

Morphology and kinetics of the formation of polyamide benzimidazole in N-methylpyrrolidone

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Abstract. Polymerization-optical methods were used to study the supermolecular structure in the gelation of systems based on polyamidobenzimidazole (PABI) in N-methylpyrrolidone (N-MP) and the kinetics of phase transformations during polymer coagulation from a the solution. It was found that the use of N-MP leads to the appearance in the PABI-N-MP-H₂O system of spherulites having a structure characteristic of LC structures. It is shown that the alternation of metastable structures upon gelation of the PABY – N-MP-H₂O system is consistent with the appearance of the LC phase of the cholesteric type.

1. Introduction

At present, the third generation of reinforcing fibers has become extremely important. Traditionally used materials (metals, metal alloys) are increasingly being replaced with new ones – composites, the production of which is impossible without reinforcing fibers. These include heterocyclic p-amide fibers of CBM and Armos that have the highest mechanical properties among the entire family of n-aramid fibers [1]. Such fibers are obtained from concentrated sulfuric acid solutions of polyamide benzimidazole (PABI). The study of the morphology of PABI-based systems in other types of solvents, the kinetics of phase transformations with slow gelation of the polymer-solvent-precipitant system, which are in a jelly-like state, is of independent scientific interest. On such systems, it is possible to experimentally test the methods for controlling the stiffness of macromolecules by changing the type of solvent, as well as by increasing the polymer concentration both directly in solution, and when polymer is precipitated from the solution. The latter implies the possibility of the system to possess the properties of a lyotropic liquid crystal. However, the achievement of a critical concentration of the transition to the anisotropic phase in this case should occur directly during the coagulation process.

The aim of this work is to study the morphology of PABI based systems in other types of solvents, the kinetics of phase transformations during polymer coagulation from solution, and also during slow gelation of the polymer-solvent-precipitant system, which are in a gelatinous state. Taking into account the rigid-chain nature of PABI, it can be expected that during its gelation or precipitation from solutions in other solvents, different structures will be formed, characteristic of both rigid-chain and flexible-chain polymers. This follows from Flory's theory [2], which associates the critical concentration of the transition to the LC state (C^*) with the degree of anisometry of



macromolecules. PABI in N-methylpyrrolidone (N-MP) with the length (nm) of the Kuhn statistical segment $A = 530$ nm was selected as objects of investigation. The ability of polyheteroarylenes to form an LC phase in the same solvents may be a relative stiffness criterion. For such polymers, this can be sulfuric acid. From this point of view, poly-*n*-benzamide ($C^* = 7 - 8\%$) and poly-*n*-phenylene terephthalamide ($C^* = 8 - 9\%$) should be considered the most rigid-chain of this range of polymers [3]. Further, in the series of decreasing rigidity there are PABI ($C^* = 11 - 13\%$) [4].

2. Experimental

Let us consider the kinetic features and structure of the brittle PABI, depending on the temperature and concentration conditions of gelling in the N-MP, containing 1.3% of water. For the preparation of solutions, unfractionated PABI samples were used, obtained by isolating the polymer in the form of films from a solution with an intrinsic viscosity $[\eta] = 5.8$ dl/g, measured at 20°C in dimethylacetamide. The solutions were kept in sealed cuvettes with a gap of 0.5 mm (Figure 1).

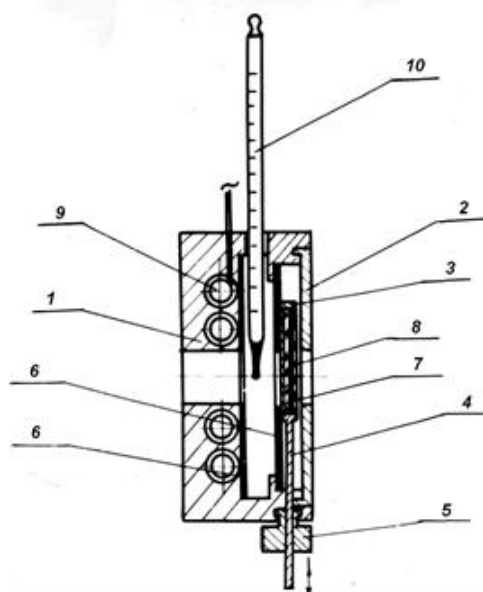


Figure 1. Scheme of the device for testing solutions and films of polymers: 1 - thermostat, 2 - thermostat cover, 3 - sample chamber, 4 - screw displacement, 5 - nut rotation, 6 - asbestos gaskets, 7 - sample, 8 - coverslips, 9 - heating element, 10 - thermometer.

The transformation of a polymer solution into a jelly during coagulation in a precipitation bath is a kinetic process, associated with structural changes that often occur within a fraction of a second. This circumstance, as well as a number of other factors, cause certain experimental difficulties during the study of the kinetics of structure formation by, for example, such methods as electron microscopy and x-ray diffraction analysis. It is known that the most important property of optically anisotropic supermolecular structures is their ability to scatter and depolarize visible light [5]. Therefore, the main methods of investigation were polarization-optical methods. According to H_v (crossed polaroids) and V_v -scattering patterns of polarized light (parallel polaroids), it is also possible to determine the type of formed mesophases [6]. Diffractograms describing the changes in the structure of the object during coagulation were obtained at the installation (Figure 2), which was designed and manufactured on the basis of the general optical scheme for small-angle polarized-light-scattering (SALS).

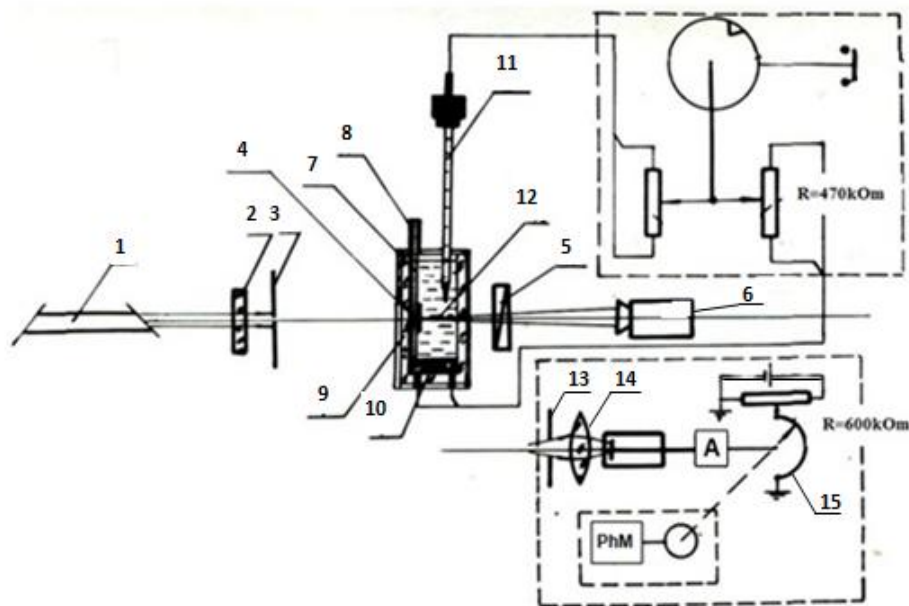


Figure 2. Scheme of experimental setup of the MRPS for study of the kinetics of rapidly-occurring structure formation processes in the precipitation of polymer from solution: 1 – laser, 2 – interference filter, 3,13 – diaphragms, 4 – specimen, 5 – analyzer, 6 – motion picture camera, 7 – object glass, 8 – guide, 9 – cuvette, 10 – heating elements, 11 – temperature sensor, 12 – precipitation bath, 14 – collecting lens, 15 – slide wire, PhM - photomultiplier.

A relatively small deterioration in the quality of the solvent leads to an increase in viscosity and gelation of the solution over time (Figure 3).

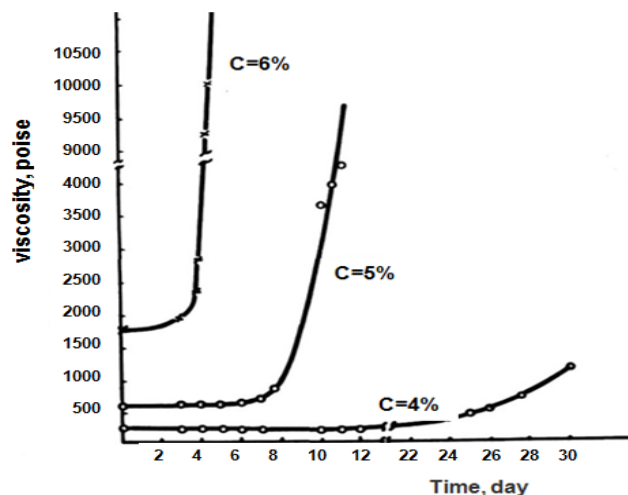


Figure 3. Change in viscosity of PABI solutions of various concentrations containing 1.8% water in N-MP, from the time of gelation.

At the same time, the transparency of the solution also changes, with solution $C = 4\%$ becoming turbid in 21 days, $C = 5\%$ in 11 days and $C = 6\%$ in 4 days. The change in the degree of turbidity of the solution is not accompanied by the appearance of any structural elements registered in sealed cuvettes by the SALS method. On the diffractometer operating in the photometer mode (Figure 2) an

increase in the overall anisotropy of the system is observed. This corresponds to aggregation at the molecular level (below the Rayleigh-Hans resolution region)

$$4\pi R(n'-1)/\lambda \ll 1,$$

where R – is the radius of the particle, n' - is the refractive index of the particle relative to the medium. In the polymer system, n' is close to unity and the Rayleigh-Hans approximation covers a wide range of particles (inhomogeneities) in size (experimentally, from 0.1 to 20 μm).

Visible changes in scattering patterns are manifested only when very high viscosity solutions (more than 10^5 poises) are reached. Solutions with a polymer concentration of less than 4%, despite a significant increase in viscosity and the appearance of small spherulites recorded by light scattering, do not form strong jelly for several months. And the transition of the system to the equilibrium state occurs through several stages of structuring and is accompanied by a variety of supramolecular structures (Figure 4).

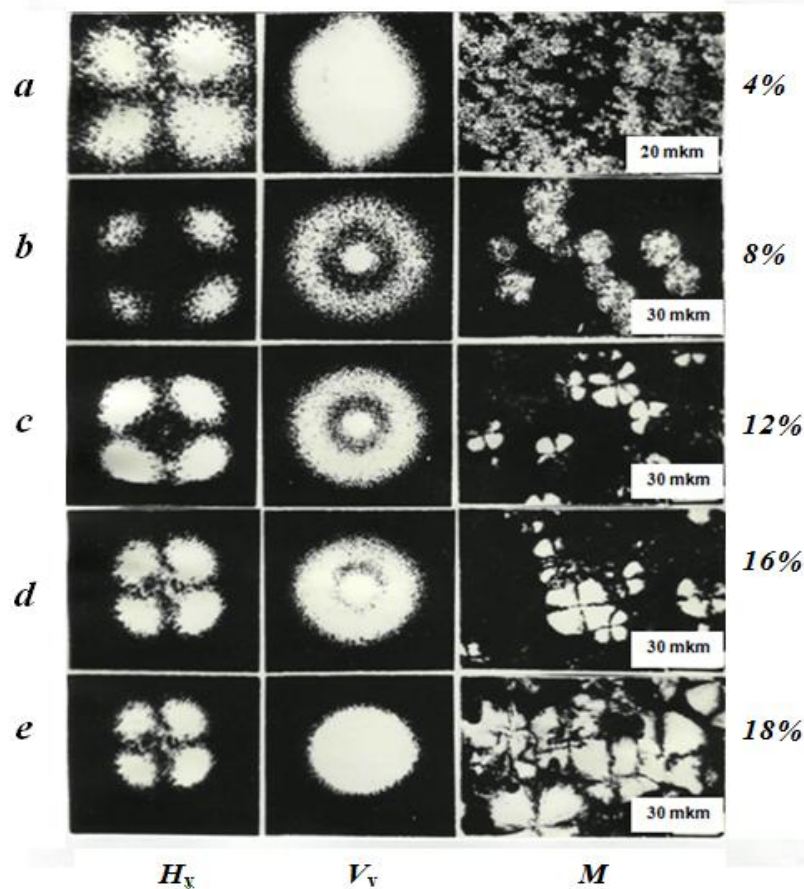


Figure 4. H_v and V_v of the light scattering pattern and microphotography (M) of PABI solutions of different concentrations in two months after preparation.

The appearance of small spherulites in the system depends on the concentration of the polymer. In 4% solutions, the spherulite structure is formed 2 months after the solution is prepared (Figure 4, a). The distribution of the polarizability ellipsoids (crystallites), as can be seen from scattering patterns, is "correct" and is for radial spherulites with dimensions of up to 3.5 μm . At large concentrations of the solution, large spherical particles (up to 30 μm) arise, the "assembly" of which occurs from the ordered material of the original spherulite structures (Figure 4, b). The optical properties of such particles differ from spherulites. In H_v , the scattering pattern gives rise to discrete reflexes, which, upon transition to V_v , merge into a ring. From the analysis of these scattering patterns it can be

concluded that the crystallites in spherical particles are oriented arbitrarily and are connected to each other in a coil by an amorphous matrix.

With increasing time and concentration, self-ordering takes place in these particles with the formation of large spherulites that exhibit a bright interference color of the quenching patterns (M) in the form of "maltese crosses" (Figure 4, c). Gradually, these structures increase in size (Figure 4, d) and at 18% fill the entire field (Figure 4, e). After 2.5 months in a 3% solution, during a certain period of time (10-13 days) three types of structures coexist simultaneously: small spherulites, spherical structures and large spherulites, "colored" in crossed nicols of a polarizing microscope. These spherulites are formed from separate ordered coils. Photomicrographs in the crossed Nicol prisms of a polarizing microscope show a change in the color of the formed spherically symmetric "prefabricated" structures with a radial-ray structure and sizes up to several microns (Figure 5).

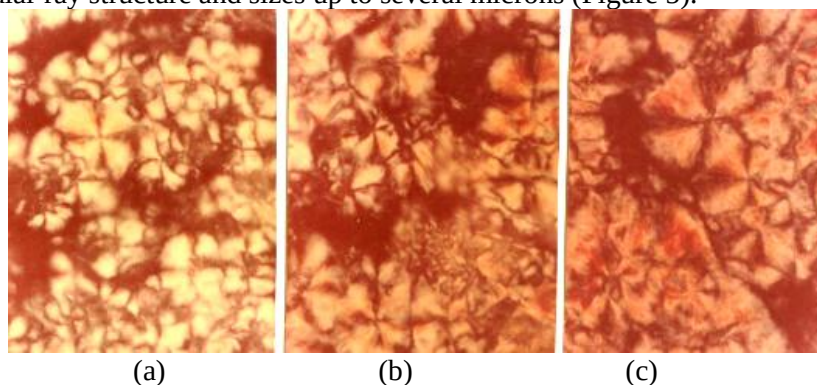


Figure 5. Microphotographs (nicols crossed) of 12% jelly PABI in N-MP at gelling times (months): a-1,5; b-2,5; c-3,5. Magnification $300\times$

The change in the interference color over time and the appearance of brighter tones indicate an internal restructuring of the spherulites. The increase in gelation time or polymer concentration in the solution is accompanied by an increase in the size and number of scattering structures in the jelly. The intensities H_v and V_v of scattering patterns become comparable in magnitude (Figure 4, d). After 5 months in 16% solutions, the number and size of the spherulites formed become so large that their collapse occurs with the appearance in the system of disorderly orientation of the scattering elements. From the point of view of the SALS theory, this indicates a predominance of orientation fluctuations in the scattering medium, which is qualitatively similar to light scattering by polymer films with a correlation structure [5]. At the same time, if the concentration of solutions is less than 2%, they only change transparency. This allows us to consider such systems as nonequilibrium, in which the establishment of thermodynamic equilibrium requires more time than in concentrated solutions.

3. Results and discussion

Polarization-optical studies of the jellied PABI in N-MP show their analogy with low-molecular-weight cholesteric liquid crystals. In particular, the scattering of light in a thin layer of cholesterol oleate is similar to the diffractograms in Figure 4, c. The "maltese crosses" observed in the microscope correspond to the confocal texture of the liquid crystal. When the low-molecular-weight cholesteric LC layer is shifted, a transition to a homogeneous planar texture occurs. The scattering pattern in this case is identical to the diffraction pattern observed when the PABI is deposited under "soft" conditions (precipitant is a 40% aqueous solution of N-MP). Diffractograms of this type correspond to a rod-like structure with orientation of the main direction of polarizability along the axis of the rod.

The alternation of metastable structures during gelation of the PABI–N-MP–H₂O system is also consistent with the previously described occurrence of the LC phase of the cholesteric type from the spherulite structure in the process of isothermal structuring in solutions of poly- γ -benzyl-*L*-glutamate [6]. Our crystal-optical experiments allow us to assume that the structure of spherulites of rigid-chain polymers of the PABI type differs significantly from spherulites in flexible-chain polymers. This is

also confirmed by the absence of a crystalline phase in the spherulite-containing studs of PABI when they are examined by x-ray diffraction. The difference between the supramolecular structure of flexible-chain and rigid-chain polymers is that for the former the folded form of the macromolecule and the formation of crystals with folded chains during crystallization is thermodynamically preferred. Their thickness is many times smaller than the length of the straightened macromolecule. It is known that in flexible-chain polymers, crystalline regions alternate with amorphous sections in the radial or tangential directions [7].

The spherulites observed in the form of brightly colored "maltese crosses" in the PABI studios can be represented as consisting of ordered macromolecules. They are distributed along the radius, and are interconnected not by an amorphous interlayer but by ordered units having a two-dimensional order at the molecular level corresponding to the liquid crystal structure. The coloring of quenching patterns is determined by the specifics of the internal structure of the PABI spherulites. The improvement of such spherulites during gelling, observed as the decomposition of the light beam into interference components, occurs by the continuous addition of parallel links of macromolecules during the gelation process. Confirmation that the PABI under certain conditions is capable of forming a cholesteric mesophase with a large spiral twist pitch $P \gg \lambda$ is indicated by experiments on the gelation of this polymer in other dipolar aprotic solvents.

References

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