Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK, S. V. VINOGRADOVA,

V. A. PANKRATOV

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK, S. V. VINOGRADOVA,
V. A. PANKRATOV

ON THE INFLUENCE OF THE STRUCTURE OF THE INITIAL BISPHENOLS ON THE PROPERTIES OF POLYARYLATES

As the initial diol components for the synthesis of polyarylates—heterochain complex polyesters—bisphenols with various substituents at the central carbon atom are used:

HO—phenylene—C—phenylene—OH (1,2).

Summarizing the data obtained in the study of a large number of polyarylates, it is possible to derive certain regularities concerning the influence of the nature of the substituents at the central carbon atom of bisphenols on the properties of the polymers synthesized on their basis.

Depending on the structure of the initial bisphenol, the polyarylates synthesized and considered by us may be conventionally divided into three types: 1) polyarylates based on bisphenols containing substituents of small volume at the central carbon atom; 2) polyarylates based on bisphenols having, at the central carbon atom, a bulky phenyl radical and a small substituent; 3) polyarylates based on bisphenols possessing aromatic bulky side substituents, closed into a five-membered ring at the central C atom.

Table 1 gives the properties of some of the synthesized polyarylates of these types. All polymers were obtained by the method of equilibrium and interfacial polycondensation in a high-boiling solvent medium C.

Polyarylates based on bisphenols containing substituents of small volume at the central carbon atom (polymers Nos. 1-9, Table 1) possess a number of properties distinguishing them from polyarylates of the other two types.

From the data of Table 1 it is evident that the polymers of terephthalic acid have high softening temperatures (350-360°). Such high softening temperatures of polyarylates of the first type based on terephthalic acid may be explained by a fairly high degree of ordering of the polymer chains of these polyarylates. X-ray structural investigation of these polymers showed that they contain a significant amount of crystalline phase. Polyarylates of isophthalic acid have substantially lower softening temperatures (280–300°).

When the methyl groups $(-CH_3)_2$ of diane are replaced by electron-acceptor trifluoromethyl groups $(-CF_3)_2$, the thermal stability and elasticity of the resulting polyarylates increase. On the basis of 2,2-bis-(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, in addition to the polymers listed in Table 1, we also obtained copolymers with other dihydric phenols and aromatic and aliphatic dicarboxylic acids, possessing high softening temperatures and good solubility in organic solvents.

The presence of six fluorine atoms in the elementary unit of the polyester (which amounts to approximately 25% F of the total weight of the polymer in the case of polyarylates of terephthalic or isophthalic acid) accounts for the fact that such polyarylates do not support combustion and, when removed from the flame, go out.

Table 1

Properties of polyarylates of various types

No.	Starting bisphenol	Acid chloride	Reduced viscosity, dl/g	Softening temperature, °C, determined in a capillary	Structure of the specimen	Solubility* chloroform	Solubility*: tricresol
1	$HOC_6H_4-CH_2-C_6H_4OH$	I	1.04	300	A crystalline phase is present	S	S
2	Same	T	–	360	Same	S. I.	S. I.
3	»	I, T	2.00	320	» »	S	S
4	$HOC_6H_4-C(CH_3)_2-C_6H_4OH$	I	0.80	280	» »	S	S
5	Same	T	–	350	» »	S. I.	S. I.
6	»	I, T	0.88	285	» »	S	S

No.	Starting bisphenol	Acid chloride	Reduced viscosity, dl/g	Softening temperature, °C, determined in a capillary	Structure of the specimen	Solubility*: chloroform	Solubility*: tricresol
7	$HOC_6H_4-C(CF_3)_2-C_6H_4OH$	I	0.60	290	» »	S	S
8	Same	T	–	350	» »	S. I.	S. I.
9	»	I, T	0.86	295	» »	S	S
10	$HOC_6H_4-C(H)(C_6H_5)-C_6H_4OH$	I	0.70	240	Amorphous	S	S
11	Same	T	1.18	280	»	S	S
12	$HOC_6H_4-C(CH_3)(C_6H_5)-C_6H_4OH$	I	0.48	265	»	S	S
13	Same	T	0.64	290	»	S	S
14	$HOC_6H_4-C(CF_3)(C_6H_5)-C_6H_4OH$	I	0.64	300	»	S	S
15	Same	T	0.70	310	»	S	S
16	$HOC_6H_4-C(C_6H_5)_2-C_6H_4OH$	I	0.34	270	»	S	S
17	Same	T	0.48	300	»	S	S
18	3,3-bis-(4-hydroxyphenyl)-phthalide	I	0.46	270	Amorphous	S	S
19	Same	T	0.80	330	»	S	S

No.	Starting bisphenol	Acid chloride	Reduced viscosity, dl/g	Softening temperature, °C, determined in a capillary	Structure of the specimen	Solubility*: chloroform	Solubility*: tricresol
20	2-phenyl-3,3-bis-(4-hydroxyphenyl)-phthalimidine	I	0.60	280	»	S	S
21	Same	T	0.64	320	»	S	S

* S —dissolves well; S. I. —dissolves only slightly.

Conventional designations in Tables 1 and 2:
I —isophthaloyl chloride; T —terephthaloyl chloride; I, T —a mixture of isophthaloyl and terephthaloyl chlorides in a molar ratio of 0.5 : 0.5.

Table 2

Dependence of tensile strength (σ, kg/cm^2) and relative elongation at break (E, %) of unoriented polyarylate films on temperature

No.	Initial bisphenol	Initial acid chloride	Intrinsic viscosity, dl/g	20° σ, kg/cm^2	20° E, %	100° σ, kg/cm^2	100° E, %	150° σ, kg/cm^2	150° E, %	200° σ, kg/cm^2	200° E, %	250° σ, kg/cm^2	250° E, %
1	$HOC_6H_4-CH_2-C_6H_4OH$	I, T	2.00	670	17	300	30	80	112	–	–	–	–
2	$HOC_6H_4-C(CH_3)_2-C_6H_4OH$	I, T	0.88	750	60	560	75	430	95	260	100	–	–
3	$HOC_6H_4-C(CF_3)_2-C_6H_4OH$	I	0.60	740	128	340	135	170	150	–	–	–	–
4	Same	I, T	0.86	850	85	390	86	190	210	–	–	–	–
5	$HOC_6H_4-C(H)(C_6H_5)-C_6H_4OH$	I	0.70	690	114	450	119	350	135	80	120	–	–
6	Same	T	1.18	980	62	710	123	570	150	300	107	90	80
7	$HOC_6H_4-C(CH_3)(C_6H_5)-C_6H_4OH$	I	0.48	690	90	520	112	510	222	510	170	300	180
8	Same	T	0.64	700	45	750	85	580	100	580	128	400	160
9	$HOC_6H_4-C(CF_3)(C_6H_5)-C_6H_4OH$	I	0.64	840	70	510	75	440	95	380	120	270	130
10	Same	T	0.70	1000	40	600	65	540	80	500	100	380	115

No.	Initial bisphenol	Initial acid chloride	Intrinsic viscosity, dl/g	20° σ, kg/cm^2	20° E, %	100° σ, kg/cm^2	100° E, %	150° σ, kg/cm^2	150° E, %	200° σ, kg/cm^2	200° E, %	250° σ, kg/cm^2	250° E, %
11	3,3-bis-(4-hydroxyphenyl)-phthalide	I	0.46	670	14	320	47	–	–	–	–	70	16
12	Same	T	0.80	650	35	630	56	–	–	540	69	–	–
13	2-phenyl-3,3-bis-(4-hydroxyphenyl)-phthalimidine	T	0.60	720	13	–	–	540	14	400	7	430	5

Note. Polyarylate films were obtained by casting from a solution in chloroform. Testing of the films was carried out on a Polyani-type dynamometer at a stretching rate of 0.0684 mm/sec. The films had a thickness of several tens of microns.

With an increase in the volume of the side substituents at the central carbon atoms of bisphenols, from hydrogens in dioxy-diphenylmethane to trifluoromethyl groups in hexafluorodiane: $2H- \to 2CH_3- \to 2CF_3-$, the softening temperatures of the polyarylates decrease somewhat.

Type 1 polyarylates based on terephthalic acid have poor solubility in organic solvents, which, together with their high softening temperatures, makes it difficult to process these polymers into articles.

When larger substituents, such as a phenyl radical, are present at the central carbon atom of the bisphenol, the solubility in organic solvents of the polyarylates obtained on the basis of such bisphenols is substantially improved, and the structure of the samples becomes amorphous (polymers Nos. 10–17, Table 1). The softening temperatures of type 2 polyarylates based on terephthalic acid are somewhat lower than the softening temperatures of type 1 polyarylates. As can be seen from the data in Table 1, type 2 polyarylates are characterized by a small difference in the softening temperatures of polymers of terephthalic and isophthalic acids (10–40°), whereas for type 1 polyarylates this difference is larger (60 –70°). The presence in type 2 polyarylates of thermally stable phenyl nuclei in the side chain, instead of aliphatic substituents (as is the case in polyarylates of dian and other type 1 polyarylates), promotes the formation of polymers more thermostable (with the exception of dioxy-diphenylphenylmethane polyarylates) than dian polyarylates.

The 3rd type of the polyarylates considered—polyarylates of 3,3-bis-(4-hydroxyphenyl)-phthalide ([3]), 2-phenyl-3,3-bis-(4-hydroxyphenyl)-phthalimidine ([4]), etc., which have aromatic bulky side substituents at the central carbon atom, closed into a five-membered ring—combines such valuable properties as a high softening temperature (320—330°), characteristic of polyarylates of the first type, and good solubility in organic solvents, inherent in type 2 polyarylates. These polymers have an amorphous structure. The high softening temperature of type 3 polyarylates can probably be explained by the great rigidity of their polymer chains due to the presence, at the central carbon atom of the initial bisphenols, of bulky cyclic substituents.

Table 2 gives the dependences of the tensile strengths and relative elongations at break of unoriented films of polyarylates of various types on the test temperature. As can be seen from Table 2, the strength of films of polyarylates based on bisphenols having substituents of small volume at the central carbon atom decreases sharply with increasing temperature, while the relative elongation at break increases markedly.

Despite the high softening temperatures of these polyarylates, their films have low strength at temperatures considerably below their softening temperatures. Thus, the tensile strength of a film of the polyarylate based on dioxyldiphenylmethane and a mixture of terephthalic and isophthalic acids at 150° is only $\sim 12\%$ of the tensile strength at 20°, whereas the softening temperature of this polyarylate is $\sim 320°$.

Films of polyarylates of the 2nd type at room temperature possess good tensile strength and comparatively large (40–114%) relative elongations at break (see polyarylates Nos. 5–10, Table 2). Moreover, films of polyarylates of this type retain considerable strength up to temperatures close to their softening temperatures. For example, the tensile strength of a film of the polyarylate based on 2,2-bis-(4-oxyphenyl)-2-phenylethane and terephthalic acid at 250° is 400 kg/cm^2. The relative elongations at break of these films increase with increasing temperature.

Films of polyarylates based on bisphenols having, at the central carbon atom, bulky aromatic substituents closed into a five-membered ring are characterized by high strength values up to their softening temperatures. Films of polyarylates of this type have low deformability. Thus, in films of the polyarylate of phenolphthalein anilide and terephthalic acid (polyarylate No. 13, Table 2), with increasing temperature the relative elongation at break does not increase but, on the contrary, decreases.

It should also be noted that films of the polyarylates under consideration based on isophthalic acid, as a rule, have at all temperatures lower tensile strength and greater relative elongation at break than films of the same polyarylates of terephthalic acid.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
27 I 1964

REFERENCES

1. V. V. Korshak, S. V. Vinogradova, *Usp. khim.*, **30**, 421 (1961).

2. V. V. Korshak, S. V. Vinogradova et al., *Izv. AN SSSR, ser. khim.*, **1964**, 141.

3. V. V. Korshak, S. V. Vinogradova, S. N. Salazkin, *Vysokomolek. soed.*, **3**, 333 (1962).

4. S. V. Vinogradova, V. V. Korshak, S. N. Salazkin, Author' s certificate No. 790825/23–4 of 13 VIII 1962.

Note: Figure translations are in progress. See original paper for figures.