Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 335–336

Mendeleev Communications

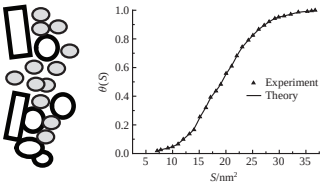
Electron beam-accelerated aggregation of formvar film macromolecules

Igor V. Melikhov, Vsevolod N. Rudin and Elmira D. Kozlovskaya*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: helbyv@mail.ru

DOI: 10.1016/j.mencom.2018.05.036

As found experimentally, macromolecules in the near-surface sections of a film prepared by solvent evaporation from a solution of polyvinylformal in dichloroethane acquired mobility under an electron beam to increase the rate of macromolecular association with the formation of nanosized aggregates by three or more orders of magnitude.



The phenomena occurring upon the irradiation of polymer solids with charged particles are of considerable importance.[1–3] We obtained experimental data on the influence of a medium energy electron beam on the properties of the near-surface sections of formvar polymer films. The films were prepared from polyvinylformal† and introduced into the electron gun of a JEM-1011 transmission electron microscope (with 80 keV electrons)[4] for taking a series of micrographs. Then, the micrographs were compared in order to reveal changes in the relief of surface films caused by the electron beam using conventional models.[5,6] Some of the films were modified with gold and carbon vapors;[7] as a result, their relief became independent of the electron beam of the microscope.[8–10]

The micrographs (Figure 1) showed that the near-surface sections of the films modified with Au consisted of elongated subnanoparticles with a width of 0.2–0.8 nm and a length of ~2.3 nm; moreover, it was obvious that many of them were the chains of condensed sections. A portion of subnanoparticles formed two- and three-dimensional aggregates of size 1.5–10 nm (nanoparticles) with a tendency toward the regulated arrangement of their subnanoparticle components. Figure 1 also shows a part of hardened Au nanodroplet formed in the film upon modification.

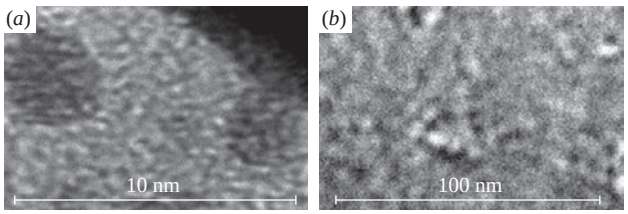


Figure 1 Micrographs of typical near-surface zones of two films: (*a*) gold-modified film, τ = 60 s; (*b*) unmodified film, τ = 480 s.

† The films were obtained by the evaporation of a solution of polyvinylformal from SPI (degree of polymerization, 350–500; molecular weight, 2.4×10^4–4×10^4; glass transition temperature, 360–370 K; dielectric strength, 20–26 mV m^{-1}; and formaldehyde content, <0.1%) in dichloroethane (Sigma, >98% purity) supported onto a polished glass plate.[4] The initial concentration and temperature of the solution were 2.0×10^{-3} g cm^{-3} and 293 K, respectively; the initial layer thickness was 30 μm, as calculated on a weight basis. After the complete removal of the solvent, a film with a thickness of 50 nm was formed, and this film was dried in air at 293 K for about 10^4 s.

Table 1 Parameters of the $\theta(S)$ distribution of film nanoparticles.

Film	S_0/nm^2	α	β
Unmodified film, τ = 480 s	9.2±0.1	0.13±0.02	0.85±0.02
Gold-modified film, τ = 60 s	2.1±0.1	2.1±0.1	0.35±0.02
Carbon-modified film, τ = 60 s	7.1±0.1	2.1±0.1	3.4±0.2

From the surface areas S of the images of nanoparticles in the micrographs, we determined the fraction $\theta(S)$ of measured nanoparticles whose image areas were smaller than S at $0.5 < Z < 5$:

$$\theta(S) = 1 - \exp[-\alpha Z(1 + \beta Z)], \quad (1)$$

where $Z = S/S_0 - 1$; and S_0, α and β are particle size distribution parameters (Table 1), which remained unchanged upon the drying of films. Equation (1) formed a basis for the quantitative description of nanoparticles.

After the introduction of the modified films into an electron beam with a frequency of 4×10^3 nm^{-2} s^{-1}; the relief of their surface remained almost unchanged in the exposure time $\tau < 500$ s because of the high dielectric strength of polyvinylformal. However, the agglomeration of nanoparticles occurred in the unmodified films under the same conditions (Figure 2); moreover, the size of the largest nanoparticles increased in accordance with the relationship:

$$S(\tau) = S_F - [S_F - S(0)] \exp[-\omega\tau(1 + \nu\tau)]. \quad (2)$$

Here, $S(0)$ = 19±2 nm^2 and $S(\tau)$ are the areas of images of the largest nanoparticles before and after irradiation for a time $0 < \tau < \tau_F$; S_F = 40±2 nm^2 is the area of images of the largest nanoparticles at the point in time $\tau_F = 10^3$ s, when their agglomeration was almost complete; $\omega = (4.2\pm0.1)\times10^{-3}$ s^{-1} and $\nu = (4.2\pm0.2)\times10^{-4}$ s^{-1} are the frequency characteristics of agglomeration.

In this case, nanosections depleted in subnanoparticles were formed around many nanoparticles (see Figure 1); at $\tau \to \tau_F$, the development of these nanosections led to the termination of nanoparticle agglomeration. The nanoparticles of the unmodified films chaotically moved over their surface under irradiation with an average velocity of 0.2 nm s^{-1} in a time from 60 to 150 s, although the initial temperature of the films was considerably lower than the glass transition temperature of polyvinylformal.

According to Figure 1, primary polymer particles were present in the layer of the evaporating solution of polyvinylformal as

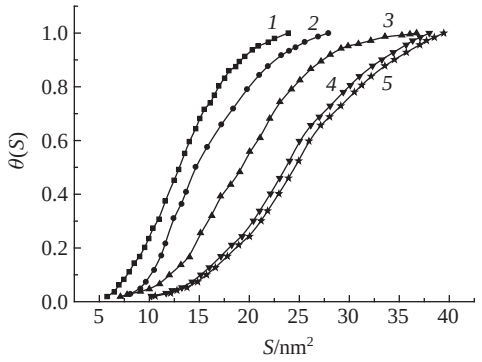


Figure 2 Distribution functions for the nanoparticles of the unmodified film in the micrographs at irradiation times of (*1*) 60, (*2*) 150, (*3*) 240, (*4*) 360 and (*5*) 480 s.

subnanoparticles. Their one-dimensional aggregates formed a disordered nanoporous network and two- and three-dimensional aggregates formed nanoparticles visible in the micrographs. In this case, relationship (1) can be represented as a solution to the Fokker–Planck equation for changes in the state of the two-dimensional aggregates of primary polymer particles in the process of film formation. Therefore, the function $\theta(S)$ can be considered as a carrier of the morphological memory of a film with respect to the formation of its aggregates.[8]

Upon the introduction of the unmodified film into the electron beam, its near-surface primary polymer particles began intensely add to the aggregates to increase their size. In this case, the frequency characteristic of the process, which was negligible before electron irradiation ($\omega < 10^{-6}$ s^{-1}) rapidly increased to $\omega = 4\times10^{-3}$ s^{-1} and to 5×10^{-3} s^{-1} after 500 s. This is evident from the experimental data given in Figure 2 and generalized as formula (2) and from the appearance of depleted nanosections near nanoparticles (see Figure 1). This fact indicates that near-surface primary polymer particles acquired electron-stimulated mobility sufficient for directed motion to the aggregates from distances commensurable with their size. The aggregates also acquired mobility, but their movement was chaotic.

For a detailed description of these phenomena, it is necessary to accumulate experimental data on relationships between the frequencies ω and ν and electron beam parameters.[11,12] It is reasonable to hypothesize that electrons absorbed by the macromolecules of a film caused their repulsion from each other to increase the mobility of the primary polymer particles and aggregates. In this case, the aggregates reflected more electrons from a beam than primary polymer particles and acquired a charge relative to their environment. The resulting electric fields stimulated aggregation on the surface of the unmodified films due to an increase in both the mobility of macromolecules and their aggregates and the probability of macromolecule incorporation into the aggregates. This stimulation was impossible on the surface of films modified with gold and carbon because of the presence of a supported modifier.

It is likely that the above behavior is not specific of polyvinylformal films, and the electron beam acceleration of aggregation will occur in any polymer with the significant frequencies ω and ν.

References

1 A. Vrancken, *J. Oil Colour Chem. Assoc*., 1984, **67** (5), 118.
2 A. K. Pikaev, *Sovremennaya radiatsionnaya khimiya. Tverdoe telo i polimery. Prikladnye aspekty* (*Modern Radiochemistry. Solid State and Polymers. Applications*), Nauka, Moscow, 1987 (in Russian).
3 L. Reimer and H. Kohl, *Transmission Electron Microscopy*, Springer, New York, 2008.
4 D. Shindo and T. Oikawa, *Analytical Electron Microscopy for Materials Science*, Springer, New York, 2002.
5 T. Kajiyama, K. Tanaka and A. Takahara, *Polymer*, 1998, **39**, 4665.
6 A. L. Valynskyi and N. F. Bakeev, *Strukturnaya samoorganizatsiya amorfnykh polimerov (Structural Self-Organisation of Amorphous Polymers)*, Fizmatlit, Moscow, 2005 (in Russian).
7 A. A. Mironov, Ya. Yu. Komissarchik and V. A. Mironov, *Metody Elektronnoi mikroskopii v biologii i meditsine (Methods of Electronic Microscopy in Biology and Medicine)*, Nauka, St. Petersburg, 1994 (in Russian).
8 I. V. Melikhov, O. V. Alekseeva, V. N. Rudin, E. D. Kozlovskaya and A. V. Noskov, *Mendeleev Commun*., 2016, **26**, 353.
9 *Flexible Polymer. Chain Dynamics in Elongation Flow. Theory and Experiment*, eds. T. Q. Nguyen and H.-H. Kausch, Springer-Verlag, Berlin, Heidelberg, 1999.
10 R. F. Egerton, *Ultramicroscopy*, 2013, **127**, 100.
11 A. H. Zewail and J. M. Thomas, *4D Electron Microscopy: Imaging in Space and Time*, Imperial College Press, London, 2010.
12 R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 3rd edn., Springer, New York, 2011.

Received: 3rd July 2017; Com. 17/5295