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Abstract

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PHYSICAL CHEMISTRY

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ON STEREOSPECIFIC EFFECTS IN INTERFACIAL POLYCONDENSATION

In a previous paper (^1) we described the synthesis of an optically active polyamide based on 1,2-*l*-propylenediamine (I) and the acid chloride of (±)-trans-cyclopropanedicarboxylic-1,2 acid (II) by the method of interfacial polycondensation.

From a number of works on the study of solid-phase polymerization ([2-]4) and of certain organic reactions proceeding in solids and at the solid–liquid interface, it is known that the crystal lattice can exert a substantial influence on the direction of the reaction and on the structure of the products formed. In this connection it was of interest to determine whether the transition from polycondensation at the interface between two liquids to polycondensation at the interface between a crystalline phase and a liquid would be accompanied by a change in the probabilities of incorporation of the (+) and (−) antipodes of II into the macromolecules of the polyamide formed. If such an effect occurs, the optical activity of the polyamide should change.

In this connection we studied* the interfacial polycondensation of I and II in the temperature range from +20 to −60°. In our experiments the aqueous phase contained 2% I and 8% KOH. As the organic phase we used a 3% solution of II in chloroform. Over the entire temperature range investigated the organic phase remains liquid. The aqueous phase remains liquid down to −7° and crystallizes upon further lowering of the temperature. Figure 1 presents the heating thermogram of the crystallized aqueous phase.** Three plateaus are observed on the thermogram, corresponding to transformations occurring in the system upon heating. The first endothermic transformation is the melting of the mixture. The nature of the second (endothermic) and third (exothermic) transformations is not clear. Thus, in the temperature interval from +20 to −60° it is possible to pass from polycondensation at a liquid–liquid interface to polycondensation at a liquid–crystal interface.

Table 1

Experiment No.	Polycondensation temperature, °C	Concentration of acid chloride, g/100 ml	Measured angle, deg., $ $436	Measured angle, deg., $ $405	Specific rotation, deg., $ $436	Specific rotation, deg., $ $405
1	+20	0.77	0.120	0.166	12.9	17.3
2	+5	1.36	0.189	0.275	12.1	17.0
3	−3	1.30	0.162	0.211	13.7	18.2
4	−3	1.83	0.320	−*	14.6	–
5	−10	0.45	0.040	0.072	7.7	–
6	−10	0.60	0.050	–	7.0	–
7	−25	0.86	0.075	0.100	7.2	9.6
8	−30	0.49	0.072	0.098	12.1	16.5
9	−30	0.35	0.057	0.072	13.0	16.3
10	−45	1.1	0.084	–	7.0	–
11	−45	0.52	0.054	–	6.8	–
12	−60	1.0	0.053	0.080	4.4	6.6
13	−60	1.1	0.069	0.109	5.2	7.2
14	−60	0.3	0.020	–	5.2	–

* Rotation was not measured because of strong absorption of light in the solution.

When carrying out the reaction with sampling of the acid chloride, it was established that under the experimental conditions, irrespective of the state of the aqueous phase containing I, the reaction is practically completed at the specified temperature.

* Student diploma candidate V. K. Zlobin took part in the experimental part of the work.

** It should be noted that the use of the concept "phase" for the system formed upon freezing an aqueous solution of I and caustic potash is conditional, since several solid phases may be formed in this case.

It should be noted that the yield of polyamides obtained at different temperatures does not change and amounts to $\sim 20\%$. After completion of the reaction, the polymers obtained were separated by centrifugation, reprecipitated from formic acid by precipitation into ammonia, again dissolved in 98% formic acid, and their optical activity in solution was determined. Measurements of optical activity were carried out using a photoelectric spectropolarimeter constructed by V. M. Potapov [(5)] on the basis of a Bellingham and Stanley polarimeter in combination with a quartz monochromator. The accuracy of measurement of the angle of rotation of the plane of polarization was $\pm 0.001^\circ$. The results of the measurements are presented in Table 1.

Fig. 1. Thermogram of heating of a frozen aqueous solution of *l*-propylenediamine (2%) and caustic potassium (8%). 1 —melting, 2 —

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Figure 1: Fig. 1. Thermogram of heating of a frozen aqueous solution of *l*-propylenediamine (2%) and caustic potassium (8%). 1—melting, 2—endothermic transition in the solid phase, 3—exothermic transition in the solid phase

Fig. 2. Dependence of the specific rotation of polyamides on the polycondensation temperature ($\lambda = 436$ mμ)

Figure 2: Fig. 2. Dependence of the specific rotation of polyamides on the polycondensation temperature ($\lambda = 436$ mμ)

endothermic transition in the solid phase, 3 —exothermic transition in the solid phase.

In Fig. 2 is shown the dependence of the specific optical activity of the synthesized polyamides on the polycondensation temperature. It is seen that at the freezing temperature of the aqueous phase there is a sharp drop in the specific optical activity, which then remains constant in the interval between the crystallization temperatures and the second endothermic transition. At the temperature of the second transition, the optical activity of the polyamide again passes through a maximum. It is characteristic that the specific rotations of the polymers obtained at +20 and −3°, i.e., under conditions when the aqueous phase is liquid, and at the temperature of the phase transition in the frozen aqueous phase, practically coincide.

It should be noted that the intrinsic viscosities in sulfuric acid of the polyamides obtained under different conditions are close and are of the order of 0.45-100 ml/g. Therefore, the observed effect is difficult to explain by fluctuations in molecular weight.

Differences in the specific optical activity of polyamides obtained at the liquid-liquid and liquid-crystal interfaces can apparently be associated with peculiarities in the occurrence of the elementary act of polycondensation on the surface of the crystalline phase containing I. It may be assumed that fixation of molecules I on the surface of the crystal lattice to some extent promotes the selection, from the racemic mixture II present in the chloroform solution, of the optically active monomer isomer "more suitable" for it.

Fig. 2. Dependence of the specific rotation of polyamides on the polycondensation temperature ($\lambda = 436$ mμ).

It is known that in the temperature region of phase transitions in solids, the mobility of molecules increases significantly. Therefore, in polycondensation at the temperature of the second phase transition ($\sim -30°$), just as in the case of

polycondensation at the liquid–liquid boundary, additional factors associated with the fixation of molecules I at the interface do not operate.

If the proposed assumption is correct, one should expect that the optical activity of the polyamide formed from pure antipodes of propylenediamine and the acid chloride of cyclopropanedicarboxylic acid should not change when the phase state of the components of the system changes. Indeed, the specific rotations of polymers obtained by polycondensation of I with the acid chloride of (+)-trans-cyclopropanedicarboxylic acid at temperatures of −3 and −60° practically coincided ($[\alpha]_D = +9°$).

It should be noted, however, that for the pair of monomers chosen by us the stereospecific effect observed is quite small. Indeed, the difference in the specific rotations of the polyamides obtained from I and II under different conditions is 6—7°, whereas the difference in the specific rotations of the polyamides synthesized by us from I and pure antipodes of the acid chloride of trans-cyclopropanedicarboxylic acid is 146°.

The specific rotations, respectively, are:

$$[\alpha]_{436} = +126° \quad (+ \text{ acid chloride}), \qquad [\alpha]_{436} = -20.2° \quad (- \text{ acid chloride}).$$

This, in all probability, is connected with the absence of measurable optical activity in trans-cyclopropanedicarboxylic acid, which was isolated after acid hydrolysis of the polyamides obtained by polycondensation of I and II at the liquid–crystal boundary.

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