Phase transitions in the product of spontaneous polymerization of the acrylamide complex of calcium nitrate

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Phase transitions in the spontaneously polymerized acrylamide—calcium nitrate system have been studied by X-ray diffraction analysis. The polymerization occurs *via* the stage of formation of crystalline particles, which exist in a homogeneous solution and are identical to crystallites in chemical composition. At the stage of particle formation, the degree of crystallinity is 60 %, the particle size is 65 nm, and paracrystallinity is 0.0208. An amorphous metal-containing polymer is the final structural state of the system.

Key words: acrylamide, calcium nitrate, complex, polymerization; X-ray diffraction analysis; phase transitions.

The development of nontraditional methods for synthesis of metal-containing polymers[1] resulted in the design of new unique objects. It has been shown previously[2] that acrylamide (AAm) is spontaneously polymerized in the presence of Cr^{III}, Bi^{III}, Pb^{II}, or Ca^{II} nitrates at the stage of synthesis of the complex at 20 °C. Assumptions about the mechanism of polymerization were advanced.[3] The recent studies[4] give grounds to believe that several intermediate structural transformations occur upon polymerization of these systems. Polymers obtained possess interesting properties. For example, the conductivity of the polymerized AAm—$Ca(NO_3)_2 \cdot 4H_2O$ system (at a molar ratio of the components of 5 : 1) can vary in a wide range. Moreover, polymerization in an electric field results in anisotropy of conductivity,[5] which indicates that structural anisotropy is possible. This assumption is unusual, because this system is very plastic at the polymerization stage and contains a considerable amount of water. An X-ray diffraction study of the AAm—$Ca(NO_3)_2 \cdot 4H_2O$ system in the process of synthesis is performed in this work.

Experimental

The procedure of the synthesis is presented in Refs. 2 and 5 and includes several stages. A concentrated aqueous solution of the AAm complex obtained begins to solidify at room temperature. In several days, depending on the salt concentration, the sample becomes entirely solid and comprises a stable glassy yellow substance. The following samples were prepared for X-ray study: when the fluidity of the system had ceased (14 h after mixing) and after complete vitrification (in 54 h). X-ray diffraction analysis was performed on a Dron-3M diffractometer according to the standard scheme (Cu was the material of the anode of the X-ray tube, and a filter for β-irradiation was used). An IBM/AT 286 personal computer was used for registration and treatment of the X-ray patterns.

Results and Discussion

The initial experiments on X-ray diffraction analysis of the product of spontaneous polymerization showed that irradiation of samples for ~5 h results in gradual decomposition of the crystalline state, and the decomposition becomes complete in 5 to 10 h. However, less than a 5-h exposure of the sample does not result in considerable changes in the X-ray patterns. Therefore, when exposures of >3 h were needed for registration of X-ray patterns, particular regions of an X-ray pattern were obtained using several objects.

The diffractogram of the polymer differs completely from diffractograms of initial components (Fig. 1). It is rather difficult to determine the structure by the diffrac-

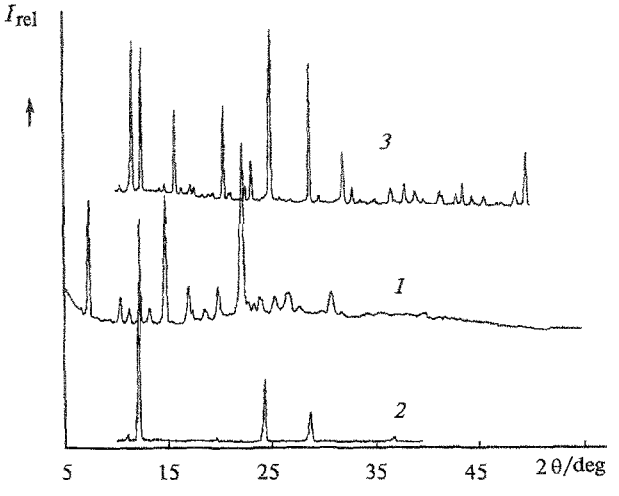

Fig. 1. Diffractograms of the AAm—$Ca(NO_3)_2 \cdot 4H_2O$ system (5 : 1 molar ratio) at 14 h after preparation (*1*), $Ca(NO_3)_2 \cdot 4H_2O$ (*2*), and AAm (*3*); 2θ is the angle of the diffractometer.

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togram of the polycrystal. The approach to the determination of the lattice by the Itoh method[6] does not allow one to identify completely all lines, which indicates that the system is multiphase. The first lines of calcium nitrate (10.43°, 11.4°, 12.45°, and 14.7°) are similar to the lines of the product (10.41°, 11.29°, 12.30°, and 14.72°). However, the ratios of their intensities in the diffractograms of the product and nitrate differ; therefore, lines obtained for the product cannot be assigned reliably to $Ca(NO_3)_2 \cdot 4H_2O$. Nevertheless, intensities and interplanar distances can considerably change in a certain situation. This is typical of small particles in the case of a substantial change in the surface energy, which can result in the appearance of a considerable strain in the crystal.[7] It is likely that small insoluble particles of AAm also should be taken into account, because the main line of the crystalline monomer, 12.07°, lies rather close.

It is known[8] that the degree of crystallinity can be determined from the X-ray pattern by the ratio of sharp peaks and the total coherent intensity. Nevertheless, in the real experiment it is rather difficult to separate amorphous and crystalline parts, if there is no exact profile of the diffraction line from the entirely amorphous product. However, a sufficiently reasonable evaluation of the profile of the amorphous component can be obtained from the enveloping of the base of reflections, taking into account superpositions in the bottom region of sharp peaks, for example, in the Gaussian approximation.[8] For curve *1* in Fig. 1 the degree of crystallinity with account for such an estimation of the amorphous component is ~60 %.

High reflectance orders are observed on the diffractogram of the product (see Fig. 1, curve *1*). The interplanar distances of 1.2, 0.6, and 0.4 nm correspond to the most intense lines, 7.32°, 14.70°, and 22.13°, respectively. This makes it possible to determine some structural parameters. The size of crystals and the degree of their perfection can be found from the following expression[9]:

$$gs = 1/L + (\pi \cdot g \cdot m)^2/d,$$

where gs is the broadening of the line expressed in units $s = 2\sin\theta/\lambda$; L is the size of the crystallites; m is the reflectance order; d is the interplanar distance; g is the paracrystalline factor, $g = (\bar{d}^2 - d^2)^{0.5}/d$; and $\bar{d}$ is the mean deviation of the lattice parameter. The broadening of the line, gs, was determined from the equation $gs = (gs_{exp}^2 - gs_{ref}^2)^{0.5}$. Crystalline AAm was used as a reference. The paracrystalline factor g was determined from the slope of the curve in the $gs = f(m^2)$ plot, which is equal to $(\pi g)^2/d$. The size of the crystallites in the product was 65 nm, $g = 0.0208$. It is shown[9] that there is an empirical dependence between the number of planes $N = L/d$ in the crystallite lattice and the paracrystallinity factor g:

$$\alpha = (L/d)^2 \cdot g. \qquad (1)$$

For thermodynamically stable crystals, α values in Eq. (1) always range within 0.15 ± 0.05. In the AAm—$Ca(NO_3)_2 \cdot 4H_2O$ system the α parameter is equal to 0.153.

The diffractograms of the amorphous-crystalline product obtained in 14 h after the beginning of the synthesis and of the almost entirely amorphous sample after the complete solidification (curves *1* and *2*, respectively) are presented in Fig. 2. Curve *3* in Fig. 2 is diffractogram *2* normalized to the amorphous component of curve *1*. The good coincidence of the shape of the diffractogram obtained for the sample at the final stage of polymerization with the amorphous component of diffractogram *1* gives grounds to believe that the coordination of the fraction of the product in the amorphous state is of the short-range order, which is similar to the coordination of the stable polymer formed from the crystalline phase. This may mean that chemical compositions of crystalline and amorphous portions are identical.

Study of the shape of diffraction reflections of various orders as a function of the degree of vitrification shows that the remaining crystallites do not change their size and degree of perfection (see curve *2* in Fig. 2). Here there is an inconsiderable remaining reflection, whose half-width is unchanged, in the region of the most intense diffraction line of the product at the polymerization stage.

Thus, it follows from the dimensional data of crystals and the high degree of crystallinity that the product obtained in 14 h after the beginning of the synthesis is a

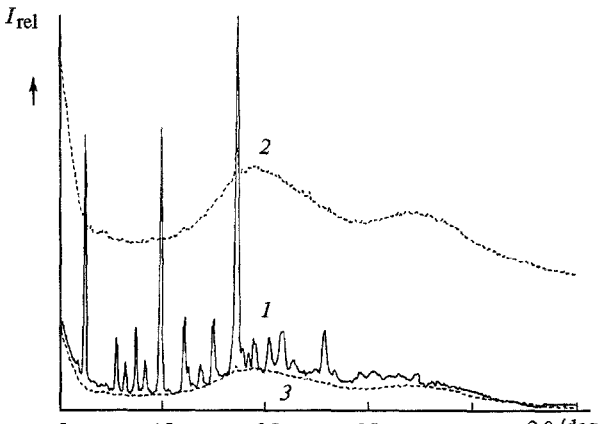

Fig. 2. Diffractograms of the AAm—$Ca(NO_3)_2 \cdot 4H_2O$ system (5 : 1 molar ratio) at 14 h after preparation (*1*) and at 54 h (*2*). Curve *3* is diffractogram *2* normalized to the background component of curve *1*; 2θ is the angle of the diffractometer.

finely dispersed massive of spherical particles[10] surrounded by the solution, which consists of chemical compounds identical to the crystal but not included in its structure. It is known that the compact packing of balls can occupy 72 % of the total volume. The degree of crystallinity of the product equal to 60 % means that particles are arranged chaotically relative to one another. The solution remaining between crystallite particles is also solidified for several days. The simultaneous amorphization of the sample is observed, and the decomposition of individual crystallites occurs due not to a decrease in their size or an increase in the imperfectness (which would result in a substantial broadening of diffraction lines), but due to the instant decomposition. This situation is not unusual, if one takes into account a small size of crystallites, whose surface energy can change jumpwise (the transition of the surroundings of particles from the liquid state to the solid state).

It can be assumed that the conductivity of the system (see Ref. 5) is mainly determined by the conductivity of particles. In fact, if it is caused by the surrounding solution, no anisotropy of the conductivity would be observed upon polymerization of the system in the electric field. It follows that the polymer possesses the high ordering degree of the short-range order despite the seeming decomposition of crystals observed by the X-ray method.

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References

1. A. D. Pomogailo and V. S. Savost'yanov, *Usp. Khim.*, 1991, **60**, 1513 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
2. V. S. Savost'yanov, V. N. Vasilets, O. V. Ermakov, E. A. Sokolov, A. D. Pomogailo, D. A. Kritskaya, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2073 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1615 (Engl. Transl.)].
3. N. P. Piven', V. S. Savost'yanov, S. D. Babenko, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 534 [*Russ. Chem. Bull.*, 1994, **43**, 494 (Engl. Transl.)].
4. D. A. Kritskaya, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1410 [*Russ. Chem. Bull.*, 1993, **42**, 1344 (Engl. Transl.)].
5. A. A. Murav'ev, S. V. Pribysh, Yu. P. Baidarovtsev, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 865 [*Russ. Chem. Bull.*, 1994, **43**, 809 (Engl. Transl.)].
6. L. Azarov and M. Burger, in *Metod poroshka v rentgenografii* [*Powder Method in X-Ray Analysis*], Izd. Inostr. Lit., Moscow, 1961, 121 (Russ. Transl.).
7. I. D. Morokhov, V. I. Petinov, L. I. Trusov, and V. F. Petrunin, *Usp. Fiz. Nauk*, 1981, **133**, 658 [*Russ. Phys. Bull.*, 1981, **133** (Engl. Transl.)].
8. B. Wunderlich, *Fizika makromolekul* [*Physics of Macromolecules*], Mir, Moscow, 1976, 455 (Russ. Transl.).
9. A. M. Hindeleh, R. Hosemann, G. Hinrichsen, and H. Springer, *J. Polym. Sci., Polym. Phys.*, 1990, **28**, 297.
10. Yu. I. Petrov, in *Fizika malykh chastits* [*Physics of Small Particles*], Nauka, Moscow, 1982, 66 (in Russian).

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