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Polymeric Chemistry

Synthesis of Polyurethanes Based on Secondary Card-Type Diols

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(Presented by Academy Member Ramaz Gakhokidze)

Abstract. The production of linear polyurethanes based on secondary diols containing a group of card and diisocyanates is disscused in the work. Among the widely used polymers, polyurethanes deserve special attention characteristic due to their unique properties. For the synthesis of homogeneous linear polyurethanes, aliphatic diols are mainly used, which explain their relatively low temperature resistance and poor solubility in conventional organic solvents. The use of carbocyclic diols for the synthesis of polyurethanes contributes to a significant increase in their physical and mechanical properties. To obtain polyurethanes with improved properties, new linear polyurethanes based on diisocyanates and secondary diols containing card groups of various structures were synthesized. For the synthesis of polyurethanes, the following secondary diols were used:1,1-bis-(4-β-hydroxypropo-xyphenyl)-cyclohexane, 2,2-bis-(4-β-hydroxypropoxyphenyl)-norbornilidene and isocyanates: 1,6-hexamethylenediisocyanate, 2,4-toluylene-diisocyanate and 4,4′-dimethylmethane-diisocyanate. The properties of the obtained polyurethanes and the basic laws of the polymer formation reaction have been studied. It has been shown that the heat resistance of polyurethanes containing card groups is higher than that of polyurethanes without card groups. The resulting polyurethane foams are characterized by good solubility in conventional organic solvents and high temperature resistance. *© 2025 Bull. Georg. Natl. Acad. Sci.*

Keywords: polyurethane, diol, bisphenol, diisocyanate, cyclohexane

Introduction

Among the numerous polymers synthesised to date, polyurethane is one of the most promising polymers in terms of diversity and scale of practical application. Polymers of this class are characterised by unique physico-mechanical and dielectric properties and have universal application in various fields of mechanical engineering and agriculture. Polyurethanes, which are characterised by both good solubility in conventional organic solvents and high heat and heat resistance, are of particular importance.

There are many studies where the issues of synthesis and recycling of polyurethanes are discussed.

First of all, it is worth mentioning the capital monograph by Saunders and Frisch, which combines almost all the works that existed at that time [1,2].

Since its appearance, polyurethane elastomers obtained from oligomers of aliphatic polyesters (polyalkyl oxides, polyoxyethylene, polyoxypropylene or their block copolymers and diisocyanates), which were used as coatings, have attracted great attention and found wide application [3-5].

The reactivity of isocyanates is influenced by both the structure of the isocyanate and the substituent. A number of works are devoted to this issue [6,7]. There are many publications in the literature that discuss the relationship between the structure of polyurethanes and their properties [8].

Prior to modern research, there were practically no reports in the literature of cases containing bisphenol fragments containing carded-type groups. It was only in the 90s that a number of works appeared on polyurethane based on cord-type bisphenols containing oxyethylated groups [9-12].

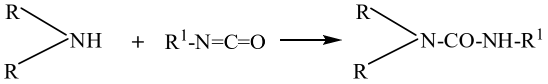
An interesting set of properties that characterises polymers of various classes obtained on the basis of bisphenols containing card groups, as well as polyurethanes containing oxyethylene groups, indicates the expediency and prospects of research on polyurethanes obtained on the basis of such diols. This explains the large number and variety of modern studies and works devoted to this issue [13-21].

The aim of our work was the synthesis of polyurethanes based on secondary diols containing fragments of substituted biphenyls of the card type, and the study of the properties of the resulting polyurethanes.

Materials and Methods

Synthesis of polyurethanes. The synthesis of polyurethanes is carried out by the interaction of secondary diols with various diisocyanates. In a flask, which was regulated by a mechanical stirrer, a reverse cooler, a thermometer and a funnel dropper, was placed a mixture of diol and chlorobenzene (the concentration of the components of the solution is 1 mol/l), diisocyanate was adde ddrop by drop (the molar ratio of the components of the solution is 1:1). The reaction lasted 8 h. Ethyl alcohol was then added to the mixture to block the isocyanate group at the bottom of the growing polymer chain. Chlorobenzene was removed from the reaction mass by steam distillation, the polymer was dissolved in chloroform and precipitates from ethyl ether. The isolated polymer was dried in a vacuum thermostat at a temperature of 70-80°C.

Determination of isocyanate number by volumetric method. This method is based on the interaction of isocyanate with dialkylamine:



$$R_2NH + R^1\text{-}N{=}C{=}O \longrightarrow R_2N\text{-}CO\text{-}NH\text{-}R^1$$

Two exact samples of a substance 0.5-1 g each containing an isocyanate group were placed in two flasks. Dry chlorobenzene and 20 ml of 0.2 N diethylamine solution were used as solvents. After 30 min, 100-120 ml of isopropyl alcohol were added to both solutions, after which the solutions were quenched with 0.1 N hydrochloric acid with the indicator bromophenol until a yellowish-green color was obtained. At the same time, a control study was conducted. The amount of isocyanate was calculated using the formula: Isocyanate number $= \frac{(a-b)\cdot 0.0032\cdot k\cdot 1000}{g}$, where a is the amount of 0.1 N HCl solution consumed on the control sample, ml; b – the amount of 0.1 N HCl solution consumed per sample of the test sample, ml; 0.0032 – the amount of the isocyanate group corresponding to 1 ml of 0.1 N HCl solution, g; k – the correction factor for the HCl titer; g – the mass of the substance, g.

Results and Discussion

The production of polyurethanes is based on a migrating polymerization reaction, in which the growing chain remains a completely independent part after all the joining processes, thus differing from free radicals and ions of intermediate chain links. Joining is carried out by migration of a moving hydrogen atom from a molecule of a hydroxyl-containing monomer to a nitrogen atom of an isocyanate group in the chain of a growing molecule. This process proceeds in stages, with a gradual increase in molecular weight. During purification, after completion of the reaction, the interaction of the isocyanate group with water forms an amino group, while the latter forms a spatial structure under the action of the isocyanate group, as a result of which the polymer loses solubility. Consequently, at the end of the reaction, the formation of isocyanate is blocked by the addition of monatomic alcohol.

Polyurethanes are synthesized on the basis of 2,2-bis-(4-β-hydroxypropoxy-phenyl)-norbornilidene, 1,1-bis-(4-β-hydroxypropoxyphenyl)-cyclohexane,

Table 1. Properties of polyurethanes synthesized on the basis of secondary diols containing the card group of cyclohexane, its phenyl derivatives and various diisocyanates

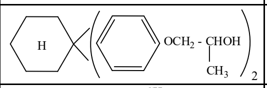
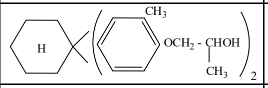
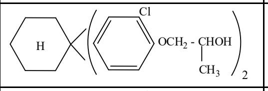
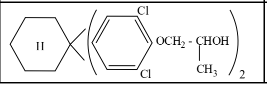
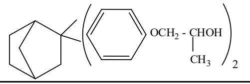
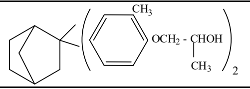
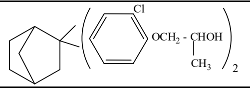
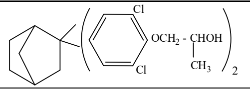
№	Chemical structure of diols	1,6-hexamethylenediisocyanate		2,4-toluylenediisocyanate		4,4'-diphenylmethanediisocyanate	
		η reduced to dl/g, chloroform 20°C	Softening temperatur, °C	η reduced to dl/g, chloroform 20°C	Softening temperature, °C	η reduced to dl/g, chloroform 20°C	Softening temperature, °C
1		0.35	75-105	0.65	240-251	0.70	255-270
2		0.40	60-70	0.70	200-212	0.80	220-255
3		0.35	65-80	0.60	195-210	0.65	200-225
4		0.45	60-75	0.45	203-217	0.50	215-240

Table 2. Properties of polyurethanes synthesized on the basis of 2,2-bis-(4-β-hydroxypropoxyphenyl)-norbornilidene, its phenyl derivatives and various diisocyanates

№	Chemical structure of diols	1,6-hexamethylenediisocyanate		2,4-toluylenediisocyanate		4,4'-diphenylmethanediisocyanate	
		η reduced to dl/g, chloroform 20°C	Softening temperature, °C	η reduced to dl/g, chloroform 20°C	Softening temperature, °C	η reduced to dl/g, chloroform 20°C	Softening temperature, °C
1		0.30	85-105	0.65	155-200	0.75	165-215
2		0.35	80-90	0.60	135-180	0.45	140-190
3		0.30	70-83	0.45	140-170	0.55	150-195
4		0.50	71-85	0.35	155-175	0.40	155-185

their phenyl derivatives and various isocyanates (1,6-hexamethylenediisocyanate, 2,4-toluylenediisocyanate, 4,4′-diphenylmethanediisocyanate).

The properties of synthesized polyurethanes have been studied. Tables 1 and 2 show data on the properties of polyurethanes obtained from 1,1-bis-(4-β-hydroxypropo-xyphenyl)-cyclohexane, 2,2-bis-(4-β-hydroxypropoxyphenyl)-norbornilidene, their phenyl derivatives and various isocyanates.

The advantage of polyurethanes based on secondary diols containing card groups is that all of them, regardless of the structure of the diisocyanate, are characterized by good solubility in conventional organic solvents and high temperature resistance. The high temperature resistance of these polyurethanes is due to the presence in the polymer chain of volumetric substitutes such as cards, which are characterized by a non-planar structure. That is why the free movement of two phenolic nuclei attached to a carbon atom of bulk cyclic groups is difficult. For the same reason, it is difficult for individual fragments of polymer molecules to move towards each other, which makes the polymer chain rigid. All this leads to an increase in heat and thermal stability of the polymer.In turn, the large volumes of these groups prevent the dense assembly of polymer chains, and despite the high concentration of aromatic nuclei in the molecule, polymers are soluble in organic solvents.

The thermal stability of polyurethane is significantly influenced by the structure of diisocyanate. When aliphatic diisocyanate is replaced with aromatic, the heat resistance increases. So, for example, if the softening temperature of polyurethanes based on 1,6-hexamethylenediisocyanate and 2,2-bis-(4-β-hydroxypropoxyphenyl)-norbornilidene is 85-105°C, respectively, then when replacing 1,6-hexamethylene-diisocyanate with 2,4-toluylenediisocyanate and 4,41-diphenylmethanediisocyanate, the softening temperature of polyurethane increases to 165-215°C, respectively. And the softening temperature of polyurethanes based on 1,6-hexamethylenediisocyanate and 1,1-bis-(4-β-hydroxypropoxyphenyl)-cyclohexane is 75-105°C, respectively, when replacing 1,6-hexamethylenediisocyanate with 2,4-toluylenediisocyanate and 4,41-diphenylmethanediisocyanate, the softening temperature of polyurethane increases to 255-270°C, respectively.

The thermal stability of polyurethanes is affected by the presence of a substituent in the phenyl core of a macromolecule. Replacing the hydrogen atom in the phenyl core with a methyl group reduces the softening temperature. For example, the softening temperature of polyurethane obtained on the basis of a diol containing a cyclohexane group and 1,6-hexamethylenediisocyanate is in the range of 80-105°C, and the softening temperature of polyurethane obtained on the basis of a diol containing a methyl substituted cyclohexane group and the same diisocyanate decreases to 60-70°C. The softening temperature of polyurethanes obtained on the basis of diol containing cyclohexane groups card and 2,4-toluylene- and 4,41-diphenylmethanediisocyanate is 240-251°C and 255-270°C, respectively. For a methyl substituted polymer, this indicator decreases to 200-220°C and 220-255°C, respectively. The softening temperature also decreases in the polymer molecule, replacing the hydrogen atom in the phenyl nucleus with the Cl atom. Diols containing a chlorine atom also deserve attention because the polyurethanes obtained on their basis are characterized by high fire resistance.

According to X-ray diffraction analysis, all cord-type polyurethanes considered to have an amorphous structure. Compared with polymers with a crystalline structure, it was expected that they would have a relatively low temperature resistance, but it turned out that the polymers withstand a high softening temperature. This is due to the fact that gimbal-type substitutes in the macromolecule cause an increase in the stiffness of the polymer chain, which leads to an increase in the strength of the polymer chain. This, in turn, causes the high temperature resistance of these polymers. The study of polymers has shown that they are characterized by a fairly high temperature resistance. According to the data of dynamic thermogravimetric analysis, at a temperature of 280-300°C, the polyurethane content in the air decreases by 10% by weight.

As can be seen from the figure, the highest temperature resistance is characterized by polyurethanes, which are obtained on the basis of 4.4'-diphenylmethanediisocyanate. Active decomposition of polyurethanes begins at a temperature of 350-400°C. At this temperature, the polymers decompose completely without forming coke.

Conclusions

The polyurethanes unknown in the literature were synthesized by migration polymerization based on diisocyanates and secondary carded diols. The influence of various factors on the course of polymerization has been studied, and it has been found that with increasing temperature, the reaction rate and the degree of transformation increase. The presence of a catalyst accelerates the reaction and increases the degree of conversion. It has been shown that the heat resistance of polyurethanes containing card groups is higher than that of polyurethanes without card groups. It has been established that the synthesized polyurethanes dissolve in chlorinated aliphatic hydrocarbons and other organic solvents. This allows them to be processed from solutions into a product. The physico-mechanical and dielectric properties of the obtained polyurethanes are investigated. It has been shown that they are significantly superior to industrial polyurethanes in these characteristics.

პოლიმერული ქიმია

პოლიურეთანების სინთეზი მეორეული კარდული ტიპის დიოლების საფუძველზე

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[*] *ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, საქართველო*
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(წარმოდგენილია აკადემიის წევრის რ. გახოკიძე მიერ)

ნაშრომში განხილულია ხაზოვანი პოლიურეთანების მიღება, კარდული ჯგუფის შემცველი მეორეული დიოლებისა და დიიზოციანატების საფუძველზე. შესწავლილია მიღებული პოლიურეთანების თვისებები. ფართოდ გამოყენებულ პოლიმერებს შორის პოლიურეთანები განსაკუთრებულ ყურადღებას იმსახურებს მათთვის დამახასიათებელი უნიკალური თვისებების გამო. ჰომოგენური ხაზოვანი პოლიურეთანების სინთეზისთვის ძირითადად გამოიყენება ალიფატური დიოლები, რაც ხსნის მათ შედარებით დაბალ თერმულ მდგრადობას და ცუდ ხსნადობას ორგანულ გამხსნელებში. კარბოციკლური დიოლების გამოყენება პოლიურეთანების სინთეზისთვის ხელს უწყობს მათი ფიზიკურ-მექანიკური თვისებების მნიშვნელოვან ზრდას. გაუმჯობესებული ფიზიკურ-მექანიკური და ქიმიური თვისებების პოლიურეთანების მისაღებად, განხორციელდა ახალი ხაზოვანი პოლიურეთანების სინთეზი დიზოციანატებისა და მეორეული დიოლების საფუძველზე, რომლებიც შეიცავს სხვადასხვა სტრუქტურის კარდულ ჯგუფებს. პოლიურეთანების სინთეზისთვის გამოყენებული იყო შემდეგი მეორეული დიოლები: 1,1-ბის-(4-β-ჰიდროქსიპროპოქსიფენილ) ციკლოჰექსანი, 2,2-ბის-((4-β-ჰიდროქსიპროპოქსიფენილ)ნორბორნილიდენი და იზოციანატები: 1,6-ჰექსამეთილენდიზოციანატი, 2,4-ტოლუილენ-დიზოციანატი და 4,4-დიმეთილმეთანდიზოციანატი. შესწავლილ იქნა მიღებული პოლიურეთანების თვისებები და პოლიმერის ფორმირების რეაქციის ძირითადი კანონზომიერებანი. დადასტურებულია, რომ პოლიურეთანების თბომედეგობა, რომლებიც შეიცავს კარდულ ჯგუფებს, უფრო მაღალია, ვიდრე პოლიურეთანების, რომლებსაც არ აქვს კარდული ჯგუფები. მიღებული პოლიურეთანები ხასიათდება კარგი ხსნადობით ორგანულ გამხსნელებში და მაღალი თერმული მედეგობით.

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