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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Amidolysis of Polyurethane Wastes

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Abstract—Chemical degradation of various grades of polyurethane under the action of ε-caprolactam was performed. The degradation rate depends on the polyurethane structure. Amidolysis of the urethane group was proved by performing model reactions.

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Steady growth of polyurethane (PU) production leads to an increase in the volume of solid wastes formed. Their elimination by incineration and disposal leads to irrevocable loss of valuable resources and gives rise to environmental problems. Therefore, the development of procedures for utilization of PU wastes with their recycling becomes an urgent problem.

Today, the best studied (and already implemented in some countries) is chemical recycling by glycolysis. The products formed in the process are used as components in synthesis of PU of the same or another type, using a standard technology [1].

At the same time, PU can be decomposed under the action of other nucleophilic agents, in particular, amines [2]. However, commercial implementation of such processes is impeded today by high cost and toxicity of amine degradation agents. In this connection, we examined in this study the chemical degradation of PU under the action of a readily available, relatively cheap, and low-toxic amine, ε-caprolactam (ε-CL).

EXPERIMENTAL

Chemical degradation experiments were performed with castable monolithic PUs of grades SKU-OM, SKU-6, and SKU-PFL, which are widely used in production of construction items. SKU-OM was prepared by the reaction of poly(ethylene butylene glycol adipate) (PEBA) with toluene 2,4-diisocyanate (TDI) in the presence of catalytic amounts of phenolic Mannich bases at the molar ratio TDI : PEBA = 1.15 : 1 [3]. SKU-PFL and SKU-6 were prepared, respectively, by the reaction of SKU-PFL-100 prepolymer with 4,4'-methylenebis(2-chloroaniline) at the molar ratio SKU-PFL-100 : MOCA = 1 : 0.8 [3, 4] and of TDI with polyethylene glycol adipate (PEA), 1,4-butanediol (BD), and 1,1,1-trimethylolpropane (TMP) at the molar ratio TDI : PEA : TMP : BD = 2 : 1 : 0.32 : 0.24. As degradation agent we used ε-CL produced by the KuibyshevAzot Joint-Stock Company.

Amidolysis was performed under argon in an oil-heated 250-ml three-necked flask equipped with a stirrer and a thermometer at 160–200°C for 2.5 h. The flask was charged with ε-CL and preliminarily ground PU in weight ratios of 80 : 20, 60 : 40, and 40 : 60.

To examine the mechanism of PU degradation, we performed model reactions with compounds that can be considered as structural models of the main chemical bonds in PU, namely, with butyl phenylcarbamate (PBC), *N,N*-diphenyl-*N*'-phenylurea (DPU), and dibutyl phthalate (DBP). The reactions of these compounds with ε-CL were performed in a two-necked flask under argon at 150°C for 2.5 h at equimolar ratio of the reactants.

The melting points of the degradation products were determined by the capillary procedure [5].

The IR spectra of the products were recorded on a Perkin–Elmer spectrophotometer (model PC-16) using KBr pellets.

The ^{1}H NMR spectra were taken on a Bruker-700 device operating at 700 MHz (for protons). The measurement error was 2%. Carbon tetrachloride was used as solvent.

The molecular weights of degradation products were determined with a Bruker OUTOFLEX 11 device. We used the MALDI TOF mass-spectrometric procedure. As an ion source we used a laser with a generation wavelength of 337 nm.

Amine and hydroxyl numbers were determined by analytical titration [5].

Chromatograms were taken with a Perkin–Elmer liquid chromatograph using a Bondapak C18 column with an internal diameter of 4 mm. The flow rate was 1 ml min^{-1}. We used a UV detector at a wavelength of 280 nm, with the sensitivity of 1.28 absorption units per whole scale. The solvent was acetonitrile.

Amidolysis under the action of ε-CL yielded light brown solids. They are readily soluble in acetone, toluene, and formic acid, in which the initial PU is insoluble. The melting points of the substances obtained are in the range 30–45°C.

The resistance of PUs to chemical degradation was evaluated by the time in which the system became homogeneous. As seen from Table 1, the degradation time increases in the order SKU-OM, SKU-6, SKU-PFL. The three-dimensional network of SKU-OM is formed by allophanate, ester, and urethane bonds; in SKU-6, by ester and urethane bonds; and in SKU-PFL, by biuret, urea, and urethane bonds. Because amidolysis involves carbonyl groups in these bonds, specifically these bonds are responsible for the thermochemical stability of polymers, which, as known, increases in the order allophanate, ester, urethane, urea bonds [6]. Therefore, for SKU-PFL containing a high concentration of urea bonds, a longer degradation time is required.

A study of the influence of temperature on the degradation showed that an increase in temperature leads to a regular decrease in the sample degradation time (Table 1). The optimal temperature is 180°C. Below this temperature PUs degrade slowly, and exceeding it leads to acceleration of thermal oxidative degradation.

Table 1. Influence of temperature and polyurethane grade on degradation time at the ratio PU : ε-CL = 40 : 60 wt %

Polyurethane grade	Degradation temperature, °C	Degradation time, min
SKU-OM	160	60
	180	30
	200	25
SKU-6	160	60
	180	40
	200	35
SKU-PFL	160	80
	180	60

The molecular weights of degradation products determined by MALDI-TOF mass spectroscopy also confirm the degradation of PU with ε-CL. The degradation product is characterized by the presence of various macromolecules with relatively low molecular weights, up to *m*/*e* 689.

Because PU degradation can involve cleavage of urethane, allophanate, biuret, urea, and ester bonds, the terminal groups of the chains should be either hydroxy or amino groups. Their content was evaluated by determining the amine and hydroxyl numbers (Table 2).

An IR study of the chemical structure of degradation products revealed the presence in them of absorption bands corresponding to hydroxy (3280 cm^{-1}) and amino (3200 cm^{-1}) groups, and also of bands at about 1640 cm^{-1}, corresponding to stretching vibrations of the carbonyl group in the lactam ring. These absorption bands are absent in the spectra of the initial PUs. This fact suggests that the degradation product is an oligomer with terminal OH and NH_2 groups, containing ε-CL fragments.

To elucidate the mechanism of PU degradation, we performed model reactions. Analysis of the chemical structure of their products by IR spectroscopy and comparison of the spectra with those of the initial compounds showed that the spectra of DBP and DPU underwent no significant changes. At the same time, the spectrum of the product formed in the reaction of BPC with ε-CL differs significantly from that of PBC (Figs. 1, 2). The absorption band at about 1065 cm^{-1}, characteristic of the $–CH_2–O–$ group in BPC, disappears in the IR spectrum of the purified reaction mixture after the action of ε-CL on BPC, which is due to replacement of the butyl group by the lactam ring. Also,

Table 2. Amine and hydroxyl numbers of polyurethane degradation products at the ratio PU : ε-CL

Product based on	Amine number, wt %	Hydroxyl number, wt %
SKU-OM	2.04	2.09
SKU-6	2.94	2.98
SKU-PFL	6.92	3.63

Table 3. Some characteristics of butyl phenylcarbamate and its degradation product, determined by liquid chromatography (solvent acetonitrile)

Compound	Retention time, min	Weight fraction, %
BPC	3.41	100.00
Product of reaction of PBC with ε-CL	3.41	89.66
	3.28	10.34

the absorption band at 3304 cm^{-1} becomes considerably broadened, confirming the presence of an NH group in secondary amides. It should also be noted that the spectrum of the final product contains an absorption band at about 800 cm^{-1}, indicative of the presence of lactam methylene groups. The absorption band at about 2930 cm^{-1}, characteristic of stretching vibrations of the $–CH_2–$ group, becomes broadened. Because the reaction occurs at a temperature exceeding the boiling point of butanol, the absorption band of the butanol hydroxy group is not observed in the spectrum.

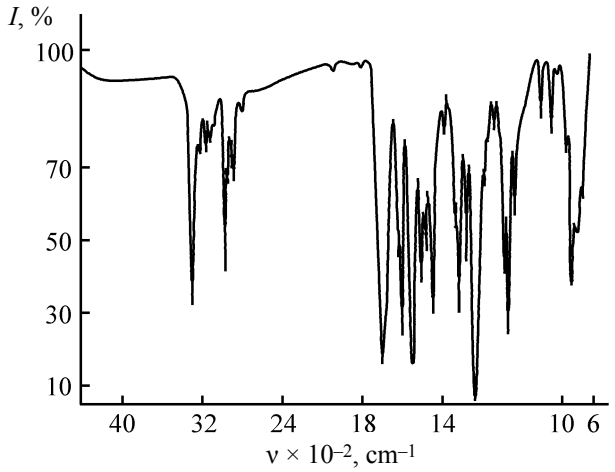


Fig. 1. IR spectrum of butyl phenylcarbamate: (ν) wavenumber and (I) absorption intensity; the same for Fig. 2.

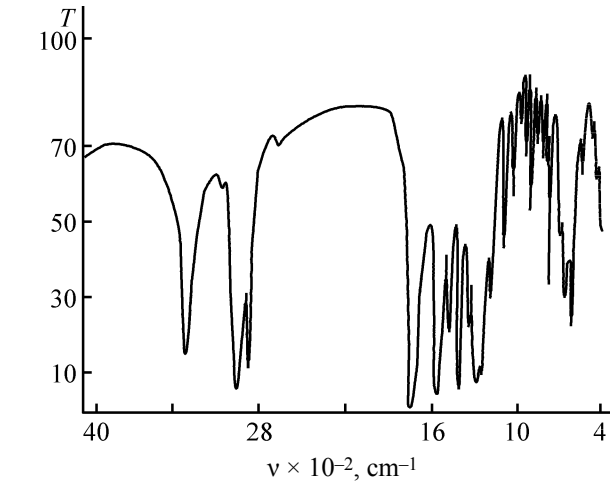


Fig. 2. IR spectrum of the purified reaction mixture after treatment of butyl phenylcarbamate with ε-caprolactam.

The NMR spectrum of the crude product of the reaction of BPC with caprolactam contains new signals in the range 7.5–6.9 ppm, suggesting changes in the surrounding of the benzene ring. Signals at 1.9–1.7, 2.5–2.3, and 2.8–2.7 ppm correspond to lactam ring protons. In addition, the proton signal of the $CH_2–N$ group of ε-CL is shifted from 3.4–3.2 to 2.8–2.7 ppm, and this is possible only in the case of addition of the lactam molecule via NH group. Calculation of the integral intensities showed that the amount of the new product is about 10% of the total sample (Fig. 3).

This conclusion was confirmed by liquid chromatography. As seen from Table 3, the product of the reaction of BPC with ε-CL {1-[phenyl(amino)carbonyl]hexahydro-2-azepinone (PCHA)} shows two peaks with different retention times, with the amount of the fraction giving the new peak being 10.34 wt %.

Thus, the reaction of ε-CL with BPC results in cleavage of the urethane group, followed by addition of the ε-CL molecule and release of butanol (see the scheme).

CONCLUSION

Chemical degradation of polyurethane of SKU-OM

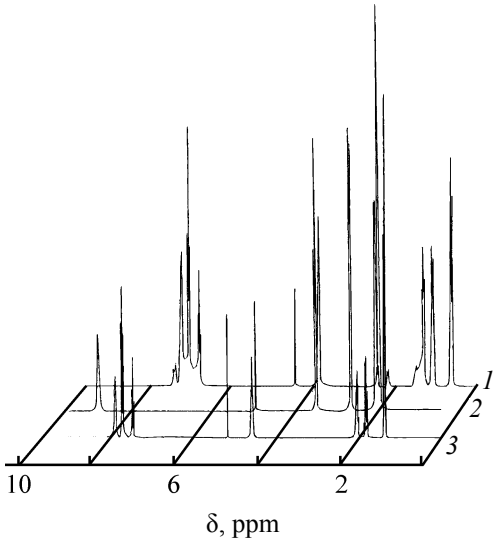
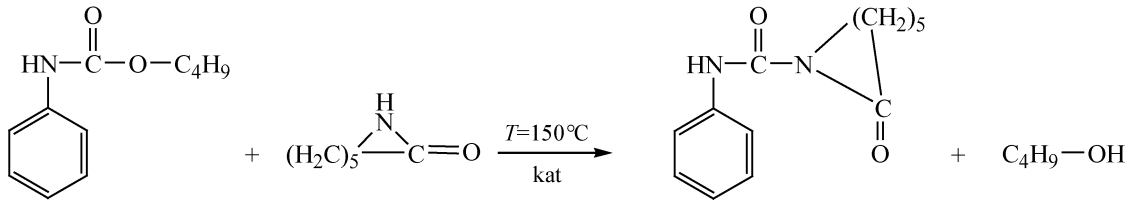


Fig. 3. ^1H NMR spectra: (*1*) butyl phenylcarbamate, (*2*) ε-caprolactam, and (*3*) product of reaction of butyl phenylcarbamate with ε-caprolactam.

Scheme.



grade under the action of ε-caprolactam occurs faster than that of SKU-PFL and SKU-6.

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