

Organic Chemistry

Polyurethanes on the Basis of Card-Type Polycyclic Bisphenols and Different Diisocyanates

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ABSTRACT. Card-Type secondary diols are synthesized by means of oxyalkylation of bisphenols. Linear homogeneous polyurethanes are obtained through interaction of diols and diisocyanates. Their physical and chemical properties, thermal and heat-resistance are studied, as well as resistance in respect of radiation emanation of polymeric compositions obtained on their basis. ©2012 Bull. Georg. Natl. Acad. Sci.

Key words: diols, diisocyanates, polyurethanes, bisphenols, card-type, oxyalkylation.

Among the homogeneous linear polyurethanes specific interest attaches to polyurethanes, which are simultaneously characterized by good solubility in trivial organic solvents and by high thermal stability. With this in view for the synthesis of polyurethanes the authors used the card-type diols of diverse structure [1-3].

The advantage of the polyurethanes synthesized on the basis of such type diols is that they are characterized by good solubility in organic solvents irrespective of the diisocyanate structures and high thermal stability. It is conditioned by the presence of non-coplanar structured polycyclic substitutes in the polymer chain near the central carbon atom, which hinders the free movement of two phenol nuclei, which are linked to the carbon atom of volumetric cyclic groups. Due to the same reason, shifting of cyclic

fragments of polymer molecules with respect to each other is complicated. It results in the increase of high heat resistance stability of the polymer. At the same time large size of the above stated groups hinders the packed placing of polymer chains. Therefore, irrespective of the great concentration of aromatic hydrocarbons in the macromolecule, polymers are well dissolved in a number of organic solvents.

The present paper deals with the synthesis and of norbornane type group containing secondary diol-5,5-bis(4- β -oxypropoxyphenyl)-hexahydro-4,7-methylenindanylidene its phenyl substituted derivatives and polyurethanes obtained on the basis of various diisocyanates.

Synthesis of polyurethanes is based on migration polymerization reaction. Addition via migration of hydrogen atom of hydroxyl in the chain of growing

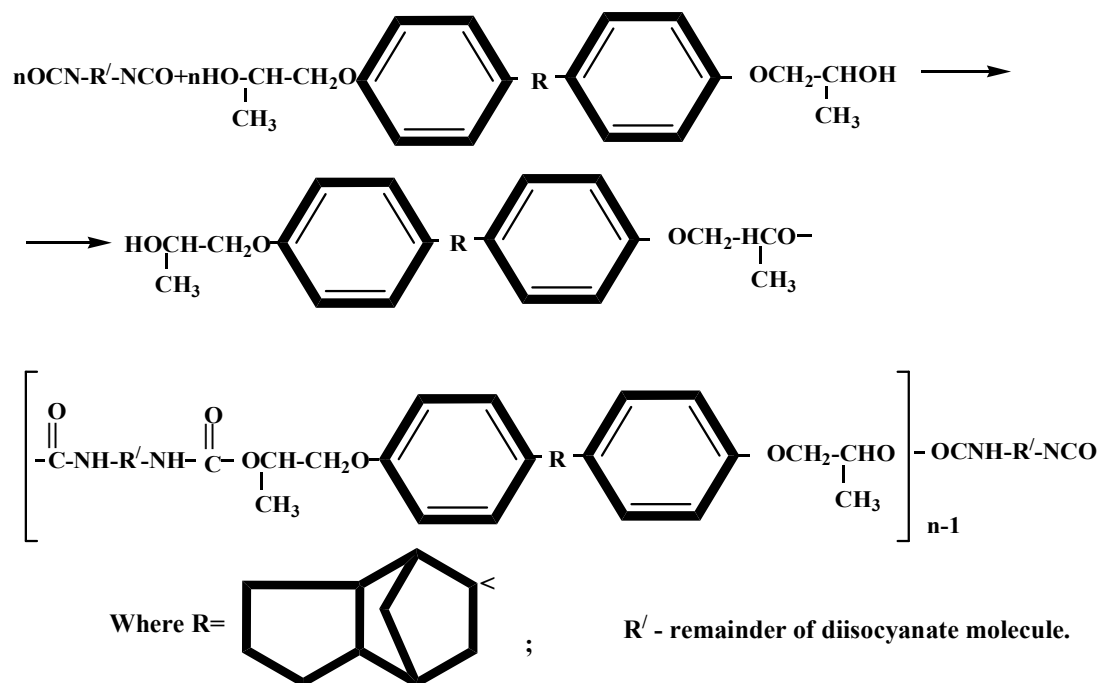


Fig. Polyurethanes on the basis of diol-5,5-bis(4- β -oxypropoxyphenyl)-hexahydro-4,7- methylenindanylidene and different diisocyanates.

molecule into the nitrogen atom of isocyanate group is realized. This process proceeds in stages with gradual increase of molecular mass. The reaction proceeds according to the scheme (Fig.).

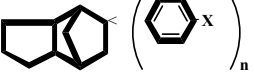
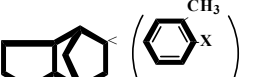

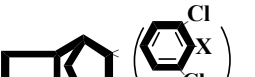
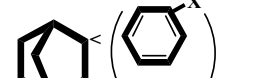
Polyurethane synthesis is carried out in chlorobenzol medium. Initial concentration of the yielded components are: 1 mol/l, mole ratio 1 : 1, reaction duration- 8 h, temperature 130 °C. Due to the fact that during the process of reaction the ends of the growing polymer chain contain isocyanate and hydroxyl groups, at the end of the reaction, during purification of the obtained products the amine group is formed as a result of interaction of isocyanate group with water. At the interaction of amine group with isocyanate group the spatial structure is formed, as a result of which polymer loses the solubility. Therefore at the end of the reaction, isocyanate groups are blocked by adding single atom alcohol. After removal of chlorobenzol the polymer is dissolved in chloroform and precipitated in ethyl ether. Isolated polymer is dried in vacuum thermostat at 70-80 °C.

The authors obtained polyurethanes on the basis of the diol synthesized by us-5,5-bis(4- β -oxypropoxyphenyl)hexahydro-4-7-methylindanylidene [1] and

its phenylsubstituted derivatives: 5,5-bis(3-methyl-4- β -oxypropoxyphenyl) hexahydro-4,7-methylindanylidene [2], 5,5-bis(3-chloro-4- β -oxypropoxyphenyl) hexahydro-4,7-methylindanylidene [3] and 5,5-bis(3,5-dichloro-4- β -oxypropoxyphenyl)hexahydro-4,7-methylenindanylidene [3, 4] and various diisocyanates, via migration polymerization.

The properties of polyurethanes are presented (Table). As seen from the thermal mechanical studies of the synthesized polyurethanes, they are characterized by high thermal stability, which, as stated above, is conditioned by non-coplanar card type substitute existing at the central carbon atom in diol component of macromolecule [4]. The studies showed that growth of volume of norbornane type card cycles in diol molecule results in the increase of the softening point of polyurethanes [5]. For example softening-points of polyurethanes obtained on the basis of diol [1] and 2,4-toluylene and 4,4'-diphenyl methane diisocyanate are 240-265 °C and 250-270 °C, respectively. While for the polyurethanes obtained on the basis of 2,2-bis-(4- β -oxypropoxyphenyl) norbornylidene and same diisocyanates (see polymer 5), where the norbornane cycle substituted at the central

Table. Properties of polyurethanes synthesized on the basis of 5,5¹-bis-(4-β-oxypoxyphenyl) hexahydro-4,7-methylenindanylidene, its phenyl-substituted derivatives and various diisocyanates^{x)}

№	Chemical structure of diols	1,6-hexamethylene-diisocyanate		2,4-toluylenediisocyanate		4,4'-diphenylmethane-diisocyanate	
		η reduced to dl/g	Softening point, °C	η reduced to dl/g	Softening point, °C	η reduced to dl/g	Softening point, °C
1		0.30	140-150	0.65	240-265	0.65	250-270
2		0.40	120-130	0.80	210-225	0.65	225-240
3		0.30	115-130	0.40	215-230	0.40	210-230
4		0.45	105-110	0.55	220-235	0.30	220-250
5		0.30	85-105	0.65	155-200	0.75	165-218

Where X= $\text{OCH}_2\text{-CH}(\text{OH})\text{-CH}_3$

carbon atom of diol component of polymer chain is of smaller size. Polymer softening temperature correspondingly was 155-200 °C and 165-218 °C (1).

Substitution of hydrogen atom in ortho-position by methyl group [2] and by Cl-atoms [3] in phenol nucleus of the diol component of macromolecules affects the thermal stability of polyurethanes. In all cases, the softening point of polyurethanes somewhat decreases [5]. Simultaneously fire resistance of polymers increases as a result of substitution of chlorine atoms.

Thermal stability of polyurethanes is also affected by diisocyanate structure. Substitution of aliphatic diisocyanate by aromatic one, results in the increase of thermal stability of polyurethanes. For example, for the polyurethanes obtained on the basis of [1] diols at the substitution of aliphatic -1,6-hexamethylenediisocyanate by aromatic - 2,4-toluylene and 4,4'-diphenylmethanes, the softening point is increased from 140-150°C to 250-270°C respectively.

According to the roentgen-structural analysis of polyurethanes the polymers synthesized by us are characterized by amorphous structure, which is conditioned by large size of card cycle of indan possessing non-coplanar structure substituted at the central carbon atom of bisphenol in diol fragment of the macromolecule. Due to the same reason the synthesized polyurethanes are characterized by good solubility in organic solvents, which enables to process polymers from the concentrated solutions.

The method of dynamic thermal-gravimetric analysis proved that decrease of polyurethane mass of synthesized polymers by 10% takes place at 250-300°C, while active decomposition starts at 350-400°C. Above this temperature, polymers are decomposed completely without formation of coke.

On the basis of the synthesized diols radiation resistant polymers are obtained, which are used as matrices in boron containing compounds possessing absorption properties.

ორგანული ქიმია

პოლიურეთანები კარდული ტიპის პოლიციკლური ბისფენოლებისა და სხვადასხვა დიიზოციანატების ბაზაზე

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(წარმოდგენილია აკადემიის წევრის შ. სამსონიას მიერ)

სინთეზირებულია კარდული ტიპის მეორეული დიოლები ბისფენოლების ოქსიალკლირებით პროპილენოქსიდის საშუალებით.

დიოლების და დიიზოციანატების ურთიერთმოქმედებით მიღებულია ხაზოვანი ერთგვაროვანი პოლიურეთანები და შესწავლილია მათი ფიზიკურ-მექანიკური თვისებები, თერმო- და თბომედვეობა, მათ საფუძველზე მიღებული პოლიმერული კომპოზიციების რადიაციული გამოსხივებისადმი მედეობა.

REFERENCES

1. G.Sh. Papava, E.Sh. Gavashelidze, I.I. Abkhazava, et al. (1994-95), Proc. Georg. Acad. Sci. Chemical Series, 1-4: 54-56.
2. G.Sh. Papava, E.Sh. Gavashelidze, I.I. Abkhazava, et al. (1991), Proc. Georg. Acad. Sci. Chemical Series, 1: 27-30.
3. G.Sh. Papava, E.Sh. Gavashelidze, N.S. Dokhturishvili, et al. (2002), Proc. Georg. Acad. Sci. Chemical Series, 3-4: 242-244.
4. H. Nakatira, T. Takata, T. Endo (1990), Macromolecules, **23**, 12: 3032-3038.
5. K. Schmidt, G. Keller, F. Gude (1970), Pat.1252896(FRG). American Chemical Society, Abstracts of papers, 72, 2: 416.

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