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Correlations microstructure—dielectric properties in thin films of high molecular weight atactic polystyrene

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The density microfluctuations $\delta\rho$ on the surface of thin films obtained from solutions of various concentrations c of high molecular weight atactic polystyrene in chloroform have been studied by electron microscopy. It is shown that the value of $\delta\rho$ and the dielectric properties of films — the dielectric permittivity ε, as well as the dielectric loss angle tangent $\mathrm{tg}\,\Delta$ change nonmonotonously on the scale of parameter c. The minimum ε and maximum $\mathrm{tg}\,\Delta$ correspond to a sharp surge in microfluctuations and fractalization of the supermolecular structure of the polymer. The discovered correlations of the „microstructure–properties" type are explained by structural transitions during film formation — aggregation of macromolecules and self-organization of particle aggregates.

Keywords: thin polymer films, electron microscopy, density microfluctuations, fractal structure, structural transitions.

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1. Introduction

Investigation of „microstructure–properties" correlations in atactic polystyrene (at-PS) thin films on the surface of solid bodies is important for theoretical and practical purposes [1–3]. at-PS films usually produced by deposition of polymer from diluted solutions in thermodynamically „good" solvents have low permittivity, low anisotropy of optical constants together with high transparency in a wide spectrum range and are used, in particular, as protective and antireflection coatings, and optical filters in IR spectroscopy and laser applications [4].

It was reported in [5] that for thin at-PS films obtained from polymer solutions in chloroform with various initial concentration c dependences of some structural and relaxation properties on c are non-monotonic. This is applicable to density and full surface energy of films as well as glass transition temperature of polymer. Later, [6] has reported complex behavior of permittivity ε of films and dielectric loss angle tangent $\mathrm{tg}\,\Delta$ during variation of c, while sharp extrema — peak $\mathrm{tg}\,\Delta$ and valley ε match each other and the maximum number of polar centers of adsorption of crystal violet on the film surfaces [7]. These effects as reported in [1,5,6] are caused by redistribution of intrachain and interchain contacts of aromatic rings as a result of interaction between segments in coil-blob [5] and order-disorder [8] type structural transitions at at-PS macromolecule coil scale level. It is important that [5,6] used a high-molecular at-PS sample with a molecular weight of $M_n = 9.1 \cdot 10^6$ and a hydrodynamic radius of $R_g = 116\,\mathrm{nm}$ [9] of the macromolecule coil in a diluted solution. For this at-PS sample, coil interpenetration and compression processes in solution take place gradually and independently of each other as the concentration c of the polymer grows [1]. These processes result in the increase in chain packing density, enhancement of contribution of aromatic rings to the interaction between macromolecule segments and induce a complex pattern of structural and relaxation properties variation in films on the c scale.

Comparative analysis of data reported in [5,6] shows that the coil interpenetration and compression of at-PS macromolecules cannot fully explain the transformation of the whole set of structural and relaxation properties of films. For example, as the initial concentration c of a film-forming solution grows, density d and full surface energy γ of films vary in a similar way along the curves with a shallow valley within $c = 0.5{-}0.6\,\mathrm{g/dl}$ and sharp peak near $c = 0.8\,\mathrm{g/dl}$ (Figure 1). Such variation of d and γ is explained by gradual overlapping of macromolecular coils and coil parts of dense blobs — regions containing coil parts of mixed macromolecule chains [5,10]. Drop of d and γ near $c > 0.8\,\mathrm{g/dl}$ is associated with microphase separation in concentrated solutions at-PS [11].

However, permittivity ε of films and dielectric loss angle tangent $\mathrm{tg}\,\Delta$ that varies inversely to it behave on the $c$scale in a different way achieving a sharp extremum (valley and peak, respectively) near $c = 0.6\,\mathrm{g/dl}$ (Figure 2). it is reasonable to suggest that such behavior of ε and $\mathrm{tg}\,\Delta$ shall be explained with the involvement of the concept of polymer density microfluctuations at a supermolecular scale level.

In [9,12], it was shown that films produced from concentrated flexible polymer solutions have submicron- and micron-scale density fluctuations. Large-scale density

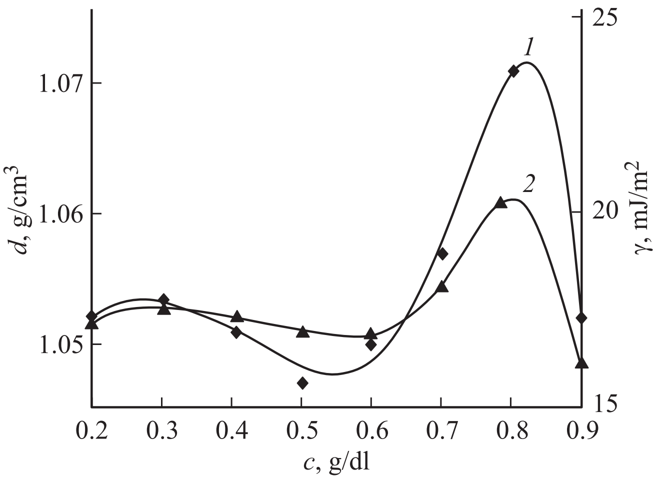

Figure 1. Dependences of density d (*1*) and full surface energy γ (*2*) of *at*-PS films on concentration c od polymer in Chl solution. According to [5].

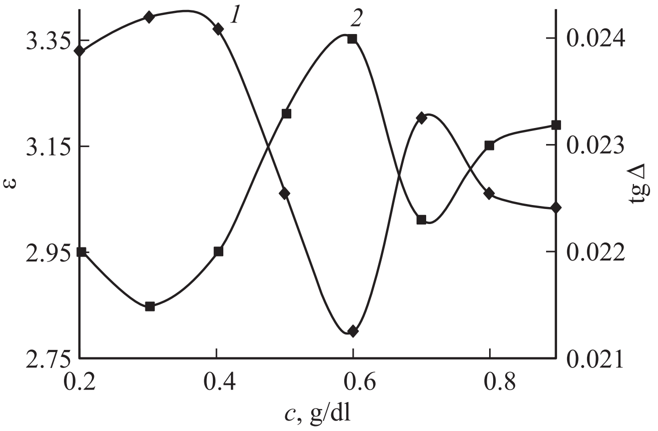

Figure 2. Dependences of permittivity ε (*1*) and dielectric loss angle tangent tgΔ (*2*) of *at*-PS films on polymer concentration c in Chl solution. According to [6].

fluctuations $\delta\rho$, whose correlation length ξ is much higher than a single coil radius R_g are formed during film formation due to the interaction between macromolecule aggregates or, otherwise, clusters [12].

Cluster-cluster aggregation and self-organization of clusters in solution predefine the topology of density microfluctuations in films and the dependence of $\delta\rho$ on the film-forming concentration condition [12]. In particular, enhancement of microphase separation effect is observed for some flexible polymers in a series of film samples produced with increasing initial concentration c of the solution. These effects are expressed in growth of macromolecule aggregate anisotropy, long-range order, ξ and, finally, in formation of a periodically inhomogeneous supermolecular polymer structure. Occurrence of periodic density oscillations in a film is preceded by film microstructure fractalization if $c \sim c_{thr}$, where c_{thr} is the „threshold" solution concentration corresponding to overlapping of macromolecule coils [12].

This study investigates the correlation between density microfluctuations and dielectric properties of *at*-PS films depending on the concentration condition for film production. The objective of the study was to use the concepts [12] of self-organization of macromolecule clusters in the film-forming solution to explain the „microstructure-properties" correlations in polymer films.

2. Experiment procedure

The study used a fractionated sample of linear *at*-PS with molecular weight $M_n = 9 \cdot 10^6$ and narrow molecular-weight distribution [5]. 7–12 μm films were formed on a flat glass from polymer solutions in chloroform (Chl) at 298 K. Initial concentration of solutions varied within $c = 0.1{-}0.9$ g/dl.

at-PS microstructure was studied using the electron microscopy by the gold decoration of film surfaces. Gold nanoparticles were made by vacuum thermal evaporation of metal on molecular bromine-activated „air" surface of films [12]. Two-dimensional images of gold-decorated samples were subjected to statistical analysis of interparticle distances in assemblies of at least 8000 decorating particles in an area of 1.5–4 μm^2. Image interpretation was based on the topological correspondence between fluctuations of ρ of spatial distribution of gold nanoparticles — on the one hand, and fluctuations of polymer macromolecule packing density — on the other hand [12].

Density — density correlations were studied using radial functions $g(R)$ of distribution and indicatrices of ρ of nanoparticles in accordance with the procedures described in [12].

Relative square fluctuations of the number of decorating nanoparticles $\sigma^2/\langle N\rangle = \langle (N - \langle N\rangle)^2\rangle/\langle N\rangle$ were calculated using $g(R)$ in accordance with the procedure described in [13].

3. Findings and discussion

Electron-microscopic images of gold-decorated *at*-PS film samples are shown in Figure 3. The most probable distance between nanoparticles is 30–40 nm, that is more than twice as low as R_g of the coil in the film-forming solution and approximately corresponds to the blob radius [5]. This fact indicates that the chosen study procedure has a quite high resolution allowing quantitative data on structural parameters of individual macromolecule coils and particle aggregates in films to be acquired.

Visual analysis of images (Figure 3) detects an increasing trend of polymer density microfluctuations as c grows. 15–30 nm gold nanoparticles on the surface of all samples form a single assembly in the form of a endless cluster that fills the surface continuously. This cluster corresponds to

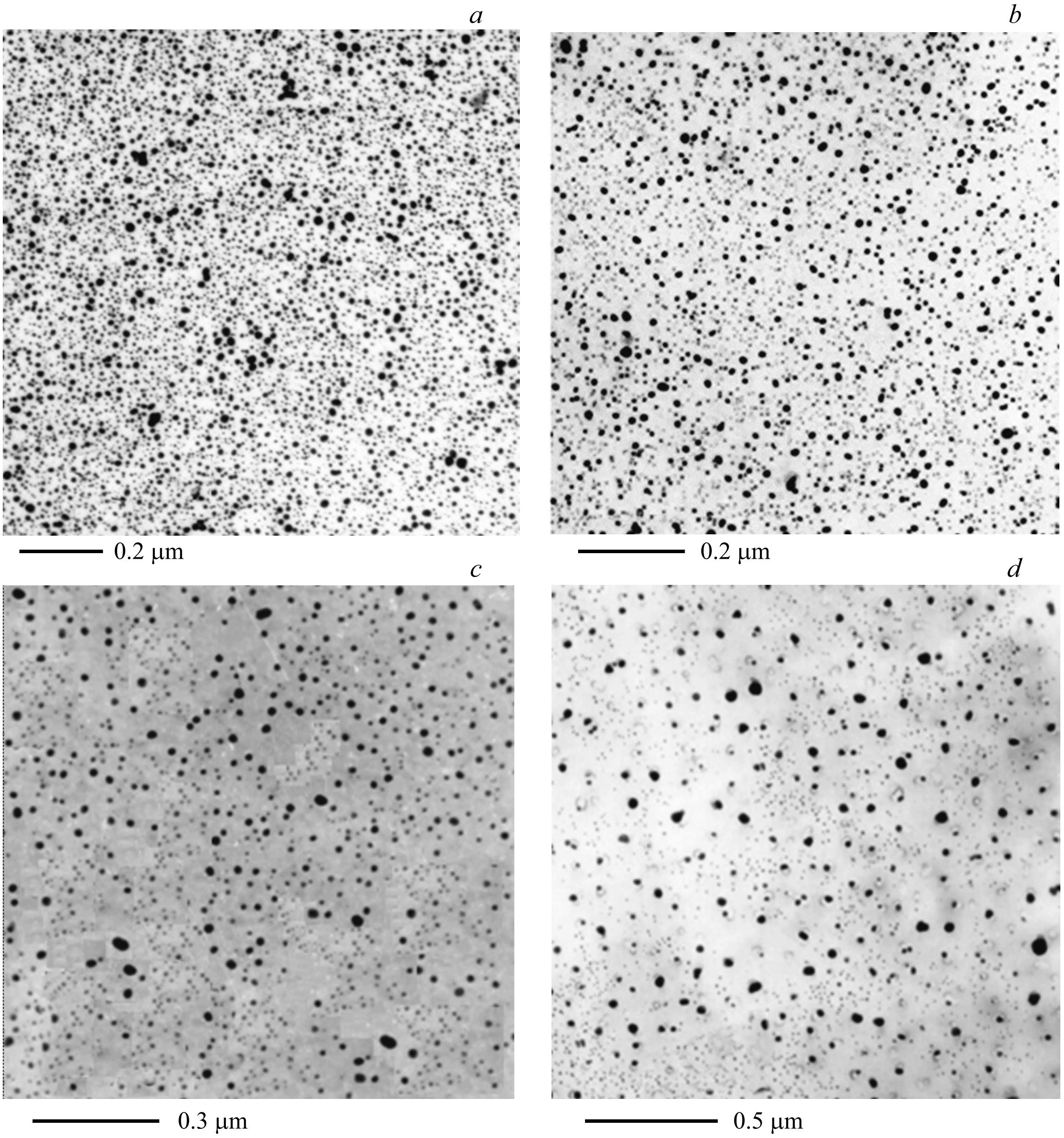

Figure 3. Electronic microphotographs of gold-decorated *at*-PS film surfaces. Solution concentration: $c = 0.1$ (a), 0.3 (b), 0.6 (c) and 0.8 (d) g/dl.

more closely-packed macromolecules [12], while the proportion of space occupied by it decreases with growth of c and approaches ~ 0.3. Individual coarse gold particles whose size exceeds 100 nm mark less dense surface areas [12]. The total area of surface segments with coarse particles increases as c grows.

The analysis of effect exerted by the film-forming concentration condition on the polymer film microstructure should be started from the review of hydrodynamic behavior of macromolecules of the high-molecular *at*-PS sample in Chl solution. According to [1], as the solution concentration grows, the hydrodynamic volume of particles [14] changes drastically at two values of c. These are the first „threshold" concentration $c_{thr1} \sim 0.3$ g/dl, at which hydrodynamic spheres of swelled coils start overlapping [15], and the second „threshold" concentration $c_{thr2} \sim 0.8$ g/dl that corresponds to formation of an endless cluster of compresses and so-called θ-coils in the solution [15]. c_{thr1} and c_{thr2} define various film-forming concentration conditions and predetermine the features of density — density spatial correlations in polymer films. Note that in *at*-PS solutions in θ-solvent (decalin), macromolecule coils have been initially compressed and, therefore, only one value of c_{thr} is recorded that satisfies $[\eta]c_{thr} \sim 2.5$, where $[\eta]$ is the intrinsic viscosity of the polymer in the solution [9].

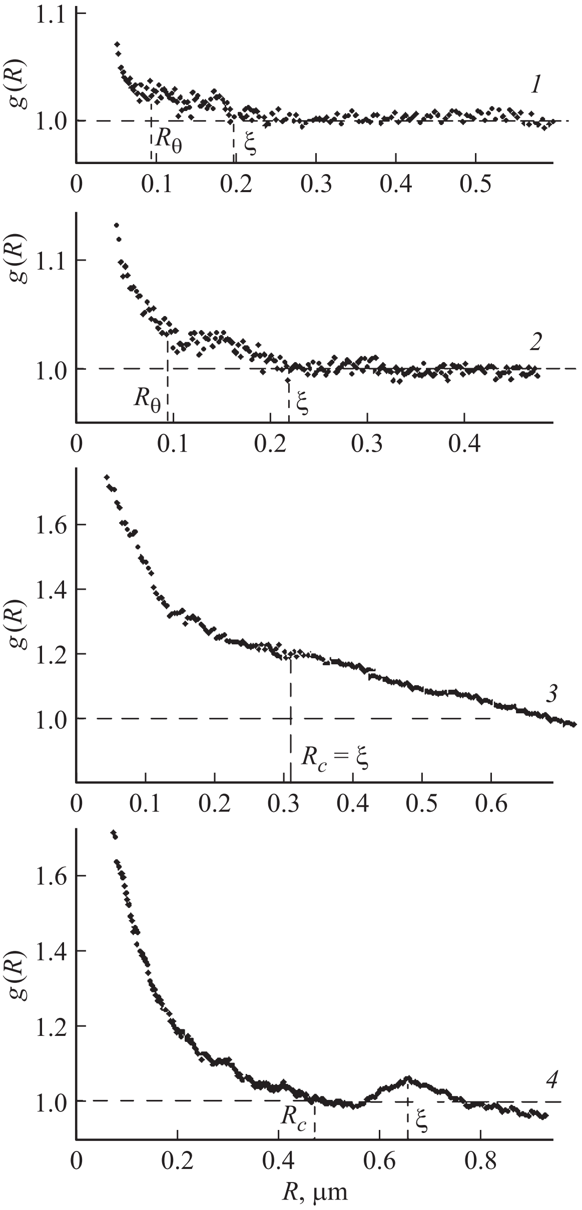

Figure 4. „Density-density coarse-grain" radial functions $g(R)$ for the decorating nanoparticle assemblies on the film sample surfaces. Surface image scanning pitch is 40–50 nm. Solution concentration $c = 0.1$ (*1*), 0.3 (*2*), 0.6 (*3*) and 0.8 (*4*) g/dl.

Figure 4 shows „coarse-grain" [12] radial functions $g(R)$ of density distribution ρ of the decorating gold particle assemblies of the polymer film sample surfaces. ρ fluctuates and the fluctuations result in non-monotonic variation of $g(R)$ as the scale R grows. In the initial segment, $g(R)$ drop as the power function $g(R) \propto R^{D-2}$ for fractal objects with the fractal dimension D [12].

In at-PS films produced at $c \leq c_{thr1}$, dimensions of the self-similar surface area are limited by the hydrodynamic radius $R_\theta = 80$ nm of θ-coil [9] (Figure 4, curves *1* and *2*). The fractal dimension of components is $D = 1.92 \pm 0.02$ and is close to $D = 2$ for θ-coil [16]. Therefore, this suggests that macromolecule chains almost do not overlap and coils retain their identity. Correlation length ξ of density fluctuations corresponds to the hydrodynamic radius R_c of clusters in the solution [9].

Transition to the film-forming condition that meets $c_{thr1} < c \leq c_{thr2}$ results in changes in film microstructure at the macromolecule coil scale level. Initial self-similar segment of $g(R)$ becomes much wider (Figure 4, curves *3* and *4*) up to the effective value R_c of macromolecule clusters in the solution and D is equal to 1.75 ± 0.02. The same value of D, according to the viscosimetry data, is specific to clusters in the solutions [1,9]. The data indicate coil entanglement and loss of their identity due to formation of blobs. Dense blobs — quasiparticles with $D = 3$ are detected in films by the X-ray small-angle scattering method [5].

$c_{thr2} = 0.8$ g/dl of polymer in the solution will result in formation of a periodically inhomogeneous microstructure. $g(R)$ has its peak at $R = \xi \sim 650$ nm that is half as high as R_c of clusters in the solution (Figure 4, curve *4*). An endless macromolecule cluster that is periodically inhomogeneous in density occurs in the films as a result of self-organization of particles during film formation [12]. An important sign of cluster self-organization is fractalization [17,18] of the supermolecular at-PS structure in the film produced at $c = 0.6$ g/dl, that precedes condition $c = c_{thr2}$ on the c scale. In this case, the density — density spatial correlations on the $R > R_c$ scale are described by $g(R)$, that drops according to $g(R) \propto R^{-0.2}$ for the endless fractal ($D \sim 1.8 \pm 0.02$) cluster of closely-packed macromolecules (Figure 4, curve *3*).

Formation of a scale-invariant [19] permolecular at-PS structure is followed by a polymer density microfluctuation surge. This is supported by the calculation of fluctuations $\sigma^2/\langle N \rangle$ of the number of decorating nanoparticles on the surface of films obtained in various film-formation concentration conditions (Figure 5). Sharp microfluctuation surge in films formed at $c = 0.6$ g/dl should be associated with the formation of a less compact and less homogeneous

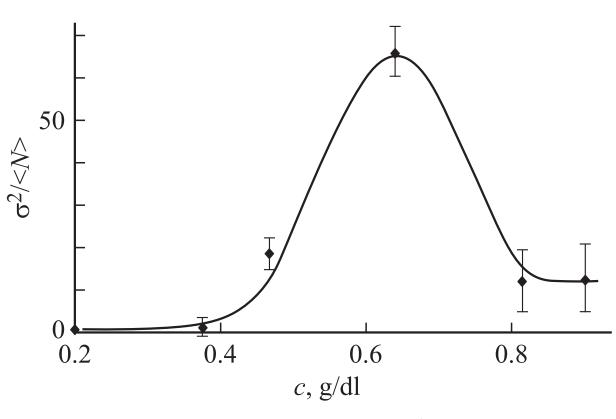

Figure 5. Dependence of fluctuations $\sigma^2/\langle N \rangle$ of the number of decorating gold nanoparticles on the film surface on solution concentration c.

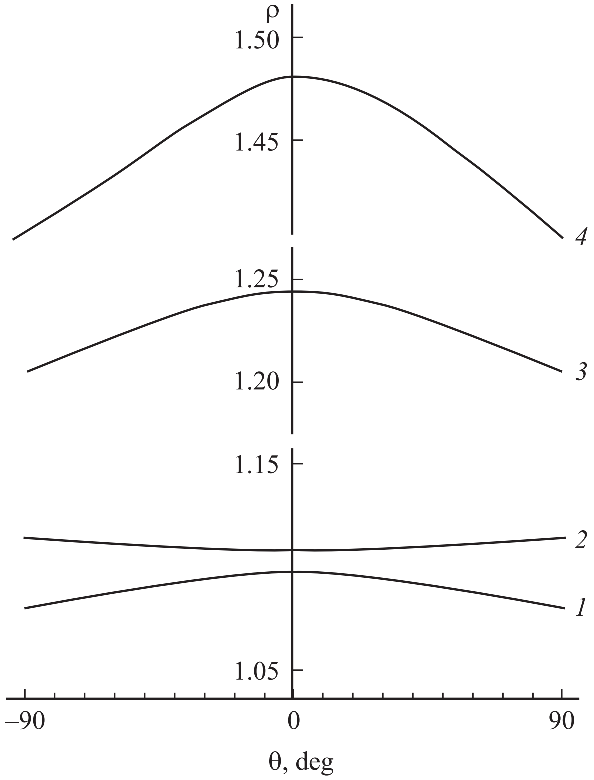

Figure 6. Indicatrices of the relative (with respect to mean surface density) density ρ of gold nanoparticle distribution on the film surfaces. Solution concentration: $c = 0.1$ (*1*), 0.3 (*2*), 0.6 (*3*) and 0.8 (*4*) g/dl. The axis of ordinates ($\theta = 0$ degrees) corresponds to the film texture axis — the direction with a maximum value of ρ.

fractal microstructure of polymer. This agrees with decrease of film density d (Figure 1), growth of the number of surface centers of adsorption [6,7] and achievement of extreme values by the permittivity ε and dielectric loss angle tangent $\mathrm{tg}\,\Delta$ (Figure 2). The established „microstructure–dielectric properties" correlations are supported in [20] where similar behavior of ε and $\mathrm{tg}\,\Delta$was detected during variation of c of the particles of barium titanate ferroelectric filler in a polymer-inorganic composite. It was shown that the sharp valley ε and peak $\mathrm{tg}\,\Delta$ correspond to $c = 30$ vol.% [20]. $c \sim 30$ vol.% corresponds to percolation threshold [19], at which the endless fractal cluster of filler particles is formed in the composite material. Thus, the findings of this study as well as findings of [20] unambiguously associated the extreme values of dielectric parameters with fractalization of the material microstructure.

With growth of the initial solution concentration c in films, anisotropy [1] of the spatial distribution of macromolecule aggregate density increases as a result of enhancement of microphase separation effects. As a result, ε (Figure 2) and d (Figure 1) of the samples drop at $c > 0.7-0.8$ g/dl. The indicatrices of the relative density ρ of decorating nanoparticle distribution demonstrate the enhancement trend of the uniaxial surface texture in the set of film samples as c grows (Figure 6). The most isotropic polymer microstructure meets $c = c_{thr1}$ that is supported, according to ATR IR spectroscopy data, by the absence of optical constant anisotropy of at-PS in the near-surface layer of thin films [1].

4. Conclusion

The film-formation concentration conditions set by the initial solution concentration c predefines both the state of individual macromolecule coils and the topology of particle aggregates in at-PS thin films. In the set of films produced with variation of c, macromolecule packing density varies as a result of order–disorder structural transitions at various scale levels. For the high-molecular at-PS sample, these transitions are clearly recorded with resolution $\sim 30-40$ nm using gold particle decoration of the film surfaces.

In at-PS films formed at $c \le c_{thr1}$, macromolecule coils are in θ-state and are not overlapping, thus, maintaining their identity. The correlation length ξ of density fluctuations is maximum twice as high as the radius R_g of the coil in the solution, while the film microstructure is quite isotropic.

Transition to the film-formation condition that meets $c_{thr1} < c \le c_{thr2}$ results in overlapping of coils and sharp increase of ξ. On the c scale, growth of ξ is followed initially by fractalization of the film surfaces and then by the occurrence of periodic spatial oscillations of the polymer density. Such microstructure transformation is explained by the self-organization of macromolecule clusters during film formation as a result of growing microphase separation effects in the solution. Formation of the scale-invariant supermolecular polymer structure is followed by the density microfluctuation surge and extreme variation of dielectric properties in the set of film samples.

Conflict of interest

The authors declare that they have no conflict of interest.

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