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Morphological memory of polystyrene bodies

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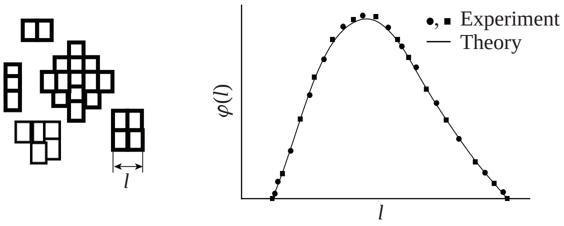
The surface of a standard polystyrene film has a microrelief. The distribution function of the size of the structural elements of the microrelief coincides with the solution of the Fokker–Planck equation for the formation of a film indicating the ability of the polystyrene film to retain information about how it was formed. This is an evidence of the morphological memory of polymer bodies, which provides access to the kinetics of processes that are inaccessible for *in situ* studying.



Experiments with polystyrene granules from Aldrich (Germany) showed that their surface had a microrelief.[1,2] A similar microrelief was observed on the surface of films formed upon solvent removal from polystyrene solutions in *o*-xylene, toluene, *etc*. (Figure 1).

In view of these facts, it was necessary to find out to what extent the microrelief of a polystyrene body retains information about the events that had occurred with the body. To answer this question, we studied the microreliefs of polystyrene films obtained under different conditions in order to identify information on the conditions of their production, which can be derived from data on the microrelief. Thus, polystyrene granules [molecular weight, $(2.5–3.5)\times10^5$ Da] were dissolved in *o*-xylene and toluene with stirring the solution in an acoustic field and recording microrelief changes during dissolution. The solution in *o*-xylene contained different amounts of C_{60} fullerene (0.03–0.1%). The mixture was applied to a glass plate in a layer thickness of 240 μm; the solvent was removed from the layer at 298–303 K; then, the plate was kept at a constant temperature of 293 K. The microrelief was examined by scanning electron microscopy (SEM) after the complete removal of the solvent. The solution of polystyrene in toluene in the absence of fullerene was applied onto a plate in a layer thickness of ~240 μm and the kinetics of toluene removal was observed under continuous layer weighing at 293 K; the microrelief was studied using SEM. The results of these studies were compared to the mesokinetic model of polymer body formation describing the possible relationship of its microrelief with the kinetics of the processes that produced the body.[3] As a result, the conclusion was made that the microrelief stored information on their formation kinetics in a form that could be studied without destruction of the body. Therefore, it can be stated that the bodies of interest had a morphological memory.[4] They retained non-equilibrium macromolecular structures formed on their surfaces, which allow the morphological characterization of these structures to be carried out without destruction. This is shown by the following facts.

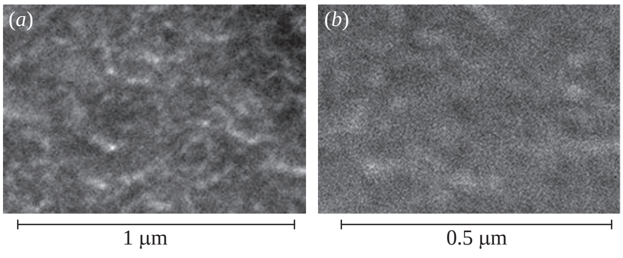


Figure 1 SEM images of (*a*) a polystyrene granule and (*b*) film (a CamScan microscope, after application of an Au film ⩽ 0.5 nm thick).

1. The near-surface zones of the test bodies consisted of particles 2–10 nm large (subnanoparticles) combined into aggregates with less than 100 nm size (nanoparticles) (Figure 1), which are combined into microparticles that form the body. The surface area *S* of the SEM image of each subnanoparticle ($j = 1$) and nanoparticle ($j = 2$) was measured, and the integral functions $\theta_j(l)$ of their size distribution $l = S^{1/2}$ were determined (Figure 2). The distribution of subnano- and nanoparticles was described by the formula

$$\theta_j(l) \equiv B_j(l)/B_{j0} = 1 - \exp(-0.693Z^q), \qquad (1)$$

where $B_j(l)$ is the number of *j*th particles measured with sizes smaller than *l*; B_{j0} is the total number of measured *j*th particles; $Z = (l - l_0)/(l_R - l_0)$; l_0, l_R and *q* are distribution parameters (see Table 1). According to the data in Table 1, the microrelief of granules was nonequilibrium. Otherwise, after the partial dissolution and subsequent drying of granules, it would returned to the original functions $\theta_j(l)$ without changes in l_R. Judging from equation (1), a nonequilibrium state is typical of all of the bodies studied; the function is related to the kinetics of their formation

$$\theta(l) = \lim_{t \to t_F} \theta(l, t),$$

where $\theta(l, t)$ is the distribution function of microrelief structural elements by *l* at any point in time *t* of its formation; and t_F is the point in time at which the body was transferred into the microscope.

2. The size distribution parameters of subnano- and nanoparticles in films depend on the preparation conditions. For

Table 1 Size distribution parameters of microrelief particles in the test bodies.

Type	Particles	l_0/nm	l_R/nm	q
$j = 1$	Film	1.8±0.1	7.3±0.2	2.1±0.1
	Granule	7.1±0.3	22±1	2.2±0.1
	Granule after contacting toluene	2.8±0.2	12.9±0.5	1.9±0.1
$j = 2$	Film	22±1	45±2	2.0±0.1
	Granule	62±3	122±5	2.4±0.1
	Granule after contacting toluene	58±3	150±7	2.2±0.1

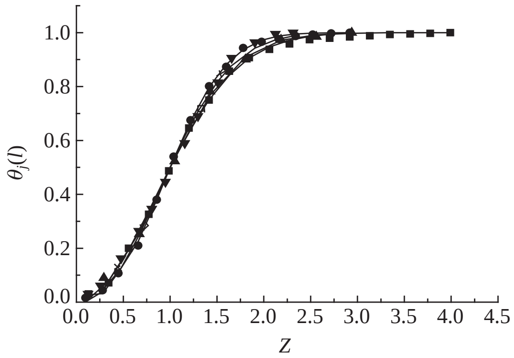


Figure 2 Integral size distribution functions of microrelief particles. (■) Film nanoparticles; (●) granule nanoparticles; (▲) film subnanoparticles; (▼) granule subnanoparticles; (□) granule nanoparticles after contacting toluene; (×) film nanoparticles at $M = 3\times10^{-4}$; lines show the results of the calculation using the Fokker–Planck equation.

example, if a film was obtained by solvent evaporation from a polystyrene solution in *o*-xylene containing C_{60} fullerene, the following relationship was observed:

$$l_R = l_{R0}(1 + \gamma M), \qquad (2)$$

where $l_{R0} = 45\pm2$ nm is the parameter of nanoparticle distribution in the absence of fullerene; $10^{-4} < M < 10^{-3}$ is the mass fraction of the fullerene with respect to polystyrene in the starting solution; $\gamma = (5.1\pm0.5)\times10^2$. The results summarized by formula (2) do not allow us to reliably evaluate the role of fullerene in the formation of nanoparticles. However, the fact that the fullerene greatly increased l_R indicates that the C_{60} molecule did not contribute to the formation of new nanoparticles, and it increased the frequency of subnanoparticle attachment to nanoparticles. These fullerene molecules, which were included in the polystyrene films, retain biological activity, as shown previously.[2]

3. The functions of microrelief distribution changed after the treatment of bodies with a solvent. For example, the short-term immersion of granules in toluene, where they started to swell and dissolve, changed the functions (see Figure 2 and Table 1).

Apparently, the granules memorized that the solvent penetrated into their bulk before dissolution moving the subnanoparticles apart. Moreover, these changes persisted upon the drying of granules. These facts indicate that information about the events that occurred with bodies is carried by the distribution functions of the microrelief structural elements by states, in particular, by the most available state parameter, namely, size *l*. The amount of this information is determined by a combination of distribution functions complemented with data on the relation of distribution parameters with the original state of bodies in the form of relationships resembling equation (1):

$$\theta(l,t) \equiv \sum_j \theta_j(l) = \sum_{\tau\to t} \lim \theta_j(l,\tau). \qquad (3)$$

The $\theta(l,t)$ distribution can be represented as the solution of a kinetic balance equation for the number of particles with size during body formation. This allows one to search for solutions where condition (3) is fulfilled. The solutions found can be considered as a result of retrieving information on how the body was formed from a morphological memory.

We performed such a search in the context of film formation during the evaporation of a layer obtained by the application of a solution of granules in *o*-xylene onto a flat support. Film formation was found to occur in three stages. At the first stage, subnanoparticles nucleated and grew in the bulk of solution; at the second stage, the association of these particles into nanoparticles predominated; and, at the third stage, the nanoparticles came into contact with each other to form microparticles. At all of the stages, the main process involved the attachment of small fragments to large particles; as a result, at the end of each stage, the function was described by equation (1) with time-dependent distribution parameters. Detailed information on the stages can be derived from the distribution parameters (Table 1) and from the fact that submicroparticles tend to form chains which are visible in Figure 1. The calculated distribution parameters indicate that, at each stage, the process occurred in compliance with the Fokker–Planck equation with the screening of the most stable aggregates and the destruction of numerous less stable forms. The established facts comply with the generally accepted concepts that polymeric bodies are formed gradually *via* the stages of formation of oligomeric particles, their aggregation into microgel particles, and aggregation to give macrogel particles.[5–7] They also comply with the notion of the slow ordering of micro- and macrogel particles that pass into a crystalline state over extremely long periods of time.[8]

Thus, one can believe that morphological memory is a feature of many polymeric bodies, along with shape memory and other kinds of memory found in polymers.

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