SYNTHESIS AND STUDY OF POLYURETHANES AND POLYUREA URETHANES BASED ON THE DIAMINO DERIVATIVES OF BIS-1, 3, 4-OXADIAZOLE

A. P. Grekov, V. P. Tkach, V. V. Medvedeva, and K. A. Kornev

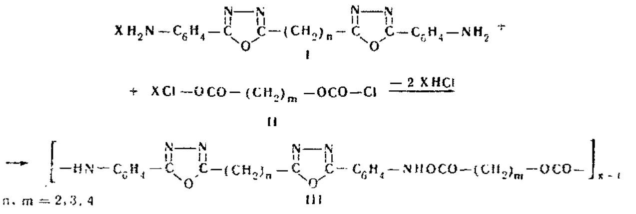
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, pp. 468–470, 1969

UDC 547.793.4.07

Polyurethanes were synthesized by condensation of diamino derivates of bis-1, 3, 4-oxadiazole with chloroformates, and polyurea urethanes were synthesized from diamino derivaties of bis-1, 3, 4-oxadiazole, diisocyanates, and ethylene glycol in a solution of dimethylformamide. Certain properties of these compounds were studied.

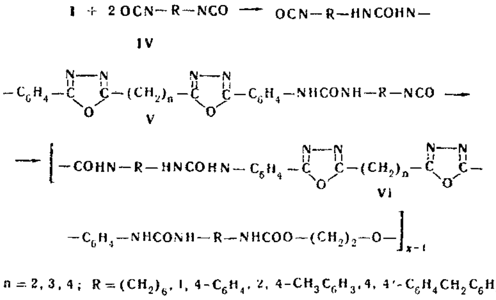
Recently increasing attention has been devoted to polymers containing 1, 3, 4-oxadiazole rings [1–7]. The polyoxadiazoles are being studied because of the fact that, in addition to the ease with they can be synthesized, the polymers obtained posses the capacity to form highly thermoresistant films and fibers which are light stable and chemically stable [1, 3, 6].

This study is devoted to the synthesis of polyurethanes and polyurea urethanes containing 1, 3, 4-oxadiazole rings. Polyurethanes are synthesized by condensing diamino derivaties of bis-1, 3, 4-oxadiazole (I) with dichloroformates (II) in a medium of dry dimethylformamide according to the scheme



The reaction readily proceeds with a yield of polymers close to the quantitative yield at a temperature of 5–10° C. An increase in reaction temperature leads to the formation of polymers with a lower molecular weight.

During the synthesis of polyurea urethanes at first a reaction occured between the diamino derivatives (I) and the diisocyanates (IV) in a molar ratio of 1 : 2 with the formation of products (V), containing terminal isocyanate groups. During the interaction between compounds V and ethylene glycol the corresponding polyurea urethanes (VI) are formed:

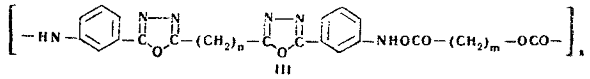


Analogous compounds VI were obtained from compounds I and products of the interaction between diisocyanates and ethylene glycol. As regards the synthesis of the polyurea urethane from 1,4-phenylene diisocyanate, this was found to be the only suitable method, as the product of the interaction between 1,4-phenylene diisocyanate and compound I is very slightly soluble in dimethylformamide.

On examination of the data presented in the tables, it is apparent that the change in length of the hydrocarbon chain in the polyurethane molecule has almost no effect either on the dissociation temperature or on its molecular weight. Introduction of the urea groups into the polyurethane increases the dissociation temperature of the polymer by approximately 100° C. The logarithmic viscosity in concentrated sulfuric acid is somewhat lower in comparison with the viscosity in m-cresol, apparently because of the partial destruction of polyurea urethanes in concentrated sulfuric acid.

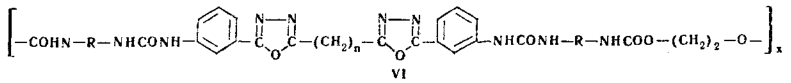
The polyurethanes and polyurea urethanes obtained are colorless powders, almost insoluble in organic solvents. In a solution of dimethylformamide they luminesce in ultraviolet light.

Table 1



n	*m*	Dissociation temperature	η	Empirical formula	N, % found	N, % calculated	Yield, %
2	2	210–220	0.22	$(C_{22}H_{18}N_6O_6)_x$	18.36	18.17	94
3	2	138–145	0.32	$(C_{23}H_{20}N_6O_6)_x$	17.83	17.64	95
4	2	145–150	0.36	$(C_{24}H_{22}N_6O_6)_x$	17.09	17.12	96
4	3	154–160	0.12	$(C_{25}H_{24}N_6O_6)_x$	16.71	16.66	97
4	4	120–130	0.44	$(C_{26}H_{26}N_6O_6)_x$	16.31	16.21	98

Table 2



VI

R	n	Dissociation temperature °C	η		Empirical formula	N, %		Yield, %
			concentrated H_2SO_4	m-cresol		found	calculated	
$(CH_2)_6$	2	256—260	0.22	0.39	$(C_{36}H_{46}N_{10}O_8)_x$	18.74	18.78	96
$(CH_2)_6$	3	218—230	0.32	0.32	$(C_{37}H_{48}N_{10}O_8)_x$	18.76	18.41	93
$(CH_2)_6$	4	197—200	0.28	0.36	$(C_{38}H_{50}N_{10}O_8)_x$	18.21	18.10	91
2,4-$CH_3C_6H_3$	2	200—205	0.10	0.18	$(C_{38}H_{34}N_{10}O_8)_x$	18.28	18.48	92
2,4-$CH_3C_6H_3$	4	216—220	0.14	0.21	$(C_{40}H_{38}N_{10}O_8)_x$	17.68	17.84	94
1,4-C_6H_4	2	329—336	—	0.24	$(C_{36}H_{30}N_{10}O_8)_x$	19.01	19.17	89
1,4-C_6H_4	4	310—320	—	0.17	$(C_{38}H_{34}N_{10}O_8)_x$	18.20	18.46	91
4,4'-$C_6H_4CH_2C_6H_4$	4	235—240	—	0.43	$(C_{52}H_{46}N_{10}O_8)_x$	15.20	14.91	92

EXPERIMENTAL

Polyurethanes (III). A 0.002 mole quantity of the diamino derivative of bis-1,3,4-oxadiazole (I) [8] in 20 ml of dry dimethylformamide in the presence of 0.5 ml pyridine in a triple-necked 50 ml-flask provided with a mechanical shaker, a calcium chloride tube, and dropping funnel was cooled to 5–10° C, and during vigorous agitation and cooling a solution of 0.002 mole dichloroformate in 3 ml of dry dimethylformamide was added. The reaction mixture was maintained at 5–10° C for 3 hr, and poured into a tenfold volume of water, after which the product was removed by filtration and dried in a vacuum desiccator over phosphorus pentoxide. The polymers were purified by reprecipitation from solution in dimethylformamide with methanol or ether.

Dissociation temperatures, logarithmic viscosity in m-cresol at 25 ± 0.05° C, and data of the analyses and yields of the synthesized polyurethanes are presented in Table 1.

Condensation between Compounds I and Diisocyanates (IV). A 0.001 mole quantity of 1,4-bis[2-(5-m-aminophenyl-1,3,4-oxadiazolyl)] butane was dissolved at room temperature in 12.5 ml dry dimethylformamide in a triple-necked 25 ml-flask provided with a mechanical shaker, a calcium chloride tube, and a dropping funnel. After 30 min a solution of 0.002 mole 1,6-hexamethylene diisocyanate in 3 ml dry dimethylformamide was added. The reaction mixture was heated to 60–65° C, and agitated for 4–5 hr (during the reaction between compound I and 2,4-toluylene diisocyanate the mixture was stirred without heating), half of the dimethylformamide was sublimed under vacuum in a current of dry nitrogen, and the residue was poured into 25 ml of dry benzene. The precipitated product was removed by filtration in a current of nitrogen and dried in a vacuum desiccator over phosphorus pentoxide. A colorless compound (V) was obtained with a dissociation temperature of 254–256° C, containing isocyanate groups at the ends of the molecule. When this compound was treated with the hydrazide of formic acid, a substance was formed with a yield of 96.3% and a melting point of 148–150° C. Found, %: N 23.23. Calculated for $C_{38}H_{52}N_{14}O_8$, %: N 23.56.

By an analogous manner other compounds V were obtained. As compounds V are formed in a sufficiently pure form with a quantitative yield, during their isolation from the reaction medium it is not essential to obtained the corresponding polyurea urethanes.

Polyurea urethanes (VI). A. A 0.001 mole quantity of ethylene glycol in 3 ml dimethylformamide was added dropwise to a solution of 0.001 mole diisocyanate (V) in 15 ml dimethylformamide. The product of the reaction was removed by filtration and dried in a vacuum desiccator over phosphorus pentoxide. Compounds (VI) were purified by boiling in dimethylformamide and reprecipitation from a solution in dimethylformamide by methanol.

B. A 0.002 mole quantity of 1,4-phenylene diisocyanate in 20 ml of dry dimethylformamide was placed in a triple-necked 50 ml-flask provided with a mechanical stirrer, a calcuim chloride tube, and a dropping funnel, and filled with nitrogen. During constant stirring a solution of 0.001 mole of ethylene glycol in 5 ml dimethylformamide was added dropwise. The reaction mixture was heated to 60–70° C, maintained for 4–5 hr, and after 30 min a solution of 0.001 mole diamine (I) in 10 ml dimethylformamide was added. The mixture was stirred for a further 5 hr and poured into a fivefold excess of water. The precipitate polymer was removed by filtration and dried in a vacuum-desiccator over phosphorus pentoxide.

The polymer from 1,4-bis[2-(5-m-aminophenyl-1,3,4-oxadiazolyl)]butane, 1,6-hexamethylene diisocyanate, and ethylene glucol was synthesized in an analogous manner. The yield, analyses and physicochemical constants correspond to those of the polymer obtained by method A.

In Table 2 are presented the dissociation temperatures, logarithmic viscosity in sulfuric acid and m-cresol, data of the analyses, and yields of the synthesized compounds VI.

REFERENCES

1. A. P. Grekov, Organic Chemistry of Hydrazine [in Russian], Tekhnika, Kiev, 1966.

2. A. P. Grekov, S. A. Malyutenko, and K. A. Kornev, KhGS [Chemistry of Heterocyclic Compounds], p. 325, 1966.

3. J. Preston and W. Black, J. Pol. Sci., B4, 267, 1966; B3, 845, 1965.

4. T. Unishi and M. Hasegawa, J. Pol. Sci., A3, 3191, 1965.

5. J. Iwakura, K. Uno, and S. Hara, Makrom. Chem., 94, 103, 1966.

6. B. Cullertson and R. Murphy, J. Pol. Sci., B4, 249, 1966.

7. A. L. Rusanov, V. V. Korshak, E. S. Krongauz, and I. B. Nemirovskaya, Vysokomol. soed., 8, 804, 1966.

8. V. P. Tkach, A. P. Grekov, V. V. Medvedeva, and K. A. Kornev, KhGS [Chemistry of Heterocyclic Compounds], 806, 1967.

15 February 1967

Institute of Chemistry of
High-Molecular Compounds
AS UkrSSR, Kiev