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Relaxation of supramolecular structures in polydimethylsiloxane films

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The surface topology of a polydimethylsiloxane film changes with time, suggesting that the supramolecular structure is reorganized; this reorganization results from relaxation of the supramolecular structure initially oriented in the field of IR radiation.

Siloxane molecules are characterized by a high thermodynamic flexibility, that is, ability of the chain to twist when exposed to thermal motion. Similarly to the ability of compounds to undergo chemical reactions, this feature is determined by the energy difference between two states. The Kuhn segment *A* is the most versatile measure for the assessment of chain flexibility. In particular, the length of the Kuhn segment experimentally measured for polydimethylsiloxane is 14.0 Å.[1] It is the small length of the Kuhn segment that determines the high conformational mobility of siloxane molecules.

The polydimethylsiloxane film was shown to form a periodic surface relief as a result of depositing a thin metal film.[2–4] When the hot metal gets in contact with the polydimethylsiloxane film in a vacuum, a strong temperature gradient appears between the top and bottom film surfaces. This results in the emergence of stresses leading to conformational chain transformations and formation of a periodic surface topology. The objective of this work was to demonstrate that for such a structure to be formed, the polydimethylsiloxane film should not necessarily be metal-coated and it would suffice to expose the film surface to IR radiation. It is also interesting to look into behaviour of such surface topologies with time.

The experiments were carried out with a siloxane elastomer prepared by hydrosilylation. The liquid composite material contains a low-molecular siloxane rubber having a molecular mass of 1500–3000 and containing terminal vinyl groups, an oligoorganosiloxane having a molecular mass of 50000–70000 and containing SiH groups, and a complex platinum catalyst. The hydride groups are arranged randomly. The ratio of the low-molecular and high-molecular components was 1:10.

Thin polydimethylsiloxane films were applied on the support surface by centrifugation. The compound was dissolved in ethyl acetate and applied onto a support mounted on a centrifuge, which was then spun up to 3000 rpm and kept in this mode until the solvent evaporated completely.

Once the film was applied, the substrate was placed in a thermostated oven. The siloxane was polymerized in the oven for 3–5 h at 150 °C. The polymerization time and temperature were selected to provide the maximum degree of polymerization.

The prepared samples were placed in an upgraded versatile vacuum device VUP-5 intended for vacuum deposition of thin films. The VUP-5 vacuum system allows a pressure down to 1.33×10^{-4} Pa to be obtained in the evacuated chamber.

Reorganization of supramolecular structures resulting in the emergence of a surface topology was carried out in the field of IR radiation *in vacuo*. A molybdenum evaporator was used as the source of IR radiation, hereinafter referred to as the radiator. The radiation power was controlled by changing the current through the radiator. The samples were mounted in a special holder at a distance of 40 cm above the radiator and the system was evacuated to 0.5×10^{-3} Pa. The pressure was kept constant during the experiment. Thermocouples were mounted both in front of the sample, in direct contact with the surface of the siloxane film, and behind the substrate. The temperature difference between the opposite film surfaces ranged from 10 to 20 °C.

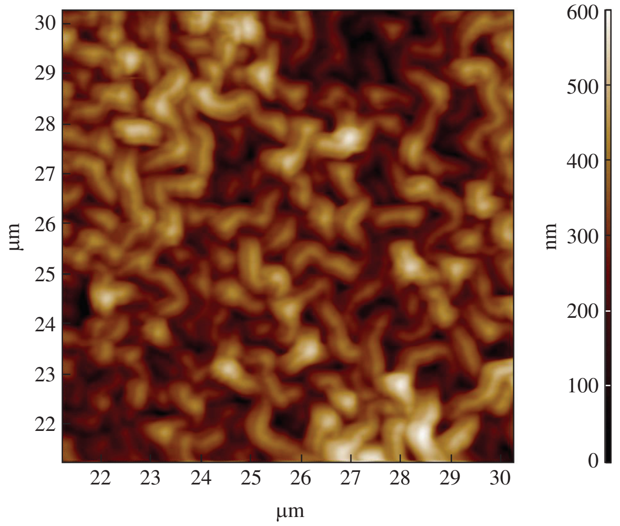

Figure 1 Surface topology of a polydimethylsiloxane film after irradiation in an IR field.

An optical system with a red semiconductor laser was assembled inside the set-up in order to monitor the siloxane film surface during the formation of supramolecular structures.

One can judge whether supramolecular structures are formed on the film surface by analyzing scattered laser radiation reflected or transmitted through the sample. Due to diffraction on supramolecular structures with spatial size comparable to the red laser wavelength (0.654 μm), the screen showed diffusion of laser radiation during their formation and gradual structuring on the film surface.

The sample was extracted from VUP-5 and the surface topology was measured using a Solver-Pro scanning probe microscope (Nt-Mdt). Figure 1 shows the topology of a polymer film on aluminum obtained by scanning probe microscopy. This struc-

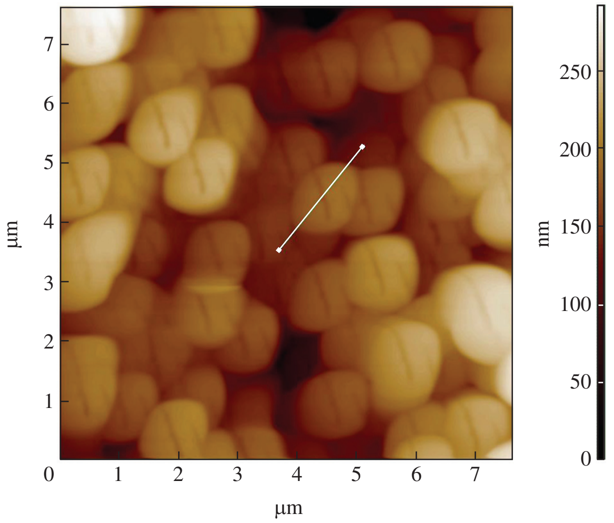

Figure 2 Surface topology of a polydimethylsiloxane film 7 months after the sample preparation. The line indicates the possibility of taking an accurate measurement between the objects.

ture is quasi-periodic with a period of 800–900 nm and a height of about 300 nm.

Observation of the structure of the film stored in a dark closed place at room temperature for two months after the preparation did not show any noticeable changes in topology. After seven months since the sample was prepared, the film surface was studied and showed changes in topology. The image obtained using the scanning probe microscope is shown in Figure 2. The film surface topology changed: disc-shaped structures appeared with diameters ranging from 1.4 to 1.55 μm and heights from 50 to 130 nm, and with a transverse band 20 nm deep on each disc.

Thus, we have established the spontaneous reorganization of the structure of a polydimethylsiloxane film. We assume that the reorganization is associated with the breakdown of the physical bonds formed during the sample irradiation in the IR field. The lifetime of bonds exponentially depends on the bond energy; therefore, breakdown of these bonds occurs with time, followed by relaxation of the supramolecular structure due to conformational transformations of polymeric molecules to minimize the total energy of the conformational states.

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