A comparison of Figs. 15 and 13 shows that the bisphenol A–terephthalic acid polyarylate is more stable to *m*-cresol than the corresponding isophthalic polyester. Thus, the terephthalic acid polyarylate is virtually unaffected by heating with *m*-cresol at 105°; after 15 h at 183° the reduced viscosity in *m*-cresol decreased by a factor of approximately 2.5 (from 0.36 to 0.14), whereas that of the isophthalic acid polyarylate was reduced threefold (0.56 to 0.18) under similar conditions.

The authors concluded from the above data that, under the influence of a large excess of *m*-cresol (0.5% solutions) at high temperatures, polyarylates undergo decomposition, by an alcoholysis mechanism:

$$\ldots-COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-\ldots + CH_3C_6H_4OH \rightarrow$$
$$\rightarrow \ldots-COC_6H_4COOC_6H_4CH_3 + HOC_6H_4C(CH_3)_2C_6H_4O-\ldots$$

The chemical decomposition of polyarylates by the action of dicarboxylic acid chlorides, dicarboxylic acids, and dihydric phenols has also been investigated (Fig. 16)[40].

Conix[47] investigated the stability of the polyarylates of structures A and B,

$[-COC_6H_4OC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-]_x$ polyarylate A,

$[-COCH=CHCOOC_6H_4C(CH_3)_2C_6H_4O-]_x$ polyarylate B,

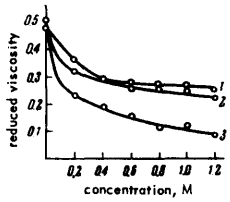


Fig. 16. Decomposition of polyarylates by bisphenol A:
1) polyarylate, prepared by homogeneous polycondensation of bisphenol A-terephthaloyl chloride; 2) polyarylate, prepared by homogeneous polycondensation of bisphenol A-isophthaloyl chloride; 3) polyarylate, prepared by interfacial polycondensation of bisphenol A-isophthaloyl chloride.

TABLE 8. Decomposition of polyarylates in boiling ethanol[47].

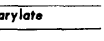
Duration of treatment, h	Reduced viscosity of the polyarylate		
	polyarylate A	polyarylate B	
0	0.82	1.3	1.0
3	0.72	0.80	0.75
66	0.66	insoluble	0.45

TABLE 9. Effect of various substances on polyarylate films[47].

Reagent	Temp., °C	Duration of treatment, h	Loss in weight (%) and property	
			polyarylate A	polyarylate B
0.1 *N* NaOH	Boiling	1	0.8 (stable, transparent)	decomposed
	»	19	3.5 (ditto)	
	»	90	13.5 (stable, opaque)	
	25	75	unchanged	19 (brittle, opaque)
	25	360	»	
$NaHCO_3$ (10%)	Boiling	24	»	8.4 (stable, opaque)
	»	164	2.3 (stable, transparent)	
NH_4OH (3.5%)	25	70	unchanged	decomposed
	25	164	»	
NH_4OH (25%)	25	60	decomposed	
0.1 *N* H_2SO_4	Boiling	24	unchanged	unchanged

to the action of boiling alcohol and solutions of acids and alkalis. His results (Tables 8 and 9) show that prolonged boiling of the polyarylates in ethanol caused some decrease in the reduced viscosity, the lowest value being obtained for the polyarylate of the aromatic dicarboxylic acid. The data in Table 9 show that films of both polyarylates are stable to the action of aqueous acids and alkalis at room temperature and even at the boiling point. They were, however, decomposed by concentrated ammonia solutions.

Eareckson[54] found that polyarylates are virtually non-inflammable. The mixed polyarylate of 4-chlororesorcinol with isophthalic and terephthalic acids was non-combustible even when the chlorine content was 12.5%. The mixed polyarylate of bisphenol A with isophthalic and terephthalic acids is particularly resistant to the hydrolytic attack of acids and alkalis. Polyarylates are stable to ultra-violet light, apart from acquiring a yellow colour. Korshak, Gribova, and Andreeva[69] described the effect of X-rays on phosphorus-containing polyarylates. They showed that the polyarylates of phosphinic acid were amenable to radiation vulcanisation. Thus, the phenoxyphosphinic acid–quinol polyester after only 30 h irradiation had a cross-linked structure, whereas 50 h irradiation was necessary to vulcanise the phenylphosphinic–quinol polyarylate.

2. Physical Properties

The physical properties of polyarylates, like those of other polymers, are intimately connected with their chemical structure, molecular weight, and polydispersity.

(a) Thermal properties. The softening temperatures of polyarylates are determined, to a considerable extent, by their chemical structure. Most polyarylates do not possess a clearly defined softening temperature; they melt over a range of temperatures. For the polycarbonates this temperature range is usually 10°–20°[3,19]. A very high melt viscosity is a characteristic of many polyarylates[3,19,20,31,46].

The softening temperatures of a number of polyarylates which are described in the literature are shown in Table 10. These data are not strictly comparable since they were obtained by different workers who used different methods for the synthesis and studies of the polymers. Nevertheless, they give an indication of the relationship between the softening temperature and the structure of the polyarylates.

Comparison of the softening temperatures of the polycarbonates of a number of dihydric phenols (Table 10, Nos. 1–26)[3] shows that the polycarbonates of di(4-hydroxyphenyl)methane and di(4-hydroxyphenyl)ethane, *i.e.* polycarbonates of dihydric phenols in which the aromatic rings are connected by unbranched methylene chains, have the highest softening temperatures.

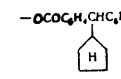
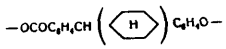
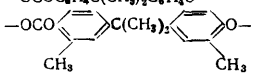
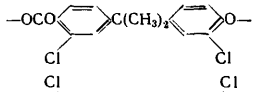
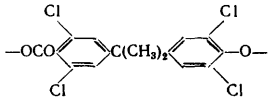
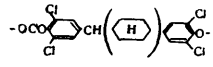
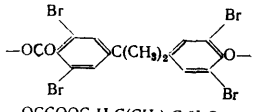
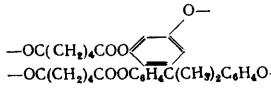
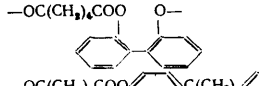
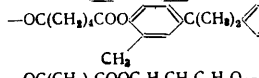
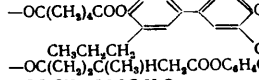
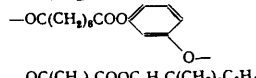
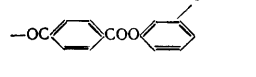
The softening temperature is reduced by substitution at one of the central hydrogen atoms of an alkyl group. If the aliphatic substituent in the bisphenol is replaced by an aromatic or alicyclic group, then the softening temperature is increased.

Korshak and Vinogradova[31,35] studied the influence of reactant structure on the softening temperatures of the polyarylates of terephthalic, isophthalic, sebacic, and adipic acids with dihydric phenols of various structures (Table 10, Nos. 31–34, 40–42, 45–48, 52–59, 63–65). They found that the softening temperatures of the polyesters were strongly dependent on the structure of the polymer chain. The polyarylate of quinol and terephthalic acid had the highest softening point. It did not melt in a capillary below 500° but merely became cream-coloured at high temperatures. At temperatures below 360° this polyarylate does not undergo deformation and, therefore, its glass temperature and softening temperature must be above 360°. Poly(quinol isophthalate) has a much lower softening temperature, although it is still relatively high; deformation begins at about 350°.

The softening temperature of a polyarylate is also dependent on the orientation of the functional groups in the dihydric phenol. The polyesters from resorcinol and terephthalic and isophthalic acids, for example, have considerably lower softening temperatures than the corresponding quinol polyesters. Thus, similar regularities are observed for the polyarylates, whose chains comprise aromatic rings and ester groups only, as those found for the polyesters derived from aromatic dicarboxylic acids and aliphatic glycols[75,76]. The polyesters of acids and dihydric phenols, in which the functional groups are in the *para*-positions, have much higher softening temperatures than those from *meta*-substituted reactants. The authors' studies[31] of the polyarylates of terephthalic and isophthalic acids with bisphenol A, di(*p*-hydroxyphenyldiphenyl)-α,α'-*p*-xylene, and dihydroxynaphthylamines confirmed this rule.

It may be concluded[35] from a comparison of the softening temperatures of the adipic and sebacic acid polyarylates with the corresponding polyesters of terephthalic acid that the substitution of an aliphatic residue for the terephthalic acid residue in the polymer chain significantly

TABLE 10. Softening temperatures of polyarylates of various structures.

No.	Repeating unit	Softening temp., °C	Reference
1	—OCOC$_6$H$_4$CH$_2$C$_6$H$_4$O—	>300	3,19,20
2	—OCOC$_6$H$_4$CH(CH$_3$)C$_6$H$_4$O—	185	3,19,20
3	—OCOC$_6$H$_4$CH(C$_3$H$_7$)C$_6$H$_4$O—	150	3,19,20
4	—OCOC$_6$H$_4$CH[CH(CH$_3$)$_2$]C$_6$H$_4$O—	170	3,19,20
5		240	3,19,20
6		250	3,19,20
7	—OCOC$_6$H$_4$CH(C$_6$H$_5$)C$_6$H$_4$O—	200	3,19
8	—OCOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	220	3,19,20
9		150	3,20
10	—OCOC$_6$H$_4$C(CH$_3$)(C$_2$H$_5$)C$_6$H$_4$O—	205	3,19,20
11	—OCOC$_6$H$_4$C(CH$_3$)(C$_3$H$_7$)C$_6$H$_4$O—	200	3,19,20
12	—OCOC$_6$H$_4$C(CH$_3$)[CH(CH$_3$)$_2$]C$_6$H$_4$O—	200	3,19
13	—OCOC$_6$H$_4$(CH$_3$)(C$_4$H$_9$)C$_6$H$_4$O—	180	3,19,20
14	—OCOC$_6$H$_4$C(CH$_3$)(C$_7$H$_{15}$)C$_6$H$_4$O—	170	3,19,20
15	—OCOC$_6$H$_4$C(CH$_3$)(C$_6$H$_5$)C$_6$H$_4$O—	210	3,19
16	—OCOC$_6$H$_4$(C$_9$H$_7$)C$_6$H$_4$O—	190	3,19,20
17	—OCOC$_6$H$_4$CH$_2$CH$_2$C$_6$H$_4$O—	290	3,19,20
18	—OCOC$_6$H$_4$C(C$_6$H$_5$)$_2$C$_6$H$_4$O—	210	20
19	—OCOC$_6$H$_4$OC$_6$H$_4$O—	230	20
20	—OCOC$_6$H$_4$SC$_6$H$_4$O—	220	20
21	—OCOC$_6$H$_4$SOC$_6$H$_4$O—	230	20
22	—OCOC$_6$H$_4$SO$_2$C$_6$H$_4$O—	200	20
23		190	20
24		250	20
25		260	20
26		240	20
27	—OCCOOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	155	54
28	—OCCH$_2$COOC$_6$H$_4$O—	230	55
29	—OCCH$_2$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	85	55
30	—OC(CH$_2$)$_2$COOC$_6$H$_4$O—	230,270	54,48
31	—OC(CH$_2$)$_4$COOC$_6$H$_4$O—	225,235, 190	35,48,49,54
32		50	35
33	—OC(CH$_2$)$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	80	35,48,54
34		55	35
35		—	48
36	—OC(CH$_2$)$_4$COOC$_6$H$_4$CH$_2$C$_6$H$_4$O—	140	48
37	—OC(CH$_2$)$_4$COOC$_6$H$_4$C$_6$H$_4$O—	300	48
38		—	48
39	—OC(CH$_2$)$_3$C(CH$_3$)HCH$_2$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	—	48
40	—OC(CH$_2$)$_8$COOC$_6$H$_4$O—	172.150	35,54
41		38	35
42	—OC(CH$_2$)$_8$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	60	35,48,54
43	—OC(CH$_2$)$_8$COOC$_6$H$_4$C(CH$_3$)(C$_2$H$_5$)C$_6$H$_4$O—	—	48
44	—OC(CH$_2$)$_8$COOC$_6$H$_4$COC$_6$H$_4$O—	50	54
45	—OCC$_6$H$_4$COOC$_6$H$_4$O—	—	31,54
46		270	31,54

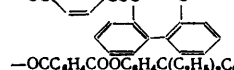
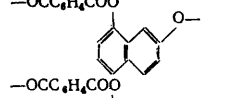
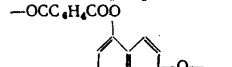
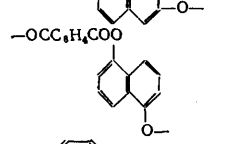
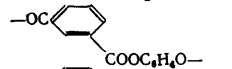
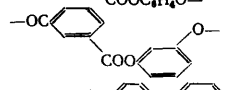
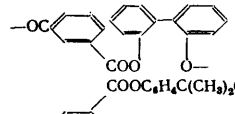
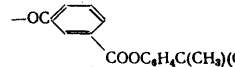
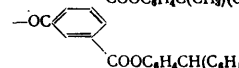
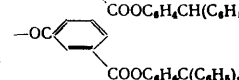
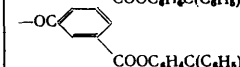
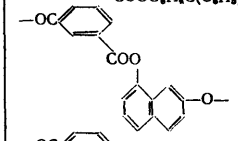
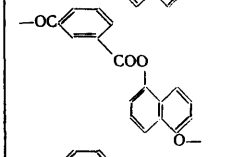
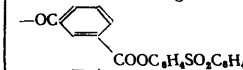
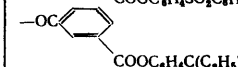
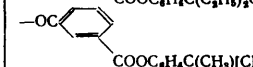
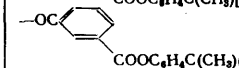
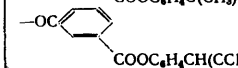
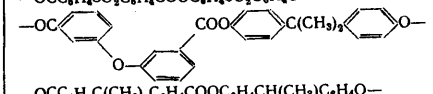
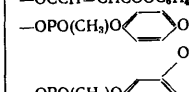
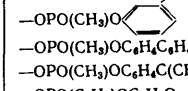
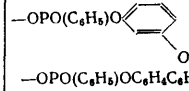
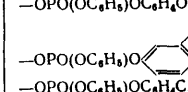
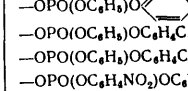
No.	Repeating unit	Softening temp., °C	Reference
47	—OCC$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	250,350	31,47,48,54
48		172	31
49	—OCC$_6$H$_4$COOC$_6$H$_4$C(C$_6$H$_5$)$_2$C$_6$H$_4$O—	150	47
50	—OCC$_6$H$_4$COOC$_6$H$_4$CH(C$_6$H$_5$)C$_6$H$_4$O—	200	47
51	—OCC$_6$H$_4$COOC$_6$H$_4$CH(CCl$_3$)C$_6$H$_4$O—	250	47
52	—OCC$_6$H$_4$COOC$_6$H$_4$C(C$_6$H$_5$)$_2$C$_6$H$_4$C(C$_6$H$_5$)$_2$C$_6$H$_4$O—	220	31
53		230	31
54		—	31
55		—	31
56		~320	
57		230,245	31,64
58		158	31
59		275,243,280	31,46,54
60		130,120	46,47
61		164,160	46,47
62		190	46,47
63		157	31
64		188	31
65		—	31
66		250	54
67		120	47
68		135	47
69		175	47
70		130	47
71	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	220,200	46,47
72	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$CH(CH$_3$)C$_6$H$_4$O—	112	47
73	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$(C$_2$H$_5$)$_2$C$_6$H$_4$O—	130	47
74	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)(C$_2$H$_5$)C$_6$H$_4$O—	160	47

TABLE 10 (contd.)

No.	Repeating unit	Softening temp., °C	Reference
75	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$CH(C$_6$H$_5$)C$_6$H$_4$O—	175	47
76	—OCC$_6$H$_4$OC$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)(C$_6$H$_5$)C$_6$H$_4$O—	160	47
77	—OCC$_6$H$_4$COC$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	160	47
78	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$COC$_6$H$_4$O—	122	47
79	—OCC$_6$H$_4$CH$_2$C$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	170	47
80	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$CH$_2$C$_6$H$_4$O—	130	47
81	—OCC$_6$H$_4$CH$_2$C$_6$H$_4$COOC$_6$H$_4$C(C$_2$H$_5$)$_2$C$_6$H$_4$O—	170	47
82	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	225	46,47
83	—OCC$_6$H$_4$SO$_2$C$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	190,230	47,54
84	—OCC$_6$H$_4$CCl$_2$C$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—]	220	47
85	—OCC$_6$H$_4$SO$_2$C$_6$H$_4$COOC$_6$H$_4$SO$_2$C$_6$H$_4$O—	—	54
86		85	46
87	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$CH(CH$_3$)C$_6$H$_4$O—	190	46
88	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$CH(C$_6$H$_{11}$)C$_6$H$_4$O—	170	46
89	—OCC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$COOC$_6$H$_4$CH(C$_6$H$_5$)C$_6$H$_4$O—	218	46
90	—OCC$_6$H$_4$CH(CH$_3$)C$_6$H$_4$COOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	225	46
91	—OCCH=CHCOOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	150,240	46,54
92	—OCCH=CHCOOC$_6$H$_4$C(CH$_3$)(C$_2$H$_5$)C$_6$H$_4$O—	130	46
93	—OCCH=CHCOOC$_6$H$_4$CH(C$_6$H$_{11}$)C$_6$H$_4$O—	180	46
94		63	41,42
95		36	42
96	—OPO(CH$_3$)OC$_6$H$_4$C$_6$H$_4$O—	110	42
97	—OPO(CH$_3$)OC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	88	42
98	—OPO(C$_6$H$_5$)OC$_6$H$_4$O—	83	41,42
99		55	42
100	—OPO(C$_6$H$_5$)OC$_6$H$_4$C$_6$H$_4$O—	120	42
101	—OPO(C$_6$H$_5$)OC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	55	42
102		23	41,42
103		17	42
104	—OPO(OC$_6$H$_5$)OC$_6$H$_4$C$_6$H$_4$O—	55	42
105	—OPO(OC$_6$H$_5$)OC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O—	12	42
106	—OPO(OC$_6$H$_4$NO$_2$)OC$_6$H$_4$O—	36	41
107	—OPO(OC$_6$H$_4$OCH$_3$)OC$_6$H$_4$O—	35	41

It has been shown[33-35] that the softening temperatures in several series of mixed polyarylates depend on the structure and proportions of the starting materials from which they were prepared. The properties of the mixed polyarylates synthesised are presented in Tables 11–14. The results show that the variation of softening temperature with composition in the aromatic dicarboxylic acid polyarylates passes through a minimum. Thus, the minimum softening temperature in the resorcinol–bisphenol A–terephthalic acid polyarylate series was observed when the resorcinol : bisphenol A ratio in the mixed polyester was 0.7 : 0.3. Clearly, with this ratio of reactants the polymer chain must be least closely packed. An increase in the concentration of either phenol, *i.e.* more than 70% resorcinol or more than 30% bisphenol A, leads to the production of a mixed polyarylate with a higher softening temperature.

The softening temperatures of polyarylates, which contain an aliphatic carboxylic acid, invariably increase with the proportion of aromatic acid in the original mixture (Tables 13 and 14). Thus, as the proportion of terephthalic acid increases, the softening temperatures of the polyarylates in the bisphenol A–adipic acid–terephthalic acid system rise from 63° to > 350°, etc. The replacement of adipic by sebacic acid in the mixed polyarylate is accompanied by a reduction in the softening temperature[34].

Schnell's results[3,20] concerning the vitrification temperature of some polycarbonates, determined by refractometry or dilatometry, are presented in Table 15, together with density and refractive index data. The vitrification temperatures of most polycarbonates lie in the 130°–170° range.

Other thermal properties of bisphenol A polycarbonate have also been studied[21]; the results are set out in Table 16.

(b) Crystallinity. The crystallinity of polyarylates is very dependent on the structure. Schnell[3] noted that the polycarbonates of di(4-hydroxyphenyl)methane and 1,2-di(4-hydroxyphenyl)ethane were very easily crystallised. The polycarbonates of bisphenol A had a somewhat lower tendency to crystallise than the above two polyesters.

reduces the softening point. Thus, the softening temperatures of the polyarylates obtained from quinol and adipic and sebacic acids were 225° and 172° respectively, while poly(quinol terephthalate) does not melt below 500°. The softening temperature of poly(resorcinol terephthalate) is 270°, whereas that of the corresponding polyadipate is only 50°. The polyarylates of adipic acid have higher softening points than the corresponding derivatives of sebacic acid. This is apparently connected with the greater flexibility of the polymer chains in the latter case owing to the reduced proportion of aromatic nuclei[35].

The synthesis and properties of the polyarylates of various phosphinic acids (Table 10, Nos. 94–107) have been described[41,42]. The softening temperature of a polyester is markedly reduced by the replacement of the carboxyl CO group by a PO(R) group. The polycarbonate of bisphenol A, for example, has a softening temperature of 220°, whereas the corresponding polyarylates with methylphosphinic, phenylphosphinic, and phenoxyphosphinic acids begin to soften at only 88°, 55°, and 12° respectively.

TABLE 11. Mixed polyesters from terephthaloyl chloride, resorcinol, and bisphenol A.

Molar ratio of components	Reduced viscosity in cresol	Softening temperature, °C: in a capillary	Softening temperature, °C: from thermomechanical curve	σ, kg cm^{-2}	ϵ, %	Dielectric constant	Dielectric loss factor at 20°, f=400 c/s	Crystallinity, %
1 : 0 : 1	insoluble	~350	>350	610	8	3.5	0.002	~10
1 : 0.2 : 0.8	0.54	310–317	310	780	20	3.6	0.0045	amorphous
1 : 0.4 : 0.6	0.69	255–280	294	720	30	3.7	0.0045	»
1 : 0.6 : 0.4	0.70	240–270	254	720	60	3.8	0.004	slight indications of crystallinity
1 : 0.7 : 0.3	0.46	180–205	188	690	14	—	—	amorphous
1 : 0.8 : 0.2	0.36	205–230	—	770	11	8.7	0.005	»
1 : 0.9 : 0.1	insoluble	245–255	233	—	—	—	—	~50
1 : 1 : 0	insoluble	270–285	275	—	—	3.6	0.006	~70

Note. The polymers were white powders. Solubilities of the samples: in ethanol 0–0.2 g litre^{-1}; in benzene 0–0.9 g litre^{-1}; in dichlorethane 0–1.4 g litre^{-1}; σ – tensile strength; ϵ – relative elongation at break.

TABLE 12. Mixed polyesters produced from quinol, bisphenol A, and terephthaloyl and isophthaloyl chlorides.

Molar ratio of components	Softening temperature, °C: in a capillary	Softening temperature, °C: from thermomechanical curve	Tensile strength, kg cm^{-2}	Relative elongation at break, %	Physical state
0.2 : 0.8 : 0.5 : 0.5	310—320	274	640	36	the sample has a completely random structure with no indication of polymer ordering
0.4 : 0.6 : 0.5 : 0.5	300—310	226	690	12	amorphous
0.5 : 0.5 : 0.5 : 0.5	300—310	265	630	10	ditto
0.6 : 0.4 : 0.5 : 0.5	310—320	—	670	11	amorphous; strong indications of an ordered structure. Ordered chains have a gas-crystal structure
0.7 : 0.3 : 0.5 : 0.5	320—340	325	610	6	ordered structure. The chains have a highly ordered arrangement
0.8 : 0.2 : 0.5 : 0.5	>350	—	—	—	ditto

TABLE 13. Mixed polyesters prepared from bisphenol A and the chlorides of adipic and terephthalic acids.

Molar ratio of components	Reduced viscosity in cresol	Softening temp., °C (from thermomechanical curve)	σ, kg cm^{-2} *	ϵ, %**	Physical state	Remarks
1 : 1 : 0	0.44	63	—	—	amorphous with little order within chains	solid. Solubility (g litre^{-1}): in alcohol 0.7, in benzene 9.9
1 : 0.8 : 0.2	0.42	88	—	—	ditto	solid
1 : 0.6 : 0.4	0.56	185	600	25	amorphous with marked order within chains	white powder
1 : 0.5 : 0.5	0.70	242	580	72	ditto	white powder solubility (g litre^{-1}) in alcohol 0.3, in benzene 9.8, in dichloroethane 0.6
1 : 0.4 : 0.6	0.58	248	700	15	»	white powder
1 : 0.2 : 0.8	0.63	350	720	22	mainly amorphous with little order within chains	white powder; solubility (g litre^{-1}) in alcohol 0, in benzene 0.6, in dichloroethane — 0.3
1 : 0 : 1	insoluble	350	610	8	~10%	white powder

* σ — tensile strength.

** ϵ — relative eleongation at break.

TABLE 14. Mixed polyesters obtained from bisphenol A and the chlorides of sebacic and terephthalic acids.

Molar ratio of components	Reduced viscosity in cresol	Softening temp., °C (from thermomechanical curve)	Physical state	Remarks
1 : 1 : 0	0.58	26		an almost solid translucent substance. Tensile strength and relative elongation at break of films ~450 kg cm^{-2} and 530%.
1 : 0.8 : 0.2	0.38	59	amorphous with little order within chains	transparent solid. Solubility (g litre^{-1}): in alcohol 0.4, in benzene 5.8, in dichloroethane 7.8
1 : 0.6 : 0.4	0.36	156	amorphous with considerable order within chains	white powder
1 : 0.5 : 0.5	0.38	171	ditto	white powder. Solubility (g litre^{-1}): in alcohol 0.2. in benzene 10.3, in dichloroethane 0.8
1 : 0.4 : 0.6	0.46	235	»	white powder
1 : 0.3 : 0.7	0.50	275	evidence of crystallinity	white powder, Solubility (g litre^{-1}): in alcohol 0, in benzene 3.7, in dichloroethane 0.3
1 : 0.2 : 0.8	0,42	305	ditto	white powder
1 : 0 : 1	insoluble	>350	~10%	white powder

TABLE 15. Vitrification temperature, density, and refractive index of some polycarbonates.

Bisphenol	Vitrification temp., °C	Density, g cm^{-3}	Refractive index
R_1R_2*-1,1-Ethane	130	1.22	1.5937
R_1R_2-1,1-Butane	123	1.17	1.5792
R_1R_2-1,1-Isobutane	149	1.18	1.5702
R_1R_2-2,2-Propane	149	1.20	1.5850
R_1R_2-2,2-Butane	134	1.18	1.5827
R_1R_2-2,2-Pentane	137	1.13	1.5745
R_1R_2-4,4-Heptane	148	1.16	1.5602
R_1-Phenylmethylmethane	176	1.21	1.6130
R_1R_2-Diphenylmethane	121	1.27	1.6539
R_1R_2-1,1-Cyclopentane	167	1.21	1.5993
R_1R_2-1,1-Cyclohexane	175	1.20	1.5900
2,2-di(4-hydroxy-3-chlorophenyl) propane	147	1.32	1.5900
2,2-di(4-hydroxy-3,5-dichlorophenyl) propane	180	1.42	1.6056
1,1-di(4-hydroxy-3,5-dichlorophenyl) cyclohexane	163	1.38	1.5858
2,2-di(4-hydroxy-3,5-dibromophenyl) propane	157	1.91	1.6147
2,2-di(4-hydroxy-3-methylphenyl) propane	95	1.22	1.5783

* R_1R_2 = di(4-hydroxyphenyl)-.

As a general rule, it appears that polycarbonates which have the more asymmetric or branched substituent at the central carbon atom of the dihydric phenol are less likely to be crystalline[19].

Many polycarbonates yield colourless transparent products after melting and cooling, irrespective of the rate of cooling or the size of sample. This indicates that if crystallites are produced their dimensions are less than the wavelength of visible light. Treatment of the polymer with a swelling agent can induce the crystallisation of certain polycarbonates.

Prietzschk[23] studied in detail the crystal structure of the polycarbonate of bisphenol A by X-ray methods. He concluded that, despite the unwieldy molecular structure, this polycarbonate may be oriented and crystallised, and its crystal lattice is very stable.

Korshak and Vinogradova[31,33-35,70] concluded, from a study of the X-ray patterns of homogeneous and mixed polyarylates of widely different structures, that a reduction of packing density of the polymer chain leads to the production of amorphous compounds. Such a reduction in packing density would result from the presence, in the aromatic reactants, of functional groups in the *meta*- or *ortho*- rather than *para*-positions (*e.g.* the polyarylates of isophthalic acid with 2,2′-dihydroxydiphenyl, resorcinol, etc.) or by the presence of side-chains in the dihydric phenol.

TABLE 16. Thermal properties of bisphenol A polycarbonate[21].

Property	Test result
Heat resistance	138°–143° with a load of 18.5 kg cm^{-2}
	140°–145° with a load of 4.6 kg cm^{-2}
Calculated shrinkage	0.005–0.007 cm cm^{-1}
Thermal conductivity	4.6×10^{-4} cal sec^{-1} cm^{-2} deg^{-1} cm
Coefficient of linear expansion	7×10^{-5} cm cm^{-1} deg^{-1}
M.p. of crystalline material	268°
Inflammability	self-extinguishing
Shrinkage on aging (after 2000 h at 125°)	0.001 cm cm^{-1}
Viscosity of melt at 300°	4000–6000 poises

Deformation under load (of a 12.7 cm cube)	Temp., °C	Load, kg	Deformation, %
	70	454	0.282
	70	227	0.080
	25	454	0.220
	25	227	0.101

Thus polyarylates of isophthalic and terephthalic acids with 2,2′-dihydroxydiphenyl and of isophthalic acid with di(*p*-hydroxyphenyldiphenyl)-α,α'-*p*-xylene are amorphous, but poly(quinol terephthalate) is crystalline.

It was also found[33,35] that the physical structure of mixed polyarylates were intimately connected with their composition (Tables 11–14). The mixed polyarylates of the resorcinol–bisphenol A–terephthalic acid series, for example, are amorphous if the resorcinol content is less than 90%. A very high resorcinol content in the polymer leads to a high degree of order in the polymer chain and hence to an increase in the extent of crystallinity.

The crystallinity of polyarylates is also dependent on the method of manufacture of articles from the polymer. Mikhailov and Eidel'nant[71], for example, found that films of bisphenol A–isophthalic acid polyarylate cast from solution were more crystalline than films obtained from the melt; generally films produced by the latter method were amorphous. A bisphenol A–terephthalic acid polyarylate with a high degree of crystallinity may be obtained by annealing a pressed sample for several hours at 320°–350°.[71]

Conix[46,47] noted, during a study of the properties of the polyarylates of aromatic dicarboxylic acids of different structures, that the presence of an asymmetric substituent at the central atom of a dihydroxydiphenyl derivative reduced the tendency of the polyester to crystallise. Thus, the polyarylate of 2,2-di(4-hydroxyphenyl)butane and isophthalic acid will not crystallise under conditions similar to those in which the corresponding bisphenol A polyester does.

(c) Mechanical properties. The mechanical properties of polyarylates have been described in a number of papers[3,19-21,31,33-35,46,47]. Schnell[3,20], Thompson and Goldbaum[21], Hechelhammer and Peilstöcker[26] and others have reported data concerning mechanical properties of polycarbonates.

It has been found that the mechanical properties of polycarbonates depend on the method of preparation, the crystallinity, and molecular weight[3,19]. Thus polycarbonates made by interfacial polycondensation have good mechanical properties only when they have relatively high molecular weights, compared with those made by homogeneous polycondensation in solution or in the melt. Schnell[3] considers that this was due to the anomalous molecular-weight distribution of the polyarylates produced at phase boundaries (Fig. 21).

Polycarbonates may be stretched[3]. The macromolecules of polycarbonates can be reoriented in the direction of a stretching force and thus acquire increased tensile strength and double refraction. The length of a polycarbonate can be increased up to double by stretching below the vitrification temperature, whereas stretching above the vitrification temperature can lead to larger increase in the length through thermoplastic deformation[3,19].

The stability characteristics of polycarbonate films of various structures are set out in Table 17.[19] The load–elongation curve for the bisphenol A polycarbonate is shown in Fig. 17. The mechanical stability of the film also depends on its method of production. Data concerning the mechanical properties of polycarbonate films prepared by different methods from bisphenol A are given in Table 18. The stability characteristics of polycarbonate films vary with temperature. The relevant data for the polycarbonate of bisphenol A are presented in Table 19.

Articles moulded from bisphenol A polycarbonate are colourless, transparent, and possess good mechanical properties (Table 20).

The mechanical properties of homogeneous and mixed polyarylates of different structures were studied by Korshak and Vinogradova[31,33-35]. It was found that the stability characteristics of unoriented polyarylate films, produced from a melt, were related to the structure of the polymer. Thus, the tensile strength and relative elongation at the breaking point for the polyarylate of sebacic acid and bisphenol A were 450 kg cm^{-2} and 530% respectively. The corresponding values for the polyterephthalate derivative of bisphenol A were 610 kg cm^{-2} and 8% only. These data demonstrate that the substitution in the polyarylate of an aliphatic dicarboxylic acid residue for the aromatic one slightly reduces the tensile strength of the film and markedly increases its elasticity.

The dependence of the mechanical properties of mixed polyarylates on their composition is evident from Tables 11–14. The tensile strengths of the mixed polyarylates of the resorcinol–bisphenol A–terephthalic acid series (Table 11) lie in the range 610–780 kg cm^{-2}. The relative

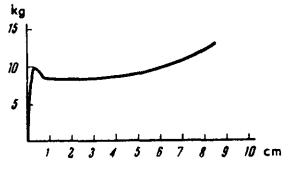


Fig. 17. Load–elongation curve for bisphenol A polycarbonate films (100μ thickness).

TABLE 17. Mechanical properties of polycarbonate films (thickness 50–60μ) prepared from solution[19].

Bisphenol	Orientation	Tensile strength, kg cm^{-2}	Elongation at break, %	Impact strength, cm kg cm^{-2}	No. of bends to failure
R_1R_2*-1,1-Ethane	unstretched	759	167	1013	>10 000
R_1R_2-1,1-Isobutane	»	775	147	300	>10 000
R_1R_2-2,2-Propane	»	820	180	900	>10 000
R_1R_2-2,2-Propane	stretched 1 : 2	1400—1700	32—40	—	>10 000
R_1R_2-2,2-Propane	stretched 1 : 4.7, crystalline	2150	15	425	>10 000
R_1R_2-2,2-Propane	stretched 1 : 11	3500	20	320	>10 000
R_1R_2-2,2-Butane	unstretched	725	70	363	5800
R_1R_2-2,2-Pentane	»	665	66	703	900
R_1R_2-Methylphenylmethane	»	824	55	172	1000
R_1R_2-1,1-Cyclohexane	»	814	56	169	5000
R_1R_2-1,1-Cyclopentane	»	708	119	552	>10 000
2,2-di(4-Hydroxy-3-dichlorophenyl) propane	»	995	19	65	>10 000
2,2-di(4-Hydroxy-3,5-dichlorophenyl) propane	»	1154	10	33	3000
2,2-di(4-Hydroxy-3,5-dibromophenyl) propane	»	1112		36	1000

* R_1R_2 = di(4-hydroxyphenyl)-.

TABLE 18. Mechanical properties of bisphenol A polycarbonate films (the polymers had Z_η = 0.087 and were flexed more than 10 000 times)[3].

Method of preparing films	Degree of orientation	Tensile strength, kg cm^{-2}	Elongation at break, %	Impact strength, cm kg cm^{-2}
Cast from solution	unstretched	820	180	900
ditto	stretched 200%	1400—1700	32—40	—
Blown	not further stretched	890	155	700

TABLE 19. Temperature variation of the strength of polycarbonate films (cast from solution), with differing degrees of orientation[3].

Temp., °C	Original film		Film stretched 1.5 times		Film stretched 1.9 times	
	tensile strength, kg cm^{-2}	elongation at break, %	tensile strength, kg cm^{-2}	elongation at break, %	tensile strength, kg cm^{-2}	elongation at break, %
30	680	96	891	9	1110	17
50	640	99	871	18	970	19
100	475	133	555	22	826	44
150	100	460	186	54	411	66

TABLE 20. Physical properties of polycarbonate articles cast under pressure.

Property	Numerical value
Flexural strength, kg cm^{-2}	800—1000
Impact strength	100%, not broken
Resistance to thermal shock, kg cm^{-2}	9—10
Yield point, kg cm^{-2}	650—700
Brinell hardness after 10 sec	930
Brinell hardness after 60 sec	900
Modulus of elasticity, kg cm^{-2}	22 000
Heat resistance (Martens), °C	125
Heat resistance (Vica), °C	165
Heat distortion point, °C	140

elongations of these films at the breaking point were between 8–60%. The polyarylate film obtained from a 60% resorcinol–40% bisphenol A mixture was the most elastic, *i.e.* it had the greatest relative elongation.

Conix has measured[46] the mechanical properties of a number of polyarylate films, obtained from solution in chlorinated hydrocarbons (Table 21). Similar data for cellulose triacetate, polystyrene, and bisphenol A polycarbonate films are given for comparison. Conix noted that, although the mechanical properties of his unoriented polyarylate films depended on their chemical structure, they varied only within the following ranges: tensile strength 6–9 kg mm^{-2}, the yield point 5 to 8 kg mm^{-2}, elongation at rupture 20–100%, and the modulus of elasticity 170 to 250 kg mm^{-2}. The good mechanical properties of a polyarylate are maintained right up to the softening temperature. Orientation of polyarylate films, in two directions, can significantly improve their mechanical properties. The tensile strengths of oriented polyarylates vary from 15 to 20 kg mm^{-2} and the elongation at rupture from 15 to 30%.[47]

According to Conix[46], the reduced viscosity of polyarylates (in 1,2-dichloroethane or tetrachloroethane) must be at least 0.4–0.5 if they are to possess film-forming properties. For fibre formation a reduced viscosity of ~ 1.0 is necessary.

(d) Electrical properties. The electrical properties of polycarbonates were studied by Schnell[3,20] (Table 22) especially those of bisphenol A polycarbonate (Table 23).[3,19,20,21]

It has been shown that the dielectric loss factor (tan δ) and the dielectric constant of bisphenol A polycarbonate vary only slightly at temperatures below 150°. Above the vitrification temperature, these constants tend to a maximum at 175°.[3,19]

The dielectric properties of the polyarylates of several dicarboxylic acids are given by Korshak and Vinogradova[33] (Table 11), and Mikhailov and Eidel'nant[71,72]. The latter workers[71] studied the temperature dependence of the dielectric loss factor (tan δ) and the dielectric constant of bisphenol A polycarbonate and the polyarylates of bisphenol A with sebacic, terephthalic, and isophthalic acids. It can be seen from Fig. 18 that the variation of the dielectric loss factor (tan δ) with temperature proceeds through two maxima. One maximum in tan δ occurs above 20°. The authors concluded, from the nature and mechanism of this

TABLE 21. Physical properties of various polymer films[46].

Property	Cellulose triacetate	Polystyrene	Polycarbonate	Polyarylate A	Polyarylate B	Polyarylate C
Tensile strength, kg mm^{-2}	11	6.3	8.4	8.4	7.0	6.3
Yield point, kg mm^{-2}	8	—	6.0	5.8	7.0	5.8
Elongation at the break, %	27—35	2.5—3.5	160	80	90	50
Modulus of elasticity, kg mm^{-2}	340	315	210	200	220	200
Softening temperature, °C	—	70—80	160	220	250	160
Absorption of water, % (after 24 h immersion)	4.3	0.5	0.2	0.3	0.2	0.3
Density, g cm^{-3}	1.28—1.30	1.05	1.20	1.21	—	—
Refractive index	1.48	1.59	1.58	1.62	1.61	1.60
Reduced viscosity	—	—	1.0	1.1	1.0	0.8

Note. Polyarylate A — $\left[-CO\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O-\right]_n$;

Polyarylate B — $\left[-CO\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O-\right]_x$;

Polyarylate C — $\left[-COCH{=}CHCOO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O-\right]_n$.

The polymers were plasticised with 15% triphenyl phosphate.

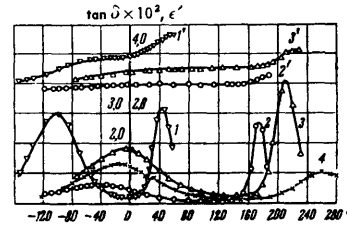


Fig. 18. Temperature dependence of the dielectric loss factor (1–4) and the dielectric constant (1′–4′) for bisphenol A polyarylates:
1) and 1′) with sebacic acid; 2) and 2′) with carbonic acid; 3) and 3′) with isophthalic acid; 4) and 4′) with terephthalic acid.

TABLE 22. Electrical properties of polycarbonates of various structures[22].

Bisphenol	Dielectric loss factor (tan δ) × 10^4, at 1000 c/s and 25°	Dielectric constant, at 1000 c/s and 25°	Dielectric loss factor × 10^4, at 1000 c/s and 100°	Dielectric constant, at 1000 c/s and 100°
R_1R_2*-1,1-Ethane	4.9	2.9	4.9	2.9
R_1R_2-1,1-Butane	5.2	3.3	5.2	3.3
R_1R_2-1,1-Isobutane	5.2	2.4	5.2	2.4
R_1R_2-2,2-Propane	4.9	2.8	4.9	2.8
R_1R_2-2,2-Butane	4.5	3.1	4.5	3.1
R_1R_2-2,2-Pentane	4.2	2.3	4.2	2.3
R_1R_2-Methylphenylmethane	5.0	3.3	5.0	3.3
R_1R_2-1,1-Cyclopentane	5.0	2.9	5.0	2.9
R_1R_2-1,1-Cyclohexane	11.2	3.0	11.2	3.0
1,1-di(4-Hydroxy-3-methylphenyl)ethane	9.9	3.4	90.0	3.6
2,2-di(4-Hydroxy-3-methylphenyl)propane	20.4	2.5	40.0	2.6
2,2-di(4-Hydroxy-3-chlorophenyl)propane	11.5	3.3	16.0	3.6
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	10.0	3.0	37.0	3.0
1,1-di(4-Hydroxy-3,5-dichlorophenyl)cyclohexane	5.0	2.6	40.0	2.6
2,2-di(4-Hydroxy-3,5-dibromophenyl)propane	20	2.7	38.0	2.7

* R_1R_2 = di(4-hydroxyphenyl)-.

TABLE 23. Electrical properties of bisphenol A polycarbonate (Lexan)[21].

Property	Temperature, °C				
	−30	−3	23	100	125
Dielectric constant at 60 c/s	3.12	3.12	3.17	3.15	3.13
Dielectric constant at 10^6 c/s	—	—	2.96	—	—
Dielectric loss factor (tan δ) at 60 c/s	0.005	0.004	0.0009	0.009	0.0011
Dielectric loss factor (tan δ) at 10^6 c/s	—	—	0.01	—	—
Bulk resistivity, ohm cm	$>10^{17}$	$>10^{17}$	2.1×10^{16}	2.1×10^{15}	2.0×10^{14}
Arc stability, stainless steel plate electrodes	—	—	10—11 sec	—	—
Dielectric strength, during short-time tests at 25°	98000 V mm^{-1} at sample thickness 0.038 mm 77250 V mm^{-1} at sample thickness 0.075 mm 64200 V mm^{-1} at sample thickness 0.120 mm 28300 V mm^{-1} at sample thickness 0.575 mm 10000 V mm^{-1} at sample thickness 3.125 mm				
Dielectric strength, during short-time tests at 100°	85000 V mm^{-1} at sample thickness 0.075 mm 31400 V mm^{-1} at sample thickness 0.575 mm 15000 V mm^{-1} at sample thickness 3.125 mm				
Resistance to electron radiation	No change up to 50 μr dose				

dielectric loss, that it may be related to "dipole-elasticity" losses. The other maximum in tan δ, which occurs below 20°, was considered by the authors to be connected with losses of the dipole-radical type. They assigned "dipole--radical" losses of the polyesters to vibrations of the ester parts of the chain. Dipole-elasticity losses were assigned to the relaxation of segments of the macromolecule.

It has been reported[71] that an increase in the concentration of aromatic nuclei in a polyarylate increases the temperature of the maximum dipole-elasticity losses (t_{max}); this indicates an increase in the relaxation time (Table 24).

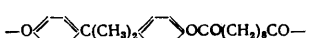
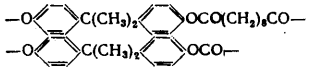
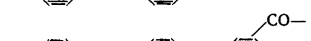
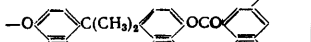
The relaxation time is also affected by the crystallinity of the polymer and the concentration and distribution of polar groups in the chain. Mikhailov and Eidel'nant considered that the differences in t_{max} for dipole-elasticity losses in polyarylates of bisphenol A possessing similar concentrations of polar groups were connected with their different crystallinities.

The temperature variation of tan δ for polyarylates, of differing degrees of crystallinity, obtained by pressing and by extrusion from solution, and of annealed samples, is shown in Fig. 19. It can be seen that the maximum in dipole-elasticity losses for the annealed sample is shifted to a much higher temperature (by ~ 40°); the maximum in dipole-radical losses is reduced. An increase in the crystallinity of the bisphenol A-terephthalic acid polyarylate after annealing is thus indicated.

The dielectric properties (Table 25) of a number of mixed polyarylates have also been studied[72]. It was established that the dipole-elasticity losses in mixed polyarylates are due to the relaxation of amorphous parts of the polymer. The temperature for the maximum dielectric loss factor (tan δ) is determined by the composition of the mixed polyester. In the vitreous state two maxima for dipole-radical losses were observed, corresponding to the two acids of the mixed polyarylate.

(e) Solubility. The solubility of polyarylates depends on their chemical structure and molecular weight. Polycarbonates obtained from quinol or from other symmetrical dihydric phenols, which contain small substituents between the aromatic rings, are reported to be insoluble,

TABLE 24. Values of tan δ_{max} and t_{max} for "dipole-elasticity" and "dipole-radical" losses at 20 kc/s [71].

Polyarylate	Concn. of aromatic rings in the chain	"Dipole-elasticity" losses		"Dipole-radical" losses	
		tan δ_{max}	t_{max}	tan δ_{max}	t_{max}
	0.154	3.1	47	3.0	—100
	0.500	2.65	174	0.6	— 40
	0.600	4.0	210	1.85	— 9
	0.600	1.0	260	1.30	— 13

Note. The concentration of aromatic rings in the chain was determined from the ratio of the number of aromatic rings to the total number of other groups in a unit.

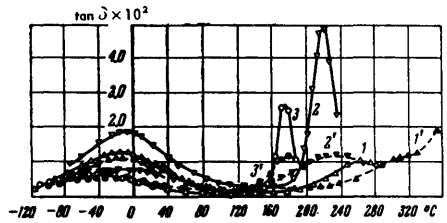


Fig. 19. Variation of the dielectric loss factor (tan δ) for bisphenol A polyarylates of different degrees of crystallinity:
1) and 1') with terephthalic acid, non-annealed and annealed; 2) and 2') with isophthalic acid, amorphous and partly crystalline; 3) and 3') with carbonic acid, amorphous and partly crystalline.

TABLE 25. Values of tan δ_{max}, temperature (t_{max}) of maximum dipole-elasticity losses at 60 c/s, and the concentration of aromatic rings (n) in the mixed-polyester chain.

Molar proportions of polyester components	n	tan δ_{max} × $\times 10^2$	t_{max}, °C
Terephthalic a. (0.8), adipic a. (0.2), bisphenol A	0.483	1.50	212
Terephthalic a. (0.6), adipic a. (0.4), bisphenol A	0.394	3.35	188
Terephthalic a. (0.6), sebacic a. (0.4), dian (1)	0.317	3.45	151

or only very slightly soluble, in organic compounds. Polycarbonates from dihydric phenols which contain asymmetric or branched radicals between the aromatic rings have considerably higher solubilities [20]. Most of the polycarbonates described are soluble in the usual organic solvents, methylene chloride, *m*-cresol, tetrahydrofuran, etc. [3,20,24].

The polyarylates of mononuclear aromatic dicarboxylic acids and dihydric phenols — poly(resorcinol terephthalate), poly(quinol terephthalate), poly(resorcinol isophthalate), and poly(quinol isophthalate) — are insoluble in organic solvents [31].

The presence of a side-chain in the acid or dihydric phenol molecule increases the solubility of the polyarylate. Thus, the bisphenol A–isophthalic acid polyarylate is soluble in cresol [31], in 1,2,2-trichloroethane and *sym*-tetrachloroethane [46]. The polyarylates of isophthalic acid with 2,2-di(4-hydroxyphenyl)butane and di(4-hydroxyphenyl)-methane are soluble in methyl chloride, 1,2-dichloroethane, 1,2,2-trichloroethane, and tetrachloroethane.

The solubility data for a number of homogeneous and mixed polyarylates of various structures are presented in Tables 11, 13, 14, and 26. [31,33-35,40]

Eareckson [54] presented solubility data for the mixed polyarylates of the bisphenol A–isophthalic acid–terephthalic acid series. He observed that the solubility of the mixed polyarylates was considerably greater than that of the homogeneous polymers. The mixed product of composition 1 : 0.5 : 0.5 possessed the greatest solubility in dioxan, tetrahydrofuran, ketones, chlorinated hydrocarbons, amides, esters, and nitro-compounds. The mixed polyarylates of this series swell considerably in aromatic hydrocarbons. They, however, neither swell nor dissolve in alcohols or aliphatic hydrocarbons.

(f) Molecular weight. Schnell [3] noted that the viscosity number for bisphenol A polycarbonates was not a linear function of the molecular weight, determined by osmometry. The logarithms of these two properties were, however, linearly related (Fig. 20). Schnell [3] expressed the relationship between the viscosity of the polycarbonate and its molecular weight as follows:

$$Z_\eta = 1.23 \times 10^{-5} M^{0.83}.$$

Schulz and Horbach [24] have proposed that the molecular weight of bisphenol A polycarbonate may be calculated from the formulae

$$M = 1.03 \times 10^2 [\eta]^{1.43} \text{ or } M = 2.4 \times 10^2 [\eta]^{1.22}.$$

The first equation concerns the relationship of the molecular weight of the polycarbonate and the reduced viscosity in tetrahydrofuran solution whereas the second formula refers to a methylene chloride solution.

Eareckson [54] has presented data (Table 27) concerning the molecular weights of mixed polyarylates determined by light-scattering methods, and their reduced viscosities in a mixture of tetrachloroethane and phenol (40/60 w/w) at 30°.

The polyarylate of bisphenol A and isophthalic acid, synthesised by Korshak and coworkers [33-35] by the interfacial method, with a reduced viscosity (in cresol) of 1.0, had a molecular weight (determined by light scattering) of 90 000.

No other information concerning the determination of the molecular weights of polyarylates has been published so far.

TABLE 26. Solubility of the polyarylates of bisphenol A with terephthalic and isophthalic acids in various solvents. [The reduced (inherent) viscosities of the polymers in cresol were 0.50 and 0.54 respectively][40].

Solvent	Solubility, g litre^{-1}	
	polytere-phthalate	polyiso-phthalate
Ethanol	0	0.1
Dioxan	3.9	~20.6
Chloroform	8.2	12.4
NN-Dimethylformamide	1.3	~ 3.8
Ethyl methyl ketone	0.4	0.7
Chlorobenzene	2	~13.3
p-Xylene	0.7	0.9
Benzene	1.0	2.1
Tetrachloroethane	95	19.0
Tetrachloroethylene	0.6	1.1
Carbon tetrachloride	0.3	0.8
Heptane	0	0
Methylene chloride	5.7	~32
Tetrahydrofuran	1.8	5.3

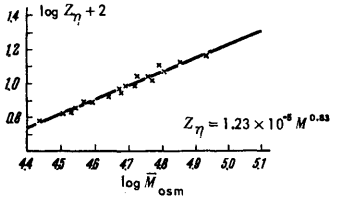


Fig. 20. Relationship between the logarithm of the viscosity number and the logarithm of the molecular weight (determined from osmotic pressure) for bisphenol A polycarbonate.

TABLE 27. The molecular weight and reduced (inherent) viscosity of the mixed polyarylate with the composition bisphenol A:isophthalic acid: :terephthalic acid = 1:0.5: :0.5.

η^*_{inh}	Reduced viscosity*	$\bar{M}$**
0.77	0.61	24000
1.03	0.89	60000
1.18	1.00	68000
1.51	1.10	88000

* $\eta_{inh} = ln\,\eta_{rel}/c$ determined in solution of tetrachloroethane and phenol (40/60 w/w), where η_{rel} is the relative viscosity and c the concentration (0.5%).

** The molecular weight was determined by the light-scattering method in chloroform solution.

TABLE 28. Steam permeability of polycarbonates[20].

Bisphenol	Steam permeability, g cm^{-1} h^{-1} × ×(10^{-8} mm Hg)$^{-1}$
2,2-di(4-Hydroxyphenyl)propane	3.0
1,1-di(4-Hydroxyphenyl)cyclohexane	1.0
1,1-di(4-Hydroxyphenyl)cyclopentane	1.5
Di-(4-hydroxyphenyl)methylphenylmethane	2.4
2,2-di(4-Hydroxy-3-chlorophenyl)propane	0.56
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	2.1
1,1-di(4-Hydroxy-3,5-dichlorophenyl) cyclohexane	1.14
2,2-di(4-Hydroxy-3,5-dibromophenyl)propane	2.3

TABLE 29. Gas permeability of bisphenol A polycarbonate[20].

Gas	Gas permeability, g cm^{-1} h^{-1} × ×(10^{-8} mm Hg)$^{-1}$, at 20°
Hydrogen	1.35
Carbon dioxide	0.75
Oxygen	0.18
Air	0.04
Nitrogen	0.01

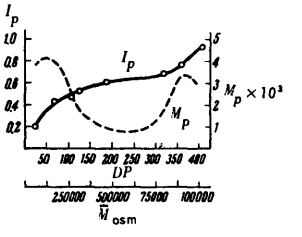


Fig. 21. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared by the interfacial method. I_p—overall weight fraction, $I_p = \int dc/d\bar{M}$; c — weight fraction; $\bar{M}$ — mol.wt.; $M_p = dc/d\bar{M}$.

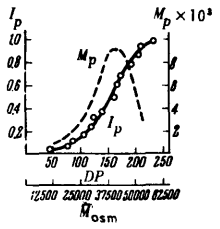


Fig. 22. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared in solution. I_p — overall weight fraction, $I_p = \int dc/d\bar{M}$; c — weight fraction; $\bar{M}$ — mol. wt.; $M_p - dc/d\bar{M}$.

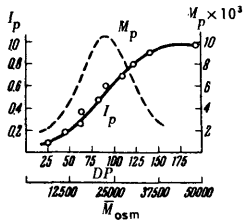


Fig. 23. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared in the melt. I_p — overall weight fraction, $I_p = \int dc/d\bar{M}$; c — weight fraction; $\bar{M}$ — mol. wt.; $M_p - dc/d\bar{M}$.

(g) Other properties. Schnell[20] giving data relating to the steam- and gas-permeability of polycarbonates (Tables 28 and 29).

The molecular-weight distributions of the bisphenol A polycarbonates obtained by both the heterogeneous and homogeneous (in solution or in the melt) polycondensations were compared by Schnell[3]. The integral and differential curves for the molecular-weight distribution in these polymers are shown in Figs. 21–23; there is an anomalous distribution (two maxima) in the polycarbonate obtained by the interfacial polycondensation.

Molecular-weight distribution data for polyarylates of other dicarboxylic acids have not been described so far. There are, however, good reasons to believe that polyarylates produced by the interfacial technique will have different distributions from those produced by homogeneous polycondensation.

IV. USES OF POLYARYLATES

The polycarbonate of bisphenol A currently finds practical application under the trade names Lexan and Makrolon. Lexan was introduced by the General Electric Company of America[21] and Makrolon is produced by the German firm Farbenfabrieken Bayer (Federal German Republic).[26] Articles can be manufactured from this polycarbonate by various methods; under pressure, by extrusion, vacuum moulding, etc.[26] It is used as a building or structural material in a number of technical fields. Lexan is particularly suitable where a high impact stability is required because of its exceptionally high specific impact strength ($\sim$ 354 cm kg cm^{-3}), its dimensional stability, and thermal stability. Bisphenol A polycarbonate is used for the manufacture of calculating-machine casings, tubing, moulds, films, sheets, etc. It is widely used in high-precision mechanical engineering[21,26]. It may be possible to utilise Lexan for the production of lenses and inspection windows, and also for the formulation of adhesive compositions which can maintain their stability over a wide temperature range[21].

Polyarylates of other dicarboxylic acids do not yet find practical applications. Since, however, their physicochemical properties (high softening temperatures, thermal stability, resistance to chemical attack, good dielectric properties, etc.) surpass in some respects those of the polycarbonates (*e.g.* thermal and dielectric properties), there are good grounds for believing that their application will not be delayed for long.

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ORGANOMETALLIC COMPLEXES — OLEFINE POLYMERISATION CATALYSTS

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After the discovery by Ziegler of a new method of synthesising polyethylene, complex organometallic catalysts came to be widely used in macromolecular chemistry.

The most important act in the intricate process of polymerisation, using organometallic complex catalysts, is the formation of the complex. The different aspects of the mechanism of the formation, and the catalytic action of organometallic complexes, have been widely discussed in the literature, including this journal[1]. However, recent work necessitates a reassessment of the concepts regarding the nature of the activity of organometallic catalysts in the polymerisation of unsaturated hydrocarbons.