

Structure of Crystallizable Polymer Solutions

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Abstract: Visually transparent solutions of crystallizable polymers in wide concentration and temperature ranges contain supramolecular particles which are fragments of the most perfect crystallites of condensed polymer. Though the fraction of these particles is usually with in 0.001-0.1wt % of the total polymer, their presence in a solution of macromolecules severely affects its physicochemical and technological properties (performance) and complicates (or even does not allow) the application of structurally-sensitive research techniques (e.g. lights cattering, dynamic birefringence, etc.). The parameters of the first-level supramolecular particles (just after visual dissolution) depend on the conditions of dissolution, storage, and the preliminary treatment temperature of the polymer. In wide polymer concentration and temperature ranges, a second level of the supramolecular particles ensemble is formed, with characteristic features of crystallization. From the formation rate of the second-level supramolecular particles, a microliquidus curve for them can be plotted. The paper presents data for the poly (vinyl alcohol) + water system which lack the area of liquid-liquid phase separation. Supramolecular particles parameters (average sizes, numerical and mass-volume concentration) were determined by means of the turbidity spectrum method.

Keywords: Crystallizable polymer, supramolecular particles, crystallites, light scattering, turbidity spectrum method.

INTRODUCTION

Complete dissolution of any crystallizable polymer proceeds when the configurative point on the state diagram is outside the binodal area for binary systems (outside the amorphous-type phase separation range on a quasi-binary section for polynary systems) and above the liquidus curve. By virtue of some peculiarities of the crystallization of macromolecules there exist rich-morphology crystallites in condensed polymer, each type having its own liquidus curve. The curve corresponding to the most perfect crystallites with an almost negligible weight fraction (~0.1 wt %) located at low polymer concentrations and high temperatures.

Polymer dissolution is frequently judged by the visual transparency and homogeneity of the polymer+low-molecular-weight (P+LMWL) system. However, the turbidity spectrum method often helps the researcher to detect, even on common colorimeters, so-called supramolecular particles (SMP) (fragments of the most perfect crystallites from the condensed, source crystallizable polymer) and to estimate their parameters (average size, numerical and mass-volume concentration). On heating or dissolution, SMP melt or dissolve as these actions drive the configurative point out of the corresponding liquidus area. The presence of SMP in polymer solutions, in spite of their negligible amount with respect to the total content, may drastically affect the physicochemical, technological

properties and performance of such structurally-complex solutions of crystallizable polymers.

During storage of such solutions, a second level of supramolecular order is formed by crystallization within wide temperature and concentration ranges. It should be emphasized that the second-level SMP are formed under the conditions unchanged after polymer dissolution (the annealing effect).

Our previous series of experiments [1, 2] has revealed no liquid-liquid phase separation range in the poly (vinyl alcohol) (PVA) + water system at least below 150°C.

Therefore, those SMP which are present in solution on visual dissolution (the first level of supramolecular order (SMO)) or formed with in wide temperature and concentration ranges are of crystal nature [2-17]. Hence, the structure of PVA solutions is generally the same as in any solution of a crystallizable polymer.

The present paper pays special attention to the properties of the first-level SMP as depend on the preparation conditions of visually transparent PVA solutions and on the soft conditions of polymer pretreatment.

First-Level SMP

Commercial samples of PVA (brand VN-1, Nevinnomyssk Azot Corp., Russia) with the following characteristics: $\bar{M}_n = 100\text{kDa}$, 0.3 wt % of acetyl groups, were used. The average-viscosity molecular mass was calculated according to Matsumoto & Ohyanagi [18].

$$[\eta]_{30} = 4.28 \cdot 10^{-4} \bar{M}_n^{0.64}$$

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The SMP parameters in aqueous PVA solutions (average radius and mass-volume concentration) were estimated on a KFK-2M colorimeter by means of the turbidity spectrum method [2, 3, 10]. The following procedure was applied to prepare visually transparent PVA solutions and to characterize their first-level SMP (the first series of our experiments).

Before dissolution, polymer samples had swollen in water at room temperature ($\sim 20^\circ\text{C}$) during 7 days. Then the flasks with these PVA-water mixtures were placed into a water bath with a temperature $80 \pm 1^\circ\text{C}$ maintained. From time to time, they were being shaken to mix the content until visually transparent solutions obtained. As a rule, this procedure took 5–6 h depending on concentration. Figure 1 presents the results for five parallel solutions prepared.

Therefore, visually transparent solutions of crystallizable polymers contain an ensemble of SMP which are fragments of the perfect crystallites from the source condensed polymer. The mass concentration of SMP is of the order of 10^{-3} – 10^{-2} wt %.

The average SMP sizes show concentration dependence peculiar for the given polymer, solvent, and dissolution technique (Figure 1a).

The decrease of the average SMP sizes on dilution is a common feature of this dependence i.e. an increase of the solvent content leads to an increase in the SMP dispersity degree, which seems quite natural.

With other conditions being equal, a lower polymer concentration promotes the hydrodynamic effect on the

polymer–solvent system at polymer dissolution under stirring due to a lower viscosity.

The frequently observed (for other systems as well) size maximum at medium concentrations is explained by predominant dissolution of relatively small SMP to raise the average size of SMP. At lower concentrations, fragments of the crystallites disaggregate over the whole size range, and the average size reduces down to its minimum value.

When the concentration is as low as no turbidity is detected ($\tau \approx 0$), the solution must be of molecular degree of dispersity, which is confirmed by means of the classical light scattering technique (Debye–Zimm) [1, 2, 11].

If SMP occur in solution but are not detected on a colorimeter, their parameters can be measured by the scattering spectrum method (e.g. at 45°) on a NFM nephelometer (a Russian brand) [12].

The reduced turbidity τ/c is independent of concentration for structurally-homogeneous particles (e.g. latexes). The concentration dependence of τ/c experimentally obtained for SMP speaks for a more dense structure of them in dilute solution (a higher value of the relative refractive index m), which seems quite natural.

Stirring the PVA-water system after 7-day swelling with a magnetic stirrer (instead of regular shaking and rocking flasks) has led to the same results (Figure 1) but the dispersion of mean sizes has become smaller.

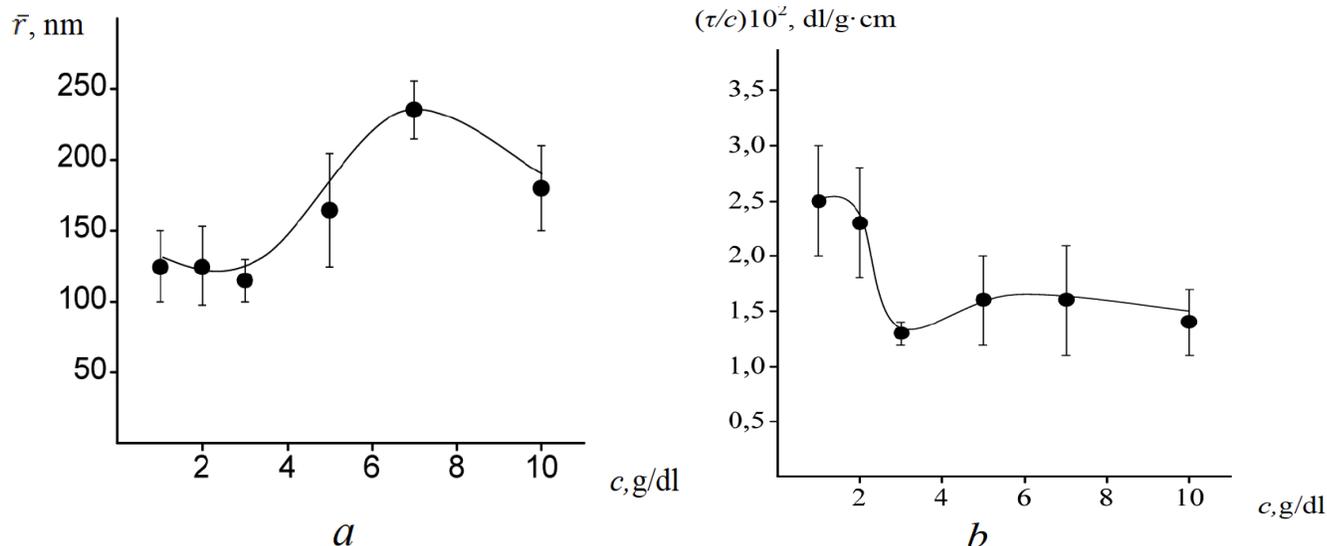


Figure 1: Average sizes and reduced turbidity at $\lambda = 465\text{nm}$ of the first-level SMP ensemble: after visual dissolution at $t=80 \pm 1^\circ\text{C}$, after 7-day swelling in water at room temperature ($\sim 20^\circ\text{C}$): 5 parallel experiments.

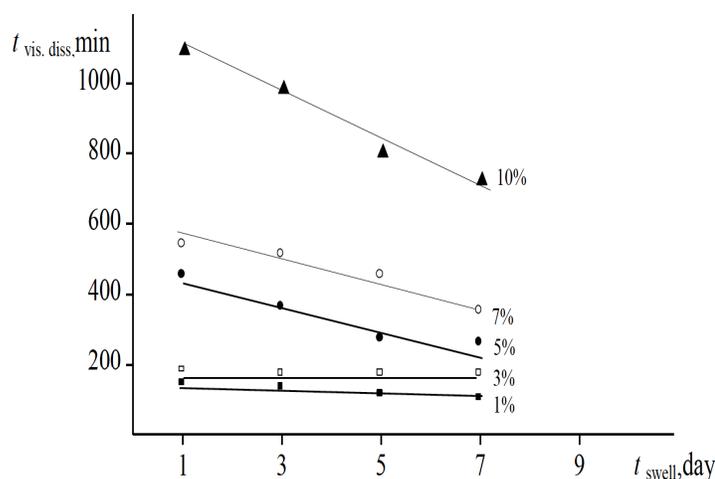


Figure 2: Dependence of the visual dissolution duration ($t_{\text{vis.diss}}$) at $t=95\pm 3^\circ\text{C}$ on the preliminary swelling duration (t_{swell}): water, $t=23\text{--}25^\circ\text{C}$.

In the second series of experiments, polymer samples were dissolved inside a water bath ($95\pm 3^\circ\text{C}$) at regular shaking the flasks on preliminary polymer swelling during 1-10 days at $24\pm 1^\circ\text{C}$. The concentration range was 1–10 wt %, the duration of visual dissolution (Figure 2) and the mean sizes of first-level SMP on dissolution (Figure 3) were measured.

The longer the preliminary swelling, the faster the dissolution until visual transparency, and this phenomenon can be explained by effective penetration of solvent molecules into the amorphous regions of condensed polymer.

Meanwhile, polymer crystallizes during its preliminary swelling, which manifests itself as a rise of the average first-level SMP sizes over the whole concentration range studied; this had been observed earlier as well [13].

In the third series of experiments the polymer was dissolved in water on a water bath ($85\pm 1^\circ\text{C}$) with a magnetic stirrer, the sample had swollen during 24h. This way of PVA dissolution in water leads to the same sizes of first-level SMP within the 2-10 wt % concentration range (Figure 4).

Our further studies took advantage of the latter dissolution method: every time the initial solution structure corresponded to Figure 4. Let us here in after refer to this method as the standard one.

Effect of Polymer Pretreatment on Solution Structure after Visual Dissolution

Polymer samples were thermostated during 5-120min at a certain temperature within $70\text{--}110^\circ\text{C}$, and then a PVA solution was prepared using the standard method. Worthwhile noting is the fact that even rather

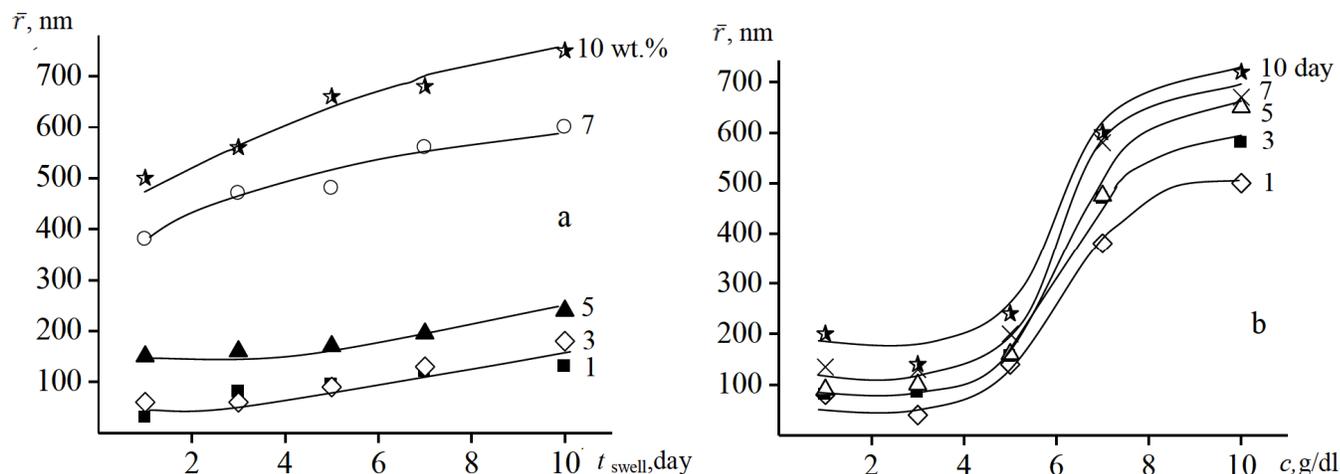


Figure 3: First-level SMP average sizes as a function of the preliminary swelling duration (t_{sw}) at a number of concentrations (a) and that of the polymer concentration at a number of swelling duration (b).

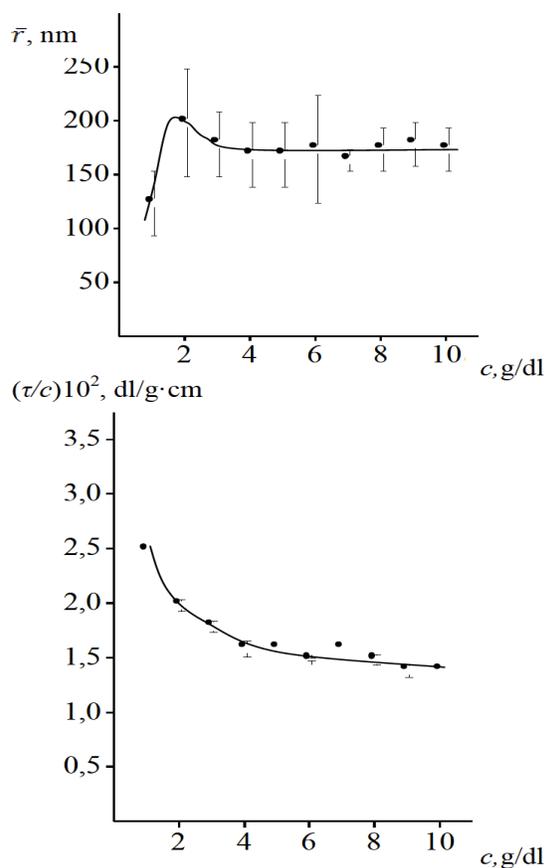


Figure 4: Average sizes and reduced turbidity at $\lambda = 465\text{nm}$ of the first-level SMP ensemble after visual dissolution at $t = 85 \pm 1^\circ\text{C}$, after one-day swelling in water at room temperature: 7 parallel experiments.

a soft thermal impact on the polymer (70°C , 5min) causes significant decreases in the initial level of SMO (Figure 5) and in the duration of visual dissolution (Table 1).

Table 1: Pretreatment Temperature Dependence of the Visual Dissolution Duration, the Duration of Pretreatment 5 to 120 min

Conc. wt %	Initial Polymer	Temperature of Pretreatment, $^\circ\text{C}$		
		80	90	110
	Duration of Visual Dissolution, min			
1	60	45	35	30
3	85	40	40	35
7	100	45	45	40
10	120	50	45	40

The 5-min polymer pretreatment at other temperatures leads to almost the same results. However, prolongation of the thermal pretreatment causes

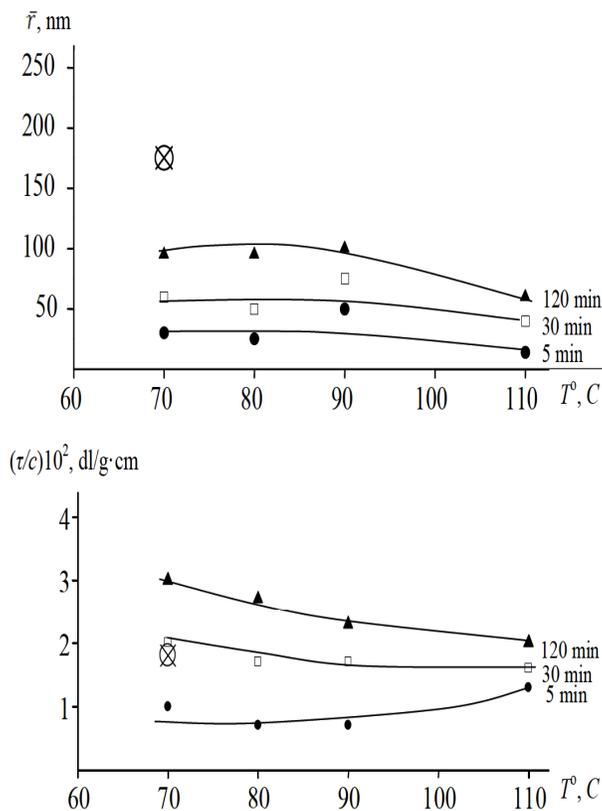


Figure 5: Average sizes and reduced turbidity at $\lambda = 465\text{nm}$ of the first-level SMP ensemble after visual dissolution at $t = 85 \pm 1^\circ\text{C}$, after preliminary thermostating of the initial polymer sample within $70\text{--}110^\circ\text{C}$ from 5 to 120min. The solution concentration is 3 wt%. The crossed circles correspond to the data obtained for the initial polymer solution.

additional crystallization, which promotes growth of the average first-level SMP sizes and increases the reduced turbidity of visually transparent solutions.

The duration of visual dissolution under standard conditions diminishes for the pretreated polymer samples (Table 1).

For the 7% solution the reduced turbidity of the solution of the pretreated sample was higher at every T and pretreatment duration while the mean SMP sizes were smaller i.e. a plenty of petty SMP arose after 30 and 120-min polymer thermostating (Figure 6).

However, as the pretreatment was performed longer at every fixed temperature, the SMP sizes increased.

Therefore, the first-level SMP properties can be controlled by means of rather soft treatment of condensed polymer or by an appropriate change in the swelling duration. Despite of a negligibly small part of polymer included into SMP, the fact of their existence itself and, of course, variations of their properties may

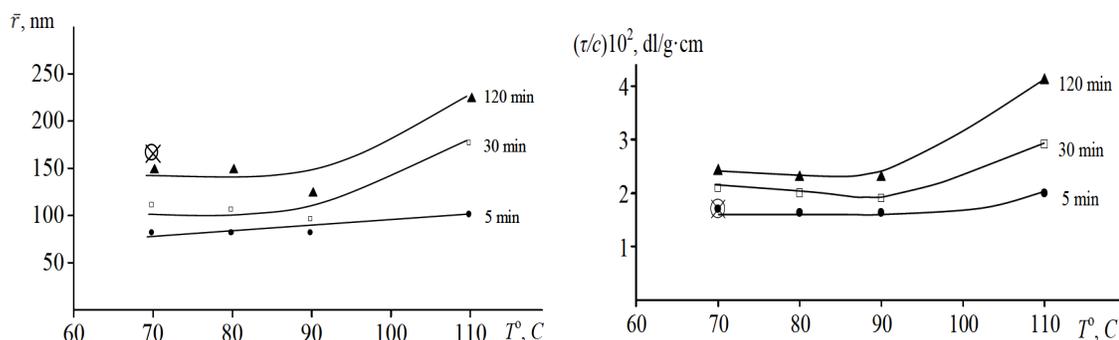


Figure 6: Average sizes and reduced turbidity at $\lambda = 465\text{nm}$ of the first-level SMP ensemble after visual dissolution after preliminary thermostating of the initial polymer sample within 70–110°C from 5 to 120min. The solution concentration is 7 wt%. The crossed circles correspond to the data obtained for the initial polymer solution.

influence the consumer properties of crystallizable polymer solutions, this effect being either negative or positive.

Besides, the first-level SMP ensemble somewhat characterizes the morphology of the source condensed polymer sample, which influences the consumer properties of things made of this polymer.

FORMATION OF A SECOND LEVEL OF SUPRAMOLECULAR ORDER

Second-level SMP are formed during thermostating of crystallizable polymer solutions within wide ranges of temperature and concentration. The kinetics of this process shows each and every indication of polymer crystallization in the presence of a solvent [1-9, 14-17]. The temperature dependence of the second-level SMP formation rate goes through a maximum.

Extrapolation of the right-hand (high-temperature) branch of this curve to zero rate gives the liquidus temperature (T_l), the same procedure on the left-hand

(low-temperature) branch does the vitrification temperature (T_v). The kinetics of SMP formation includes the stages of fast (crystallization itself) and slow (post-crystallization) growth of new-phase particles.

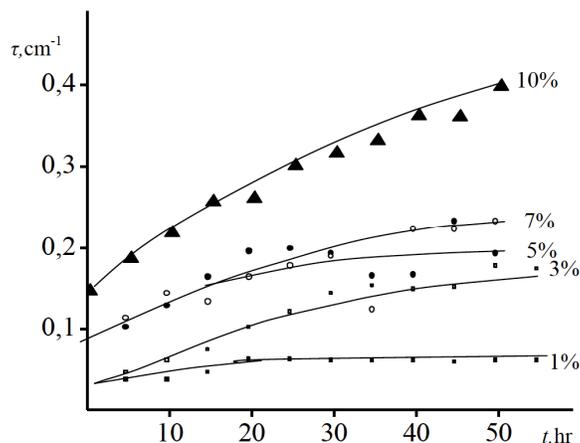


Figure 7: Increase of the turbidity at $\lambda = 465\text{nm}$ in the course of the formation of second-level SMP at 30°C. The polymer concentrations are indicated near the curves.

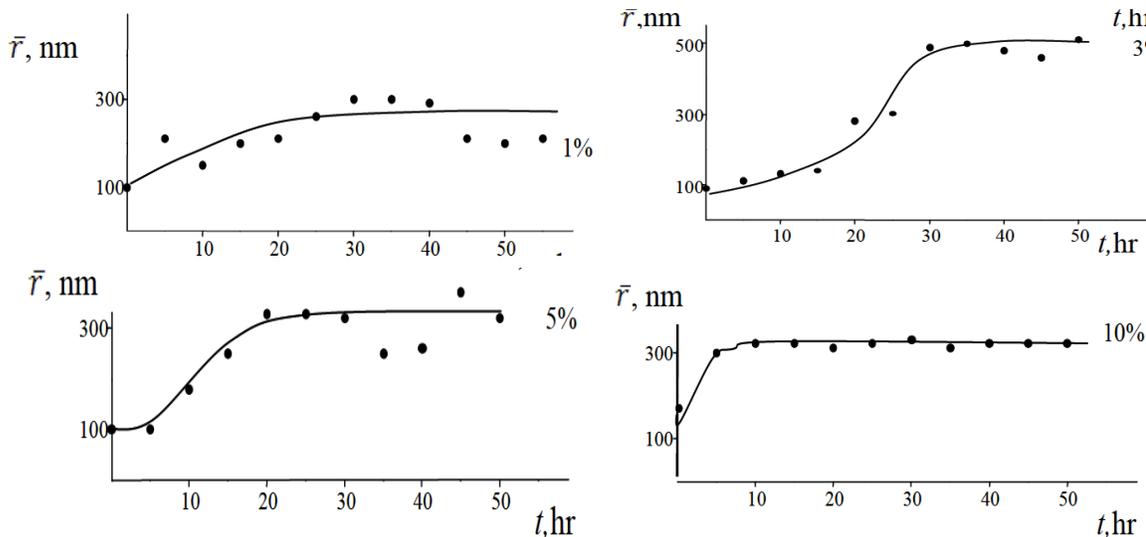


Figure 8: Kinetics of second-level SMP growth at 30°C. The polymer concentrations are indicated near the curves.

An induction period of particle formation is frequently observed.

The solutions with the initial SMO level reflected in Figure 1 were subjected to second-level SMP formation within 20-60°C. Figures 7 and 8 show the turbidity of the system and the SMP sizes in the course of SMP formation at 30°C.

The rate of growth was estimated using the initial slope of the $\tau=\tau(t)$ curves:

$$V_{\tau} = \frac{\Delta\tau}{\tau_0\Delta t} (\text{h}^{-1}),$$

Where τ_0 is the turbidity of the initial system at $t=0$ (first-level SMP) (Figure 9).

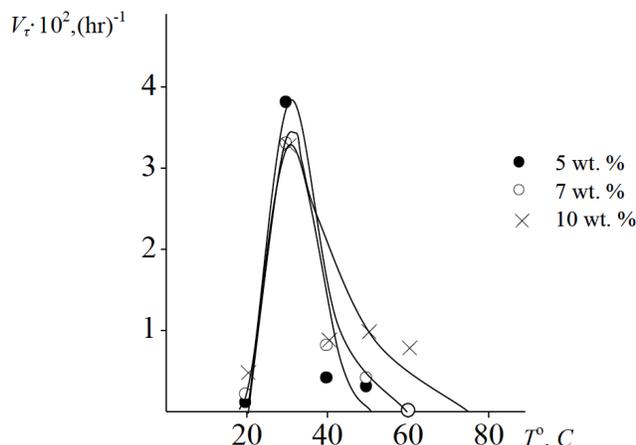


Figure 9: Temperature dependence of the second-level SMP formation rate.

The $V_{\tau} \rightarrow 0$ extrapolation provides the liquidus (l) and vitrification (v) curves for the given sample (Figure 10).

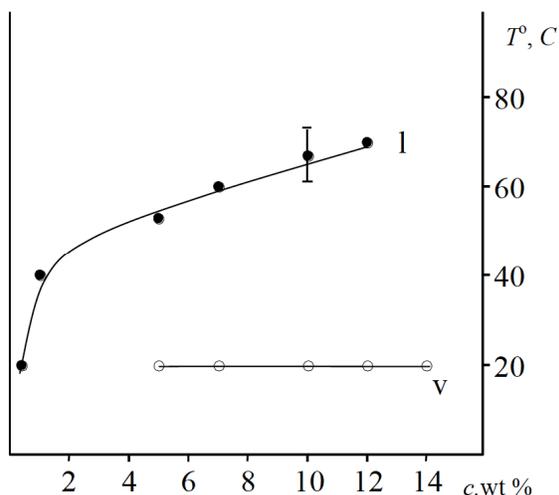


Figure 10: Liquidus (l) and vitrification temperature (v) according to the data on the second-level SMP formation rate.

As a rule, the concentration dependence of the isothermal second-level SMP formation rate has a maximum as well. In this case, the extrapolation of the left-hand branch $V_{\tau} \rightarrow 0$ (at a lower polymer concentration) gives a configurative point (T_l, c_l) of the liquidus while that of the right-hand branch does a configurative point of the vitrification curve (T_v, c_v).

CONCLUSIONS

- SMP (fragments of the perfect crystallites from condensed polymer) occur in visually transparent solutions of a crystallizable polymer.
- The parameters of such SMP (average sizes, numeric and mass-volume concentration) are reliably measured by means of the turbidity spectrum method on any colorimeter [10]. The scattering spectrum method can be employed to detect SMP in very dilute solutions [12].
- The SMP which are presented in solution immediately after visual dissolution constitute the first (initial) level of SMO. As a rule, their weight or mass concentration is rather small (10^{-3} – 10^{-2} wt %), but this amount is nevertheless enough to influence the essential properties of such structurally-complex polymeric solutions.
- The presence of SMP may lead to great difficulties in analysis of such solutions since many techniques are sensitive to small particles (molecular light scattering, dynamic birefringence, etc). As a rule, SMP do not influence the viscosity of dilute solutions and their intrinsic viscosity. No SMP are permissible in polymer solutions used as plasma-substituting solutions and other ones of medical purposes. On the other hand, there are data on decreasing the hydrodynamic resistance of a turbulent flow where in SMP occur.
- The sizes of first-level SMP have a peculiar concentration dependence to reflect some morphological features of condensed polymer, features of solvent, conditions of preliminary swelling and dissolution.
- As a rule, the SMP size diminishes on dilution. If the configurative point of the preparation conditions turns out to be on the left of the liquidus curve, a molecular SMP-free solution will result.

- Second-level SMPs are being gradually formed in solutions with the first-level SMP within wide ranges of concentration and temperature, which have some features of polymer crystallization in solution.
- In particular, a new phase is formed under the same conditions which were maintained in the preparation of the solution with first-level SMP (annealing phenomenon), which speaks for the crystal nature of SMP.
- The conventional techniques of structure-phase analysis (X-ray diffraction, differential thermography etc.) may turn out to be insensitive to the crystal nature of SMP even in concentrated solutions because of their negligible fraction and structural imperfectness.
- On prolonged storage under usual conditions, crystallization occurs in crystallizable polymers. The sizes of first-level SMP therefore increase on visual dissolution, the morphology becomes more perfect, and the turbidity of the solution obtained rises. The crystallites appearing in condensed polymer act as links to hinder dissolution even in thermodynamically good solvents. So, prolonged storage may cause complete loss in dissolution under common conditions. The ability to dissolve can be restored by thermal treatment at a configurative point above the liquidus curve.

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