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SYNTHESIS OF POLYESTERS BY THE METHOD OF EQUILIBRIUM POLYCONDENSATION

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ABSTRACT

Aromatic polyesters were synthesized on the base of policiclicbisphenols and dichloroanhydride of aromatic dicarboxylic acid by the method of equilibrium polycondensation in solvent. The obtained polymers are characterized by high heat- and thermal stability, are well soluble in chlorinated hydrocarbons and they form transparent films from solutions which are characterized by good mechanical and dielectric properties.

KEYWORDS

aromatic, polyester, bisphenol, dichloroanhydride, polycondensation, macromolecule, films, fibres, plasticity, flexibility.

Introduction. Development of a series of branches of new technology, such as space engineering, aviation, rocket technology, radio electronics and others ask for the creation of new type materials, which should preserve high strength at strict conditions of exploitation at high temperature, at high mechanical charges. With this in view the polymers, which are characterized by high heat- and thermal resistance, high strength and other significant indices are most interesting.

As has been shown by the researches, with the view of heat- and thermal stability, the polymers with macromolecules which contain aromatic and heterocyclic rings are most perspective materials, but because of high rigidity of recurrent cycles of such polymers, often it becomes impossible to use them for obtaining films, fibres and other articles, where materials must possess high plasticity, flexibility, high dielectric and other specific properties. General method to obtain such polymers is creation of the polymers, macromolecules of which, together with aromatic and heterocyclic rings would contain relatively more flexible groups such as ester, ether and the like.
bonds; creation of such macromolecules can be achieved either in the process of polymer synthesis, when such bonds are formed in the reaction process, e.g. polyarylates, polyimides, epoxy, silicon-containing or other polymers, or by inculation of such fragments into polymer chain by the use of the monomers, which contain such groups. With this in view the so-called card-type polymers are perspective polymers, which in their recurrent ring contain side cyclic groups, one of the atoms of which simultaneously is in the composition of a macromolecule structure. Presence of such groups grants specific properties to the polymers, when high thermal stability of a polymer is fused with its good solubility [1-4]. It is especially important for aromatic heterocyclic polymers of rigid structure, when softening temperature of such polymers is close, or even is higher than polymer destruction temperature, which, of course complicates the process of obtaining articles from such materials.

Considering the above stated the card-type polymers, aromatic polyimides, polyamides, polyoxazoles, which in their polymer chain contain phthalide, norbornane and the like card-type groups they become important [5, 6].

In special literature there are rather scarce data about the polymers, which contain norbornane type card groups, which are very interesting because of their original spatial structure, creating closed three dimensional, volumetric cycles. Such structure distinguishes them from other card groups. This is why it was expected that for building macromolecules, it would be interesting and perspective to use the monomers, which as substituted groups contain norbornane type and other cyclic groups characterised by non-coplanar structure.

Materials and Methods.

For obtaining of heterochain polymers we used the norbornane type monomers, which contain biatomic phenols in which phenol hydroxyl groups were in various nuclei of benzol. In their synthesis we used the easily accessible material such as wastes of gas and petroleum treatment.

For the synthesis of polymers we used the following norbornane type polycyclic bisphenols: 4,4\(^1\)-(2-norbornaNYiden) diphenol; 4,4\(^1\)-(2-norbornaNYiden)di-ortho-cresol; 4,4\(^1\)-(2-norbornaNYiden)bis-2-chlorophenol; 4,4\(^1\)-(hexahydro-4,7-methylenindan-5-yliden)diphenol; 4,4\(^1\)-(hexahydro-4,7-methylenindan-5-yliden)-di-ortho-cresol; 4,4\(^1\)-(hexahydro-4,7-methylen-indan-5-yliden)bis-2-chlorophenol; 4,4\(^1\)-(decahydro-1,4,5,8-dimethylenant-2-yliden)-di-ortho-cresol; 4,4\(^1\)-(decahydro-1,4,5,8-dimethylenant-2-yliden)-bis-2-chlorophenol.

As an acid component we used 4,4\(^1\)-(diphenyldicarboxylic acid dichloroanhydride. Synthesis of polymers was performed by the method of equilibrium polycondensation in ditolylmethane. Properties of the synthesized polymers are given in Table 1.

Results and Discussion.

IR- spectroscopic studies of the synthesized polymers showed an absorption band in the 1770 cm\(^{-1}\) zone in IR spectrum, which is characteristic for polymer ester groups and an absorption band in the 1460 cm\(^{-1}\) zone, which is characteristic for bisphenolCH\(_2\) groups.

As is seen from the data of Table #1 the polymers obtained on the base of polycyclic bisphenols and aromatic dicarboxylic acid are characterized by high thermal stability. High softening temperature of the polymers is explained by high rigidity of polymer chain, which is conditioned by non-coplanarity of norbornane type cycles. These cycles have significant dimensions in all directions. This is why these groups are not capable to orientate in any definite direction, hence they can’t move in a small space between macromolecules similar to that taking place in case of alkyl or phenyl groups. By the same reason free circulation of two phenyl groups which are linked to norbornane cycle carbon atom is complicated. Due to the fact that the polymer softening and melting temperatures are associated with movement of certain definite zones of macromolecules towards each other, presence of non-coplanar polycyclic structure in polymer recurring ring conditions high softening temperature of polymers.

Polymer thermal stability was investigated by the method of thermogravimetric analysis, at heating on air (sample heating velocity – 4.5°/min). As is seen from the data of Table #1, polymers are characterized by high thermal stability. Decrease of their mass at heating on air commences above 300-400°C. Especially high heat resistance is inherent to the polymers obtained on the base of chlorine substituted bisphenols, destruction of which commences only at 470-480°C.
Table 1. Properties of polyesters obtained in solvent by equilibrium polycondensation.

| # | Structure of polymer recurring ring | Decrease of polymer mass at heating on air | Yield, % | 0.5% polymer solution in chloroform \( \eta^o_{\text{finished}, \text{dl/g}} \) | Softening temperature, °C | Polymer structure according to X-ray diffraction analysis |
|---|-----------------------------------|------------------------------------------|---------|---------------------------------|------------------------|-----------------------------------------------|
| 1 |                                   | 366 410 535 80 0.65 330-345 220 Amorphous |         |                                 |                        |                                               |
| 2 |                                   | 360 380 510 80 0.50 339-340 227 Amorphous |         |                                 |                        |                                               |
| 3 |                                   | 365 400 525 80 0.65 345-360 235 Amorphous |         |                                 |                        |                                               |
| 4 |                                   | 360 365 510 70 0.70 340-352 245 Amorphous |         |                                 |                        |                                               |
| 5 |                                   | 370 415 540 90 0.52 345-350 250 Amorphous |         |                                 |                        |                                               |
| 6 |                                   | 370 400 515 70 0.55 320-330 290 Amorphous |         |                                 |                        |                                               |
| 7 |                                   | 450 480 560 85 0.48 355-360 305 Amorphous |         |                                 |                        |                                               |
| 8 |                                   | 435 440 500 94 0.40 345-355 300 Amorphous |         |                                 |                        |                                               |
Continuation of table 1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|----|
| 9 | ![Chemical Structure](image) | ![Chemical Structure](image) | 450 | 510 | 580 | 94 | 0,40 | 360-365 | 325 | Amorphous |
| 10 | ![Chemical Structure](image) | ![Chemical Structure](image) | 445 | 490 | 500 | 80 | 0,88 | 340-345 | 320 | Amorphous |

As has been shown by the studies polyarylates which contain the polycyclic bisphenols are characterized by high resistance to water. Films prepared on the base of these polymers are characterized also by high resistance to 20% sodium alkaline solution and to ultraviolet rays. At the long-term impact of ultraviolet rays polymers factually remain unchanged. Chlorine containing polymers are characterized also by refractory properties.

**Conclusions.** Hetero chain polyesters were synthesized on the base of polycyclic bisphenols and dichloroanhydride of dicarboxylic acid by the use of equilibrium polycondensation method. The obtained polymers are characterized by high heat and thermal stability, are well soluble in chlorinated hydrocarbons. In solutions they form transparent films, which are characterized by good mechanical and dielectric properties.

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