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Abstract

Full Text

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Polycondensation at the Phase Boundary

Polyamides belong to the types of polymers that can most readily be obtained by polycondensation at the phase boundary. This method was proposed by Wittbecker and Morgan (^{1}) and, as noted by the authors of (^{2}), has a number of advantages in comparison with the previously used method of polycondensation in the melt. At present this method is being thoroughly studied from the theoretical point of view; the influence of a number of factors on the polymer yield, the magnitude of the molecular weight, and the viscosity is being clarified. The most important of these proved to be ($^{3-5}$): the nature of the organic solvent, the nature of the emulsifiers, the concentration of the reactants, and carrying out the process with stirring or without stirring. The heterogeneous process of interfacial polycondensation underlies the preparation of complex polyesters, polyamides, polyurethanes, polysulfonamides, and other heterochain polymers. Beaman et al. (^{6}) obtained 13 polyamides of different structures. In doing so they used aliphatic, aromatic, or alicyclic diamines and dichlorides of dicarboxylic acids, as well as primary and secondary diamines.

The present work is devoted to the synthesis of a polyamide from pyridine-2,6-dicarboxylic acid dichloride and hexamethylenediamine by the method of interfacial polycondensation and to the study of some of its physicochemical properties.

The process was carried out in a chemical beaker at room temperature and with stirring. The polycondensation reaction of pyridine-2,6-dicarboxylic acid dichloride with hexamethylenediamine may be represented by the following scheme:

$$\text{pyridine-2,6-dicarbonyl chloride} + NH_2(CH_2)_6NH_2 \xrightarrow[\substack{CH_3COONa \cdot 3H_2O \\ Na_2CO_3 \\ NaOH}]{} [-HN-C(=O)-C_5H_3N-C(=O)-N \tag{1}$$

As the starting material for the synthesis of the polyamide we used a lutidine-containing β-picoline fraction, which is a waste product of the chemical manufacture of the preparation phthivazide (^{7}).

Fig. 1. Thermomechanical curve of the polyamide

Figure 1: Fig. 1. Thermomechanical curve of the polyamide

Pyridine-2,6-dicarboxylic acid dichloride, obtained by boiling pyridine-2,6-dicarboxylic acid with thionyl chloride ([8]), was dissolved in benzene, and freshly distilled hexamethylenediamine was dissolved, respectively, in aqueous solutions of sodium acetate, sodium carbonate, and caustic soda. In each case, with the aid of an LP-5 tube potentiometer, the pH of precipitation of the polyamide was measured (the pH was, respectively, 3, 7—8, 10).

When the indicated solutions are simply poured together, a polymer film forms at the interface, which can be drawn out with a glass rod in the form of a thread. When the reaction is carried out with stirring, however, a polymer precipitate forms throughout the entire volume of the solution. After filtration and washing with water, the polyamide was isolated in the form of a white powder, which dis-

dissolves in pyridine, dimethylformamide, concentrated sulfuric, hydrochloric, acetic, and formic acids, and, on heating, in *m*-cresol. The polyamide could be purified only by reprecipitation, precipitating it with ether from a pyridine solution.

The viscosity of solutions of the polyamide in concentrated sulfuric acid and dimethylformamide was measured with an Ubbelohde viscometer at 20° (9–12).

The specific viscosity of each polyamide sample isolated at different pH values, equal to 3, 7-8, and 10, proved to be the same.

The polyamide is characterized by a specific viscosity equal to 0.323 at a polyamide concentration in concentrated sulfuric acid of 0.5 g/100 ml of solution, and by a reduced logarithmic viscosity calculated according to formula (5)

$$\eta_{\log} = \frac{\ln \eta_{\text{rel}}}{C} = 0.560.$$

Fig. 1. Thermomechanical curve of the polyamide

The specific and logarithmic viscosities of the polyamide in dimethylformamide solution were measured at different polymer concentrations. The results are given in Table 1.

On the basis of the Huggins equation (1), we estimated the average molecular weight of the polyamide to be approximately 20000–30000.

The thermomechanical curve, measured on Kargin' s balance and characterizing three states of the polymer, is shown in Fig. 1. An IR absorption spectrum was recorded, indicating the presence of N—H and C=O bonds. The N—H frequency is 3352-3378 cm^{-1}, and the C=O frequency is 1652 cm^{-1}. Fig. 2 (see the insert facing p. 1084) presents an X-ray diffraction pattern of the polyamide, from which it is evident that the synthesized compound has a gas-crystalline structure.

Table 1

Conc. in g/100 ml of solution	η_{sp}	η_{log}
0,1	0,033	0,322
0,2	0,113	0,533
0,3	0,202	0,610

Since the polyamide under consideration contains functional groups that could form chelate units with metals, the ability of the polyamide to react with metal salts was tested. For this purpose, the polycondensation of the dichloroanhydride of pyridine-2,6-dicarboxylic acid with hexamethylenediamine was carried out in the presence of an Fe^{II} salt. A dark-brown viscous product resembling rubber was obtained.

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