The formation of dissipative structures in polymers as a model of synergy

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Abstract. Synergetic is an interdisciplinary area and describes the emergence of various kinds of structures, using the representation of the natural sciences. In this paper we studied the conditions for the appearance of thermodynamically stable amorphous-crystalline supramolecular structures on the basis of practical importance for the production of heat-resistant high-strength polymer fibers semi-rigid systems. It is found that in the process of structure formation in the coagulation of the polymer from solutions having supramolecular structures area a definite geometric shape and dimensions. Pattern formation in such systems can simulate the processes studied synergy. This is occurring in the process of self-organization of dissipative structures, transitions from one structure to another. This most discussed matter of self-organization on the "optical" scale level, are observed spherulites have a "correct" form and certain geometric dimensions comparable to the wavelength of visible light. Previously, this polymer does not crystallize at all considered. It is shown that for the study of supramolecular structures are the most convenient and informative experimental approaches are polarization-optical methods, which are directly "tuned" to the optical anisotropy of the structure and morphology. The great advantage of these methods is also possible to study the kinetics of structure formation processes without interfering the system under study.

1 Introduction

The main problem of synergy, which is the interdisciplinary field, is to describe the occurrence of various types of structures, using the representation of the natural sciences [1]. By definition, the Hermann Haken self-organization, which resulted in the formation of highly ordered structure of nuclei, or even out of the chaos is the spontaneous transition from a disordered state to an ordered due to the combined action of many sub-systems [2]. Such ordered formation arising during no equilibrium irreversible processes were called dissipative structures [3]. The formation of such structures from chaotic state described by a decrease in entropy due to the exchange with the external environment. An example of such is the appearance of dissipative structures in the process of coagulation of supramolecular structures of various types, which ultimately determine the physical and mechanical properties of the finished product [4].

The mechanical and other physical properties of polymers depends on their molecular structure and supramolecular organization [5]. Underneath understand the internal structure, size, shape, relative location in space and the nature of the interaction between the structural elements constituting the polymeric body. Crystallized and non-crystallizing polymers of the types of structures usually divide into discrete (stable over

time) and fluctuation structure (members, globules, etc.), characterized by a finite "life time". Discrete supramolecular structures have a different set of "levels" of supramolecular organization, the nature of which is due to the phase state, the presence or absence of orientation, as well as the molecular chain rigidity [6, p.44]. Most theoretically justified manner of obtaining high performance fibers is currently spinning liquid crystal (LC) solutions of rigid para-type wholly aromatic polyamides. This fact directly indicates that the fundamentals of the structure lays in the spinning solution. It is quite obvious in the case of rigid polymers, processing of fiber which is only possible through the solution due to the high glass transition temperature, but it is less clear for flexible solutions - and semi-rigid polymers. It is therefore of great interest to study the conditions for the appearance of thermodynamically stable supramolecular structures in polymer solutions, differing in the molecular chain rigidity [7]. At the same time, the question remains about the mechanism of structure formation in the transition of isotropic polymer solutions in a condensed state in the process of coagulation. For semi-rigid polymers, despite the large amount of accumulated experimental material here is no single concept under which these questions would have enough reliable interpretation. The reason for this is that in such systems not previously observed major ordered to "optical" level spherulites type formations, single

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crystals and other supramolecular structures that could serve as targets for the correct structural experiments [8]. Such research, as a result of general principles of structural organization, have established that structural and mechanical characteristics and identified specific areas, allowing to expect the best areas of this communication, served as the theoretical basis for the creation of a number of advanced technological modes of molding synthetic fibers from melts flexible chain polyolefin [9]. In general, we can conclude that the mechanism of formation of supramolecular structures in semi-rigid polymers is not considered in the literature as a separate issue, which is of great scientific and practical importance. Unlike the variety of structural and morphological shapes formed during crystallization of flexible chain polymers, the structure of rigid polymers are less studied. Practically fibrillary structures are known only to rigid polymers and macromolecules elongated lamellar form, in the case of rigid spiral macromolecules [7].

A convenient object for studying the kinetics of growth of spherulites are sulfuric acid solutions of certain polymers, in which the formation and spherulite growth occurs in the absorption of a solution of water vapor from the air. Under these conditions, the growth rate is relatively low, which allows to observe experimentally the kinetics of the formation of spherulites. In this paper we studied the conditions for the appearance of thermodynamically stable supramolecular structures in semi-rigid polymer solutions. This mainly discussed issues of self-organization on the "optical" scale level as supramolecular structures (spherulites fibrils domains LC phase and others.) Often have the "correct" form and certain geometric dimensions comparable to the wavelength of visible light.

2 Experimental

As objects of study was selected semi-chain poly-n-phenylene-1,3,4-oxadiazole (POD) c length Kuhn statistical segment $A = 240$ nm, which is considered generally does not crystallize. This polymer is particularly interesting, because of its concentrated solutions formed high-strength, heat-resistant fiber. The structural formula of this polymer is as follows:

The concentration of the test isotropic solution under a specific viscosity $\eta_{ud} = 0.61$ was 11%, the solvent is 98% sulfuric acid. The studies were conducted on micro film projectors. The speed of the film was 2-6 shots per second, depending on the growth rate of the first system detected in spherulites. Under the same conditions a study the kinetics of spherulite growth was conducted with the help of small-angle polarized light scattering (SALS) (Figure 1).

At the same setup (Fig. 1), operating in the metering mode, the kinetic curve was obtained, which

characterized by the emergence and growth of anisotropic structures in the process of structure formation.

The average radius of the spherulites was determined microscopically and according to the small-angle light scattering. The spherulite radius dependence on the crystallization time is linear. Saturation curves for large time of crystallization due to the restriction of the spherical continuous development due to the occurrence of obstacles increase. Similar changes depending on the size of the spherulites observed in the crystallization of polypropylene melt [9]. Straight section inclination angle to the horizontal axis determines the growth rate $G = \tan \alpha$ spherulite saturation curve - an average spherulite radius R_{dif} . In the segment on the x-axis you can find the time τ_0 induction.

Fig. 1. The experimental setup for studying the kinetics of fast processes, the polymer deposition from a solution: 1 -laser, 2 - interference filter, 3, 13 - diaphragm, 4 – sample, 5 - analyzer, 6 - film camera, 7 - microscope slide, 8 - rail for the slide, 9 - cuvette, 10 - heating elements, 11 - temperature sensor, 12 - coagulation solution, 14 - collecting lens, 15 – slideware, photomultiplier registration.

3 Results and discussion

The formation of spherulites in a slow crystallization can be traced experimentally. However, the interesting details of the emergence of spherulites, as can be seen from a comparison of the photomicrographs and H_v scattering patterns for the same crystallization times (Fig. 2) lie below the limits of the possibility of optical microscopy.

As can be seen from Fig. 2 the resolution diffraction method is significantly higher than microscopic method. This allows to conduct a detailed study of the kinetics of the formation and growth of spherulites.

At the initial stage of crystallization in the intensity distribution of the scattering patterns H_v monotonically diminishes from the center, which corresponds to Fig.2,b, and a light scattering characteristic rod-like structures. At this time, only a microscopically after 10 seconds can be discerned in the form of spherulites embryos luminous dots in crossed polarizers (Fig.2, M, b, c). When crystallization times over 45 seconds in the intensity distribution of the angle $\mu = 45^\circ$ peak is observed, and the diffraction pattern has the form of imperfect spherulitic structure (Fig.2, H_v , d). In this

period photomicrographs can also judge the appearance of spherulites (Fig.2, M, d). Theoretical analysis of the H_v diffraction patterns [8] (Fig.2, a-d) showed that the formation of bar-like structures and the process of branching at the spherulite growth can be modeled by an extension of conical sectors and an increase in the angle of opening (β) (Fig. 3). This is accompanied by changes in the intensity distribution of diffraction H_v (Fig. 2a-d).

Fig. 2. Kinetika spherulite growth of POD concentrated solutions according to optical microscopy (M) and the diffraction of light at small angles (H_v) at crystallization time with: 5 (a), 10 (b), 15 (c), 20 (g) 60 (d), 100 (e), 120 (w) and 180 (h).

Fig. 3. The scheme, which simulates the formation of spherulite

To explain the growth of spherulites on the basis of light scattering diffraction patterns it is necessary to introduce two speeds - in a radial $G_R = dR / dt$ and tangential directions $G_\beta = d\beta / dt$. In the latter case, the rate of increase of the solid angle at the apex of the cone simulates branching slats to laterally until is completely formed spherulites ($\beta = 90^\circ$). This H_v diffraction patterns become characteristic spherulites committed in the form of four petals (Maltese cross) (Fig.2, H_v , e-h). The maximum in the intensity distribution at $\mu = 45^\circ$ as the formation of spherulites increases and shifts to the region of small angles θ (Fig. 5). Spherulites during collapse (Fig. 2, e), the angle β is of minimal importance and will not be changed. A slight decrease in the intensity of scattering H_v paintings at $\theta = 2^\circ 30'$, found on the installation of photoelectric recording (Fig. 1), due to the decrease in the contribution ($\alpha_r - \alpha_t$) into the equation, characterizing improvement spherulitic structure [10].

When coagulation POD in 40% aqueous H_2SO_4 H_v diffractogram is rotated through an angle of 45° relative scattering patterns shown in Fig.2.

Reflex "maltese crosses" in the paintings of extinction in this form an angle of 45° with the direction of transmission planes of the polarizer and the analyzer. This "anomalous" scattering pattern previously observed in the crystallization of polyethylene terephthalate from melts and is due to the orientation of the ellipsoids of the polarizability at an angle of 45° with respect to the radius of spherulite.

Thus, the basic structural unit in the "optical" level of supramolecular organization in semi-rigid polymers is a spherulite. It is a "design team" consisting of crystalline and amorphous regions and having a dendritic growth pattern [8]. Depending on the direction of the preferred orientation of the molecular axis with respect to the radius of spherulites can be observed in crossed nicols of a polarization microscope (blanking the picture) in the form of crosses "(tangential or radial orientation). In this case, spherulites are divided into positive (tangential orientation) and negative.

The principal difference of the supramolecular organization of rigid and flexible chain polymers, is that for the first thermodynamically preferred form of coiled macromolecule and crystallizing the formation of crystals with folded chains, the thickness of which is many times smaller than the length of the straightened macromolecules. The kinetics of formation is that they have a certain geometric and optical anisotropy and are characterized polarizability ellipsoids. A rich variety of morphological forms at various levels of scale also demonstrated semi-rigid polymers. Spherulite structure is a combination of more or less densely packed crystalline and amorphous regions, arranged spherically or cylindrically symmetric, as well as areas with intermediate levels of order. Spherulites on the internal organization may have a great influence of the impurity, as which may be monomers and oligomers. Crystallization impurities are displaced in the area between the fibrils and spherulites. This leads to disruption of the compactness of the spherulites, increase the size of the fibrils and difficult branching processes. The main elements are the microfibrils fibrillar structures that differ from those rays spherulites, in which molecular chains are oriented along the crystallographic axes with the principal axes of microfibrils. In contrast, in the positive and in negative spherulites axis substantially perpendicular to the radius of spherulite. This type of structure is also noted for a semi-rigid polymer chains.

4 Conclusions

By using polarization-optical methods able to detect several successive stages of growth of spherulites in concentrated sulfuric acid solution under. Determine their size and is a diagram modeling the process of such structures formation and growth. The process of coagulation is observed a number of different levels of supramolecular organization, each of which corresponds

to the formation of well-defined structure type. Pattern formation in such systems can simulate the processes studied synergy. The first is self-organization in complex systems, the transition from one structure to another, and dissipative structures arising in the process of self-organization. The kinetics of growth, morphology and internal structure of such structures is convenient to explore by SALS. It was found by this method that the concentrated solutions practical importance semi-rigid polymer (POD), depending on the deposition conditions, formed by the internal structure different anisotropic structure in the form of radial and annular spherulites. It was possible to compare the size of spherulites, certain diffraction and microscopy methods, and to show that the formation of spherulites of solutions subject to the general laws of kinetic growth, characteristic of the crystallization of the polymer melts.

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