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1964

SovietRxiv

## Abstract

## Full Text

## Chemistry

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# INVESTIGATION IN THE FIELD OF MIXED BLOCK POLYARYLATES

Recently a number of works have appeared devoted to the study of a new type of polyesters—polyarylates—heterochain complex polyesters of diatomic phenols, possessing such valuable qualities as high softening temperatures and heat resistance, good dielectric properties over a broad temperature range, high chemical resistance, etc. However, some of these polymers, along with valuable properties, also have a number of shortcomings. Thus, some polyarylates are very poorly soluble in organic solvents and possess low elasticity, which, in combination with their high softening temperature, sometimes lying above the decomposition temperature, makes it difficult to process polyarylates into articles and limits the number of possible fields of their practical application. Therefore the question of studying the possibility of modifying the properties of polyarylates appears very interesting. In modifying polyarylates, the primary task becomes preserving the high softening temperature characteristic of them.

One of the ways of modifying the properties of polymers is the synthesis of mixed polymers. It seemed possible to us to modify the properties of polyarylates by synthesizing block copolymers. In doing so we proceeded from the consideration that, upon incorporation into the main chain of the polyarylate of block segments of another polymer, the molar fraction of such blocks will be small even when their weight amount is rather large. As a result, such block segments of another polymer will be rarely located along the polymer chain, which will make it possible to preserve the principal packing of the polymer chains and, together with this, the high softening temperature of the polymer.

The process of formation of a mixed heterochain polymer at elevated temperature from a mixture of homopolymers or of a homopolymer and a monomer is accompanied by the formation of block copolymers ([1−4]). However, as a rule, they exist in such systems for only a short time, since these blocks, with increasing reaction time, decrease owing to the occurrence of interchain exchange processes, and when the system reaches an equilibrium state a mixed polymer is formed.

In the literature there is a small amount of information on modification of the properties of heterochain polyesters, in particular polyethylene terephthalate, by incorporation of polyethylene oxide into its polymer chain as a block component

($^{5,6}$).

We set ourselves the goal of synthesizing mixed block polyarylates containing blocks of different structure in their composition. As blocks in our work we used low-molecular bifunctional polymers with terminal hydroxyl groups, namely: penton (PN): $H[OCH_2C(CH_2Cl)_2CH_2]_{nOH}$; a silicon-containing oligomer (Si): $[HOC_6H_4C(CH_3)_2C_6H_4[OSi(CH_3)(C_6H_5)]]_2O$; polypropylene glycol (PPG): $HO[CH(CH_3)CH_2O]_{nH}$ and polyethylene glycol (PEG): $HO(CH_2CH_2O)_{nH}$. In doing so, we assumed that by introducing these blocks into polyarylates it would be possible to increase their elasticity, dyeability, solubility, and flowability, while still retaining a fairly high glass-transition temperature of the polymers.

The following were used as other starting components: acid chlorides of aromatic dicarboxylic acids and diatomic phenols of different structures.

Since, in the synthesis of mixed block polyarylates, different starting components participate in the polycondensation reaction, the functional groups of which differ in their reactivity, the following types of reactions may occur during polycondensation:

$$\begin{aligned}
&1.\quad n\mathrm{HO-A-OH} + n\mathrm{ClOC-D-COCl} \rightarrow 2n\mathrm{HCl} + -[\mathrm{OAOOCDCO}]_n-;\\
&2.\quad n\mathrm{HO-B-OH} + n\mathrm{ClOC-D-COCl} \rightarrow 2n\mathrm{HCl} + -[\mathrm{OBOOCDCO}]_n-;\\
&3.\quad n\mathrm{HO-A-OH} + 2n\mathrm{ClOC-D-COCl} + n\mathrm{HO-B-OH} \rightarrow\\
&\qquad\qquad \rightarrow 4n\mathrm{HCl} + -[\mathrm{OAOOCDCOOBOOCDCO}]_n-,
\end{aligned}$$

where A is the residue of the molecule of the block component, B is the residue of the molecule of the diatomic phenol, and D is the residue of the molecule of the acid chloride of the dicarboxylic acid.

And, finally, the interaction between polymer molecules with one another, both through terminal groups and through exchange along intermediate ester linkages, leads to averaging of the composition of the mixed block polymer along the chain. We investigated the interaction of terephthalic acid chloride with dian and with blocks of different structure under the conditions in which the synthesis of various block polyarylates was carried out. The course of the process was monitored by the amount of hydrogen chloride evolved during the reaction. From Fig. 1, where the results obtained are presented, it may be assumed that at the first stage of the reaction, when polyethylene oxide and polypropylene oxide are used as blocks, chains of copolymers enriched with these block units will be formed, whereas when penton and a silicon-containing oligomer are used, polymer chains enriched with dian molecules will be formed. As the process proceeds further, the less reactive component will also become involved in the reaction.

Fig. 1. Change in the amount of hydrogen chloride evolved during the reaction

Fig. 1. Change in the amount of hydrogen chloride evolved during the reaction of terephthalic acid chloride with: 1—PEO-2; 2—PPO-1; 3—PPO-2; 4—dian; 5—PN-3; 6—Si

Figure 1: Fig. 1. Change in the amount of hydrogen chloride evolved during the reaction of terephthalic acid chloride with: 1—PEO-2; 2—PPO-1; 3—PPO-2; 4—dian; 5—PN-3; 6—Si

of terephthalic acid chloride with: 1—PEO-2; 2—PPO-1; 3—PPO-2; 4—dian; 5—PN-3; 6—Si

On the basis of the above-mentioned blocks, we synthesized various mixed block polyarylates. The results obtained are summarized in Table 1. From the data in Table 1 it is evident that the introduction of block units causes modification of the properties of polyarylates. Thus, the softening temperatures of the polymers obtained change with the change in the amount of block in the reaction mixture. The greater the content of the block component in the mixed block polyarylate, the lower its softening temperature. In many cases, introduction of block units into the polyarylate chain noticeably improves the solubility of the polymer. An analysis of the data obtained makes it possible to conclude that, in the synthesis of a mixed block polyarylate, up to $\sim 40$ wt.% of block can be introduced into the polymer chain (see polymers Nos. 1, 2, 5—8, 11—16, 18—25, 27—30, 32—36, 38—41, 43, 44, Table 1), while still retaining a fairly high softening temperature of the polymer.

In the synthesis of mixed block polyarylates we used blocks of different molecular weight. As can be seen from the data in Table 1, copolymers containing in their composition a higher-molecular-weight block, under otherwise identical conditions,

**Table 1**

**Mixed block polyarylates based on dian, terephthalic and isophthalic acid chlorides, and various blocks: pentone, silicon-containing oligomer, polyethylene glycol, and polypropylene glycol**

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 1 | Si : D : T = 0,1 : 0,9 : 1 | 22,6 | 87 | 0,49 | 348 | 0 | 0 | 0 |
| 2 | Si : D : T = 0,2 : 0,8 : 1 | 38,6 | 85 | 0,38 | 342 | 0 | 0 | 1 |
| 3 | Si : D : T = 0,3 : 0,7 : 1 | 50,4 | 78 | n. d. | 240 | 0 | 0 | 1 |
| 4 | Si : D : I = 0,4 : 0,6 : 1 | 59,5 | 92 | n. d. | 188 | 0 | 0 | 0 |
| 5 | Si : D : I = 0,05 : 0,95 : 1 | 12,4 | 90 | 0,35[2] | 282 | 1 | 0 | 2 |
| 6 | Si : D : I = 0,1 : 0,9 : 1 | 22,6 | 95 | 0,40[2] | 283 | 1 | 0 | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 7 | Si : D : I = 0,15 : 0,85 : 1 | 31,2 | 87 | 0,35[2] | 281 | 1 | 0 | 2 |
| 8 | Si : D : I = 0,2 : 0,8 : 1 | 38,6 | 89 | 0,26[2] | 283 | 1 | 0 | 2 |
| 9 | Si : D : I = 0,3 : 0,7 : 1 | 50,4 | 92 | 0,24[2] | 237 | 1 | 0 | 2 |
| 10 | Si : D : I = 0,5 : 0,5 : 1 | 66,8 | 95 | n. d. | 134 | 1 | 0 | 0 |
| 11 | Si : F : I = 0,05 : 0,95 : 1 | 10,2 | 90 | 0,30[2] | 273 | 2 | 0 | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 12 | PN-1 : D : T = 0,011 : 0,989 : 1 | 10,7 | 88 | 0,55[2] | 283 | 2 | 2 | 2 |
| 13 | PN-1 : D : T = 0,024 : 0,976 : 1 | 20,9 | 94 | 0,60[2] | 282 | 1 | 2 | 2 |
| 14 | PN-1 : D : T = 0,05 : 0,95 : 1 | 30 | 79 | 0,51[2] | 278 | 1 | 2 | 2 |
| 15 | PN-1 : D : T = 0,07 : 0,93 : 1 | 44,3 | 83 | 0,63[2] | 273 | 2 | 2 | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | ηsp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 16 | PN-1 : D : T = 0,1 : 0,9 : 1 | 53,7 | 95 | 0,40[2] | 266 | 2 | 2 | 2 |
| 17 | PN-1 : D : T = 0,5 : 0,5 : 1 | 88,8 | 86 | 0,16[2] | 159 | 2 | 2 | 2 |
| 18 | PN-3 : D : T = 0,018 : 0,982 : 1 | 20,7 | 79 | 0,76[2] | 340 | 1 | 1 | 2 |
| 19 | PN-3 : F : T = 0,022 : 0,978 : 1 | 20,3 | 91 | 0,82[2] | 294 | 1 | 1 | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | ηsp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 20 | PN-2 : D : T = 0,033 : 0,967 : 1 | 30,3 | 92 | 0,44[2] | 328 | 1 | 1 | 2 |
| 21 | PN-2 : D : I = 0,033 : 0,967 : 1 | 30,3 | 89 | 0,42[2] | 292 | 1 | 1 | 2 |
| 22 | PEO-3 : D : T = 0,0125 : 0,9875 : 1 | 10,8 | 80 | 0,40 | 339 | 0 | – | 1 |
| 23 | PEO-3 : D : T = 0,025 : 0,975 : 1 | 19,7 | 77 | 0,32 | 328 | 0 | – | 1 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 24 | PEO-3 : D : T = 0,05 : 0,95 : 1 | 33,3 | 92 | 0,36 | 318 | 0 | – | 1 |
| 25 | PEO-3 : D : T = 0,1 : 0,9 : 1 | 50,8 | 88 | 0,36 | 291 | 1 | – | 2 |
| 26 | PEO-3 : D : T = 0,2 : 0,8 : 1 | 68,9 | 91 | 0,48 | 121 | 2 | – | 2 |
| 27 | PEO-2 : D : I = 0,07 : 0,93 : 1 | 33,8 | 79 | 0,44 | 248 | 2 | – | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 28 | PEO-2 : F : T = 0,085 : 0,915 : 1 | 33,5 | 74 | 0,44 | 128 | 2 | – | 2 |
| 29 | PEO-1 : D : T = 0,05 : 0,95 : 1 | 10,3 | 93 | 0,36 | 336 | | | |
| 30 | PEO-1 : D : T = 0,1 : 0,9 : 1 | 19,2 | 90 | 0,34 | 320 | 1 | – | 2 |
| 31 | PEO-1 : D : T = 0,2 : 0,8 : 1 | 33,8 | 91 | 0,40 | 305 | 2 | – | 2 |
| 32 | PEO-1 : D : T = 0,3 : 0,7 : 1 | 45,3 | 94 | 0,46 | 270 | 2 | – | 2 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | ηsp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 33 | PPO-2 : D : T = 0,025 : 0,975 : 1 | 11,7 | 77 | 0,39 | 338 | 1 | – | 1 |
| 34 | PPO-2 : D : T = 0,05 : 0,95 : 1 | 21,3 | 72 | 0,38 | 335 | 1 | – | 1 |
| 35 | PPO-2 : D : T = 0,1 : 0,9 : 1 | 35,9 | 60 | 0,52 | 332 | 1 | – | 1 |
| 36 | PPO-2 : D : T = 0,2 : 0,8 : 1 | 49,3 | 88 | 0,47 | 295 | 1 | – | 1 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 37 | PPO-2 : D : T = 0,25 : 0,75 : 1 | 60,9 | 88 | 0,44 | 232 | 2 | – | 2 |
| 38 | PPO-1 : D : T = 0,1 : 0,9 : 1 | 11,1 | 72 | 0,33 | 326 | 1 | – | 1 |
| 39 | PPO-1 : D : T = 0,2 : 0,8 : 1 | 21,1 | 64 | 0,30 | 318 | 1 | – | 1 |
| 40 | PPO-1 : D : T = 0,3 : 0,7 : 1 | 30,3 | 72 | 0,26 | 302 | 1 | – | 1 |
| 41 | PPO-1 : D : T = 0,4 : 0,6 : 1 | 38,6 | 68 | 0,28 | 286 | 1 | – | 1 |

| No. | Starting substances and their ratio, mol[1] | Block content, wt. % | Yield, % | $\eta$sp/c of polymer in tricresol, dl/g[2] | Softening temp. in capillary, °C[3] | Solubility[4] in chloroform | Solubility[4] in cyclohexanone | Solubility[4] in tetrachloroethane |
|---|---|---|---|---|---|---|---|---|
| 42 | PPO-1 : D : T = 0,45 : 0,55 : 1 | 42,5 | 92 | 0,34 | 146 | 1 | – | 1 |
| 43 | PPO-2 : D : I = 0,1 : 0,9 : 1 | 35,9 | 85 | 0,20 | 261 | 1 | – | 2 |
| 44 | PPO-2 : F : T = 0,03 : 0,097 : 1 | 11,3 | 77 | 0,28 | 264 | 2 | – | 2 |
| 45 | D : T = 1 : 1 | – | – | 0,44 | 350 | 1 | – | 1 |
| 46 | D : I = 1 : 1 | – | – | 0,45 | 300 | 1 | 0 | 2 |

[1] F—phenolphthalein; D—dian; T—terephthalic acid chloride; I—isophthalic acid chloride; PN-1 mol. wt. 3900; PN-2 mol. wt. 4640; PN-3 mol. wt. 5130; Si mol. wt. 980–1000; PEO-1 mol. wt. 800; PEO-3 mol. wt. 3470; PEO-2 mol. wt. 890; PPO-1 mol. wt. 420; PPO-2 mol. wt. 1880.

[2] Viscosity was determined in tetrachloroethane. n. d.—practically insoluble.

[3] The softening temperature was taken as the temperature at which the polymer

in the capillary completely passes into the melt.
[4] 0—the polymer is practically insoluble in the given solvent; 1—the polymer is partially soluble; 2—the polymer is completely soluble.

at the same percentage content, melt higher than copolymers containing a low-molecular-weight block (cf. polymers Nos. 13 and 18, 14 and 20, and other polymers, Table 1).

The results obtained also show that, by synthesizing mixed block polymers, it is possible to obtain polymers whose softening temperature will be considerably higher than the softening temperature of the corresponding polymer block. Thus, if the softening temperature of pentone is 178–180°, then in the mixed block polyarylate based on terephthalic acid and dian, containing up to ~54 wt. % pentone, it rises to 266° (see No. 16, Table 1).

The data presented in Table 1 also show how the properties of mixed block polyarylates change depending on the structure of the initial diatomic phenol and the acid chloride of the dicarboxylic acid. From them

it is evident that in all cases replacement of terephthalic acid chloride by isophthalic acid chloride causes a decrease in the softening temperature of the copolymer, while the mixed block polyarylates of phenolphthalein melt lower than the corresponding copolymers based on dian.

As Coleman' s study^(5) showed, a substantial drawback of polyethylene terephthalate containing ethylene glycol as a block in its composition is that it is unstable to the action of ultraviolet rays. Table 2 gives the results obtained by us upon irradiation, under rather severe conditions, of solutions of various block polyarylates in tetrachloroethane.

**Table 2**

Change in the viscosity of a solution of a mixed block polyarylate in tetrachloroethane under the action of ultraviolet rays for 1 hour

| No. | Starting substances and their ratio, mol* | Block content, wt. % | $\eta_{pr}$ of polymer solution in tetrachloroethane, dl/g before irradiation | $\eta_{pr}$ of polymer solution in tetrachloroethane, dl/g after irradiation | Degree of destruction, % (by viscosity) |
|---:|---|---:|---:|---:|---:|
| 1 | PEO-4 : G : T = 0.007 : 0.993 : 1 | 14.1 | 0.37 | 0.22 | 40.5 |

| No. | Starting substances and their ratio, mol* | Block content, wt. % | $\eta_{pr}$ of polymer solution in tetrachloroethane, dl/g before irradiation | $\eta_{pr}$ of polymer solution in tetrachloroethane, dl/g after irradiation | Degree of destruction, % (by viscosity) |
|---|---|---|---|---|---|
| 2 | PEO-1 : D : T = 0.1 : 0.9 : 1 | 19.2 | 0.32 | 0.27 | 15.6 |
| 3 | PPO-2 : D : T = 0.05 : 0.95 : 1 | 21.3 | 0.36 | 0.32 | 11.1 |

* PEO-4 mol. wt. 4500; G—ethylene glycol. The other designations are given in Table 1.

As is evident from the data of Table 2, mixed block polyarylates are characterized by considerably greater light resistance than the polyethylene-terephthalate-containing block. Thus, if $\eta_{pr}$ of polyethylene terephthalate containing polyethylene glycol falls after irradiation by 40-odd percent, the viscosity of mixed block polyarylates based on dian and terephthalic acid with polyethylene glycol and polypropylene glycol, containing a larger amount of block segments in their composition, decreases after irradiation by only 15 and 11%, respectively.

X-ray structural analysis of the synthesized mixed block polyarylates (see polymers Nos. 5–8 and Nos. 11–15, Table 1) shows that they have a crystalline structure with a high degree of ordering of the crystalline regions, whereas the block components used by us—penton, a silicon-containing oligomer, and polypropylene glycol—have an amorphous structure, and the homopolyarylates of dian and terephthalic and isophthalic acids have a crystalline structure with low ordering of the crystalline regions. Since polyarylates are characterized by a rather rigid structure, the inclusion in their polymer chain of more elastic block segments—penton, a silicon-containing oligomer, polyethylene glycol, and polypropylene glycol—evidently increases the mobility of the chains of the polyarylate molecules and makes it possible for them to pack better into bundles, which is manifested in an increase in the crystallinity of the block copolymers obtained.

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Received
5 II 1964

## CITED LITERATURE

1. V. V. Korshak, T. M. Frunze, Lu In-nan, *Vysokomolek. soed.*, **2**, 984 (1960).
2. V. V. Korshak, S. V. Vinogradova et al., *DAN*, **147**, 1365 (1962).
3. M. M. Brubaker, D. D. Coffman, F. C. Meger, U.S. Pat. 2 339 237, 1944.
4. C. Ayers, *J. Appl. Chem.*, **4**, 444 (1954).
5. D. Coleman, *J. Polym. Sci.*, **14**, 15 (1954).
6. U.S. Pat. 3 038 880, 1962; *Chem. Abstr.*, **58**, 6948g (1963).

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