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Polyurethanes based on derivatives of bicyclic bisureas, hexamethylenediisocyanate and adipic acid

The present work is devoted to the research of possibility of bicyclic bisureas fragments inclusion in polyurethane polymer structure and, as a consequence, improvement of mechanical properties of known polyurethane polymers. The most convenient from stereometric point of view linear monomers such as adipic acid and hexamethylenediisocyanate were chosen for interaction with bicyclic monomer, namely tetra-N-methylolglycoluril. The optimal conditions of tetraol preparation were found and influence of various factors on its efficiency was shown. Polyurethanes were synthesized by step-growth polymerization, molar masses of polymers synthesized were determined, and some physical& mechanical properties were studied.

Key words: polyurethanes, bicyclic bisureas, tetra-N-methylolglycoluril, step-growth polymerization.

Introduction

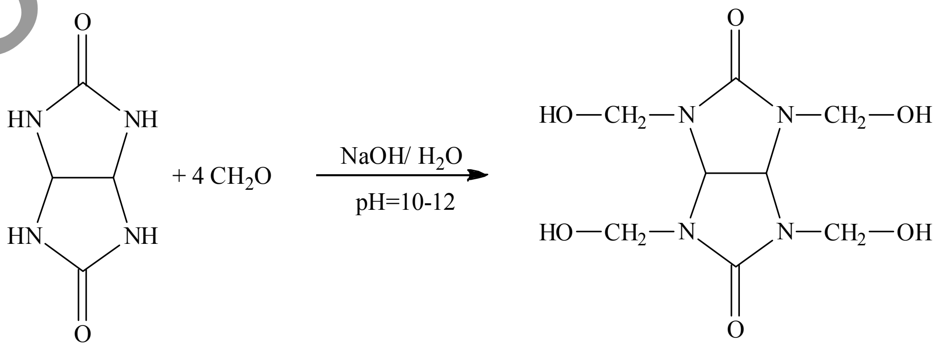
In spite of impressive success achieved in the sphere of synthesis of polymers possessing specific properties searching of new ways of step-growth polymerization, identifying of macromolecular designing principals, development of new prospective polymeric materials and deep researching its properties are still up-to-date issues. Progress in the sphere of polyurethane technology is reflected in development of industrial (or semi-industrial) production of plastics, fibres and films which are widely used in different fields of engineering and house holding in our country and abroad [1, 2].

At present time teachers of Chair of Organic Chemistry and Polymers of Buketov Karaganda State University deal with working out and studying of process of polymers obtaining on a basis of hydroxyl derivatives of bicyclic bisureas and diisocyanates. It is connected with the variety of specific features exhibited by such compounds.

Results and Discussion

Tetra-N-methylolglycoluril that we used as the monomer in synthesis of polyurethanes is referred to a derivative of glycoluril which belongs to the class of bicyclic bisureas of octane raw.

Glycoluril and its derivatives are widely applied in different fields of industry: they are used in water purifying, as flame retardants, in paper production, as intermediates for disinfectants synthesis, detergents, as activators of bleachings, explosives, antioxidants, etc. [3]. Tetra-N-methylolglycoluril may be applied as the crosslinking agent at obtaining of polyurethane resin. It is known [4] that N-hydroxymethylglycoluril is easily formed by interaction of glycoluril and formaldehyde in the alkaline medium. We carried out tetraol synthesis by reaction of glycoluril with 40 % aqueous solution of formaldehyde (formalin) at temperature of 50°C in the presence of NaOH for indicating pH meaning equal to 9–10 and stirring during 2 hours. Tetra-N-methylolglycoluril was obtained with high yield (73 %). Scheme of tetraol synthesis is following:



For tetra-N-methylolglycoluril preparation in a crystalline form distillation of water under vacuum was carried out. It should be mentioned that precise controlling of quantity of water distilled essentially influences on the yield of crystalline tetra-N-methylolglycoluril. Experimentally it was established that distillation of 70 % mass of reactionary water is optimal value (Table).

Table

Dependence of the distilled water mass on the yield and physical state of tetra-N-methylolglycoluril

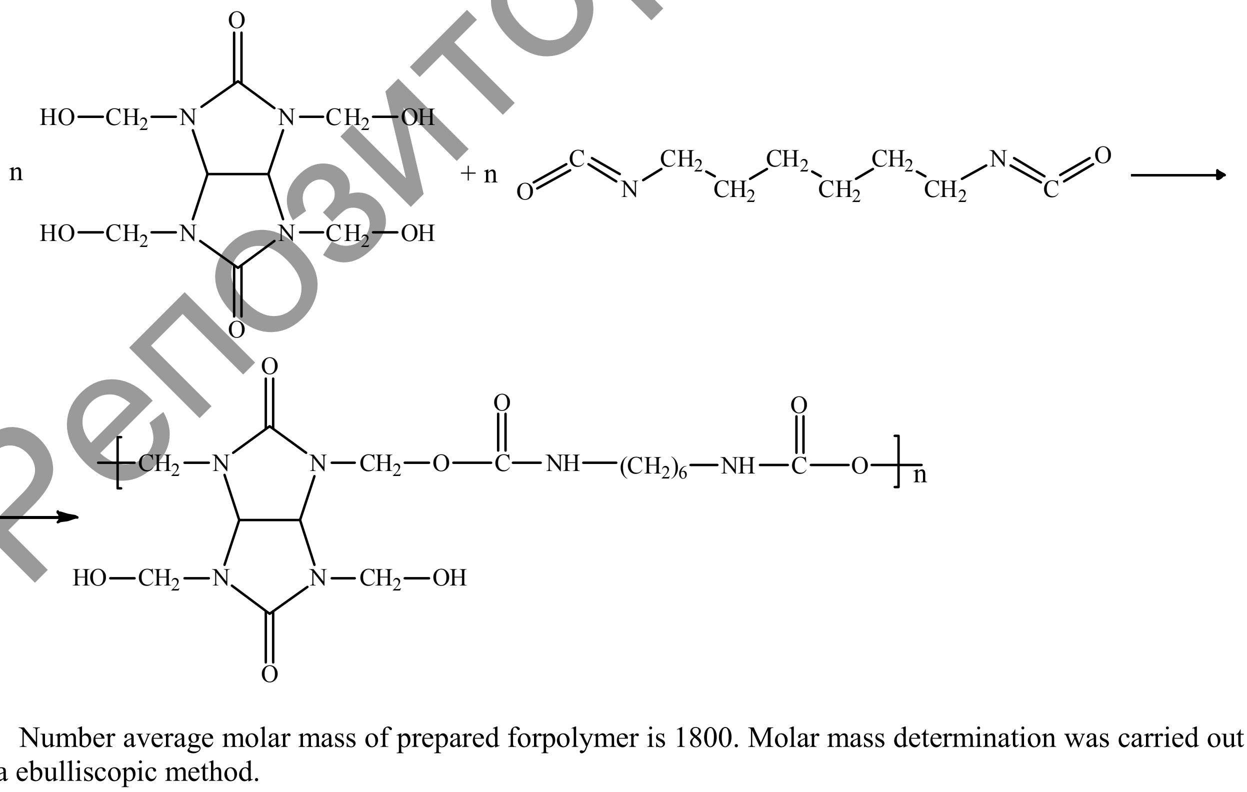
Water mass, %	Distilled water mass, g	Physical state of tetraol	Yield of target product, %
50.6	24.0	Viscous mass	22.3
60.5	28.8	Viscous mass	34.6
70.1	33.6	White crystals	73.0
80.4	38.4	Amorphous solidified mass («caramel» mass)	61.2

According preliminary researches it is known that tetraol in crystalline state is more active than in others, hence it can be used for the further transformations.

Besides it was established that for achievement of maximum possible high yields of target product it is necessary to control precisely a temperature mode of both synthesis process and distilling of water. Optimal temperature range is 50–55 ºC.

As tetra-N-methylolglycoluril is the multifunctional compound containing free hydroxyl groups we assume that this compound can be monomer for synthesis of polyurethanes. From a wide choice of diisocyanates used in the industry for polyurethanes production the hexamethylenediisocyanate was chosen as it has linear structure and, accordingly, the most favorable spatial configuration relatively to bicyclic tetraol. It was experimentally established that an optimal method of polyaddition of tetra-N-methylolglycoluril and hexamethylenediisocyanate is a stepwise polymerization in a solution. A mixture of chlorobenzene with *o*-dichlorobenzene was chosen as a solvent because, as it was mentioned above, namely crystalline tetraol is more active reagent.

Interaction of tetra-N-methylolglycoluril with hexamethylenediisocyanate is presented at the following scheme:



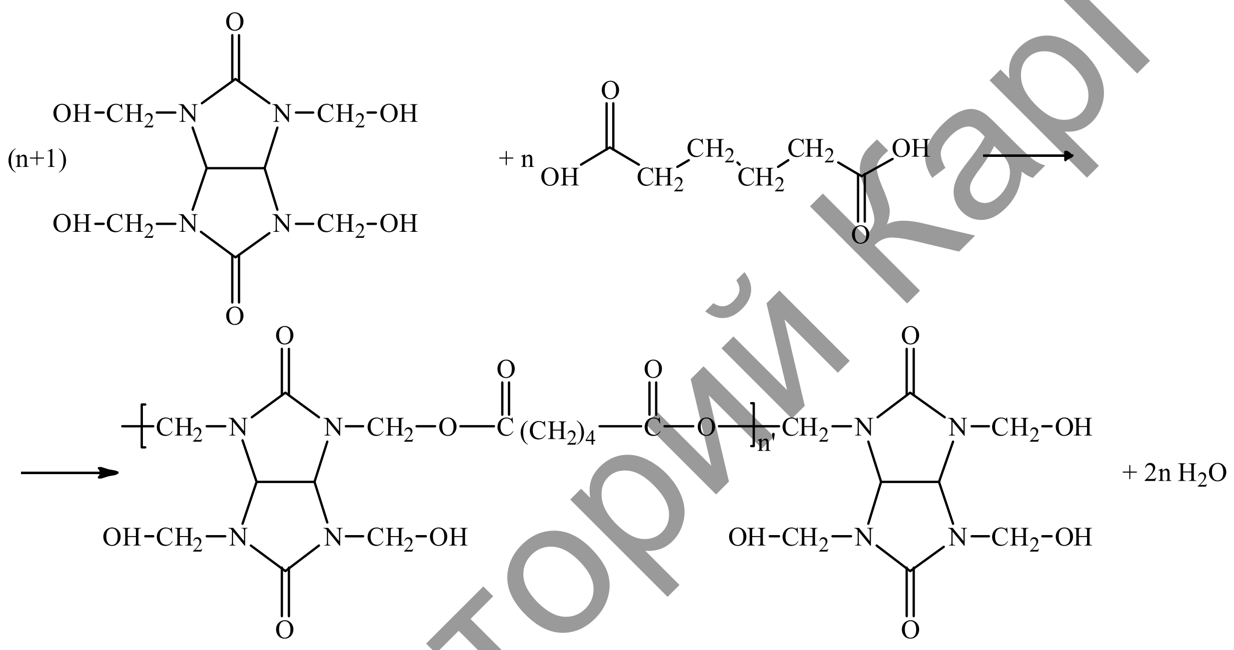
Number average molar mass of prepared forpolymer is 1800. Molar mass determination was carried out by a ebulliscopic method.

According references [2, 5] it is known that molar mass of polyurethane prepolymer can be increased when using chain extenders. Polyethers and polyesters are used as chain extenders in synthesis and manufacture of polyurethanes.

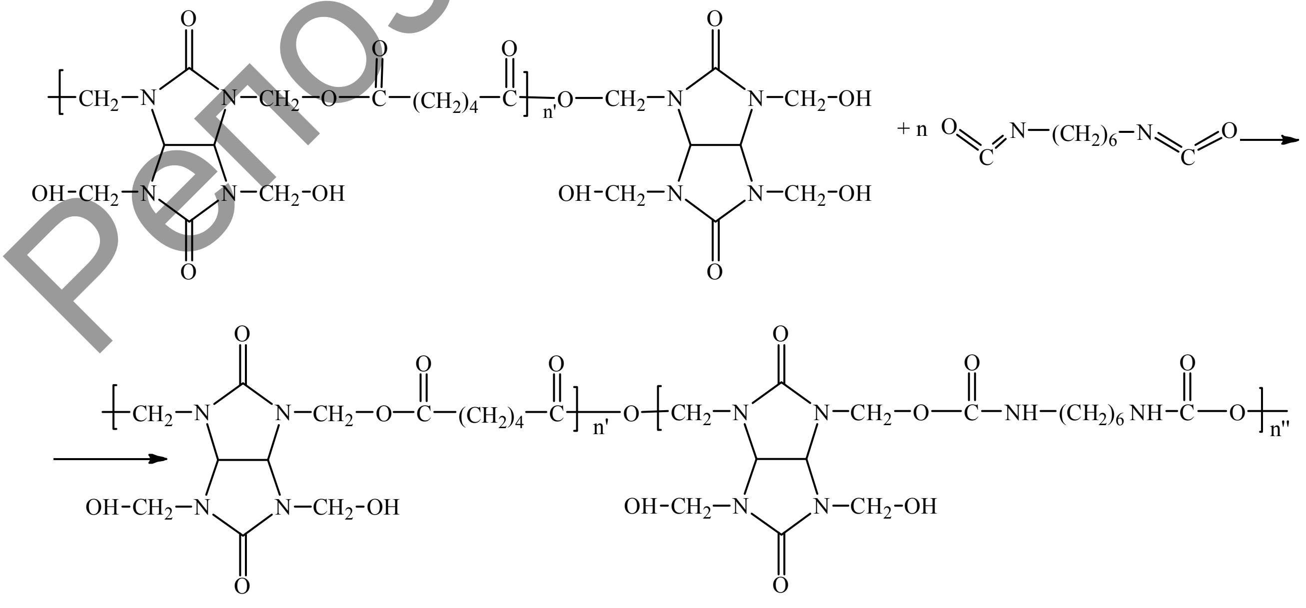
Polyesters as extenders must have hydroxyl end group, therefore usually conditions for interaction of excess of hydroxyl containing monomers in reaction with the dicarboxylic acid are created. Excess of polyol is usually 5 to 20 mol. %.

Proceeding from availability of accessible reactants we carried out step-growth polymerization of tetraol with adipic acid in melt having obtained polyester such as polytetra-N-methylolglycouryladipinate. As a result of polyesterification reaction the mixture of oligomers was obtained. According well known techniques [6] the acidic (2.5) and hydroxyl (31.1) numbers were calculated. Considering the hydroxyl number an average molar mass of polytetra-N- methylolglycoluryladipinate was calculated, it was equal to 2860.

The scheme of interaction of tetraol and dicarboxylic (adipic) acid is presented below:



We introduced this polyester into reaction with diisocyanate by a known technique [6] having obtained polyesterurethane. Synthesis was carried out under vacuum at pressure of 10 mm of mercury column in order to avoid foaming.



The polymer obtained is a solid waxlike product, poorly soluble in organic solvents, its molar mass is equal to 4310. Molar mass was also determined by a ebulliscopic method. Shore hardness is 39 on D scale, it was measured by means of portable durometer Metrotest TPS-TD2. The presence of various functional groups such as urethane, polyesher, carbonyl, hydroxyl, methylene chains, frame fragments of bicyclic bisurea derivative in composition of polyetherurethane synthezised assumes a complex of various physical and chemical properties, researching of which will be continued.

Thus as a result of researches new polymers based on hydroxyl derivarive of glycoluril, hexamethylenediisocyanate and adipic acid were synthesized, the molar masses of polymers obtained were determined, some physical and chemical properties of polymers were studied.

Experimental part

Tetra-N-methylolglycoluril preparation

20 % Solution of sodium hydroxide was added to suspension 28.4 g (0.2 mole) of glycoluril and 80 g of 40 % solution of formaldehyde up to adjustment of pH equal to10–12, then a reactionary mixture was held at temperature of 50°C and stirred during 2 h. After that solvent was distilled and tetra-N-methylolglycoluril was recrystallized.

T_m=136.5ºC, IR spectrum (KBr), ν, sm^{-1}: 1682.51 (C=O), 3268.18 (OH); NMR ^1H (DMSO-d6), δ, ppm: 5.47 (N-CH), 4.626–4.797 (N-CH2); NMR ^{13}C (DMSO-d6), δ, ppm.: 65.736 (CH), 156.913 (C=O).

Prepolymer preparation

Dry three-necked flask of 1 liter volume provided with a stirrer, gas inlet tube and the reflux condenser protected by a desiccating tube was filled with nitrogen and after that solution of 7.9 g (0.03 mole) purified tetra-N-methylolglycoluril into 100 ml of a chlorobenzene and *o*-dichlorobenzene (4:1) mixture was loaded. A gas inlet tube was replaced with a dropping funnel and a solution was heated up to boiling. Solution of 8.4 g (0.05 mole) of hexamethylenediisocyanate was added a in 50 ml of solvent by means of dropping funnel; then a half of diisocyanate solution was quickly added at vigorous stirring, and the rest amount of diisocyanate was added within 3–4 hours, then it was held for 1 hour at boiling temperature. At cooling the solution to room temperature the precipitation of prepolymer was formed and solvent was decanted. Polymer obtained was dissolved in 50 ml of hot DMFA and 50 ml of ethanol was added in still warm solution. Transparent solution was left in the refrigerator for the night and polymer precipitated was separated by filtering and was dried within 24 hours in vacuum desiccator at 0.1 mm of mercury column [6].

Synthesis of olygomeric polyester

Mixture of 0.033 mole (8.7 g) of tetraol and 0.03 mole (4.4) of adipic acid was loaded into a flask provided with reflux condenser, then it was heated on a sand bath until to melting of monomer. Then at stirring the temperature of a reactionary mixture raised up to 160°C.Reaction was carried on with periodical selecting samples before achievement of acidic number of polyester approximately equal to 2. When reaction was over a hot product was poured out in a porcelain glass.

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Бициклді бисмочевина туындылары, гексаметилендиизоцианат және адипин қышқылының негізіндегі полиуретандар

Мақала полиуретандық полимерлердің құрылысына бициклді бисмочевиналардың фрагменттерін енгізу мүмкіндігін зерттеуге және нәтижесінде белгілі полиуретандық полимерлердің механикалық қасиеттерін жақсартуға арналған. Бициклді мономер — тетра-N-метилогликоурилмен — стереометриялық тұрғыдан әрекеттестіру үшін өте қолайлы сызықтық мономерлер таңдалған: адипин қышқылы және гексаметилендиизоцианат. Тетраолды синтездеудің оңтайлы жағдайлары табылып, әр түрлі факторлардың оның шығымына әсері көрсетілген. Синтезделген полимерлердің молекулалық массалары аңықталып, физика-механикалық қасиеттері зерттелді, сондай-ақ полиуретандар поликонденсация реакциясы арқылы синтезделді.

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Полиуретаны на основе производных бициклических бисмочевин, гексаметилендиизоцианата и адипиновой кислоты

Статья посвящена исследованию возможности включения в структуру полиуретанового полимера фрагментов бициклических бисмочевин и, как следствие, улучшению механических свойств известных полиуретановых полимеров. Для взаимодействия с бициклическим мономером — тетра-N-метилолгликолурилом — были выбраны наиболее удобные со стереометрической точки зрения линейные мономеры: адипиновая кислота и гексаметилендиизоцианат. Также были найдены оптимальные условия синтеза тетраола и показано влияние различных факторов на его выход. Полиуретаны были синтезированы реакцией поликонденсации, определены молекулярные массы синтезированных полимеров и изучены их физико-механические свойства.