Microprinting – a new approach to study competitive structure formation on surfaces

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(Received: August 17, 1998; revised: February 16, 1999)

SUMMARY: A new approach to the experimental investigation of heterogeneous crystallization on surfaces with molecularly defined structures is demonstrated. Crystallization and competitive dewetting processes of polyethylene on heterogeneous micropatterned surfaces were studied using molecular imprinting techniques for structured chemical modification of surfaces on micrometer scale in laterally defined areas. Examination of spherulitic textures by low-voltage SEM and AFM shows remarkable differences in spherulite sizes due to surface chemical influences. The results are discussed in terms of a diffusion limited aggregation process which causes the dendritic and spherulitic structures and which is influenced by the dewetting process.

Introduction

The knowledge of correlations between surface chemistry, arrangement of molecules on surfaces and its influence on the nucleation behaviour and crystal growth on surfaces is of great importance for the understanding of heterogeneous nucleation in polymer science and also in the biomimetic approach to the preparation of materials with new structural features1, 2). Crystallization processes are extremely sensitive towards a number of different parameters, some of them being even of statistical nature. To run crystallization experiments in a reproducible way is extremely difficult. An experimental setup in which surface areas of different chemical properties within the same sample appear in laterally well-defined patterned motifs would allow one to compare the influence of the different molecular features on the crystallization, while all other parameters influencing crystallization are kept constant within a single experiment.

Recently Whitesides3, 4) demonstrated an elegant route for the chemical heterogenization of surfaces on a molecular level by microprinting with polymer stamps (polydimethylsiloxane [PDMS]), producing monomolecular self-assembling layers on surfaces of micrometer respectively submicrometer scale.

The essential features for the surface modification by microprinting and its application in crystallization experiments are shown in Scheme 1. Structural features of a 3-d object taken from a microstructured siliconwafer are replicated into a flexible polymer material, e.g. polydimethylsiloxane (PDMS), producing a relief structure. The PDMS replica has the function of a stamp which can be coated with a suitable “ink” used for surface modification. The PDMS replica has the function of a stamp which can be coated with a suitable “ink” used for surface modification of surfaces. The “ink” molecules need to be anchored on surfaces by reactive groups, for example, thiol groups in case of an Au surface. It was checked by STM5) that the molecular packing of thiol-terminated molecules transferred to a gold surface by microprinting is surprisingly homogeneous. While chemisorption favours up to four different chain packings of alkanethiols on the gold surface, only one modification was detected applying microprinting.

In our experiments the polyethylene is in contact with the modified surface shown in Scheme 1 during crystallization. The crystallization process occurs during solvent evaporation from the polyethylene solution.

In this short communication the influence of the heterogenized surface on the spherulitic texture of polyethylene crystallized in thin films from xylene solution is demonstrated. Spherulitic structures were observed by low voltage scanning electron microscopy (LVSEM) of uncoated specimens. Fine structures of dendrites were investigated by AFM.
Experimental part

An elastomeric mold was fabricated from poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) by casting PDMS against a master that contained a pattern complementary to that to be reproduced. The silica master was prepared by conventional microfabrication techniques.

The stamps were wetted with a few drops of a $10^{-3}$ mol/l ethanol solution of 11-mercaptoundecanoic acid (Aldrich). Excess solvent was removed with nitrogen gas. For micro-printing the impregnated stamp was contacted with gold surfaces.

Gold layers of 30 nm thickness were prepared by thermal evaporation of gold (Goodfellow) with an evaporation rate of 0.03 nm/s onto glass substrates which were precoated with a 2 nm Cr layer as adhesive interface.

For crystallization experiments, a 0.2 wt-% solution of polyethylene ($M_w = 125000$, density 0.945 g/cm$^3$, Poly-Science) in xylene was prepared at 100°C. Gold substrates modified with the 11-mercaptoundecanoic acid were dipped into the solution for some seconds, removed and dried in air.

The polyethylene films were examined by low-voltage scanning electron microscopy (LVSEM) (LEO Gemini 982). Accelerating voltages of 1 KeV or below guarantee imaging without charging, although the samples were not sputter-coated as usual. In addition the penetration depth of electrons in the sample is very low (<50 nm) and favours the characterization of surface structures.

For high resolution studies, an AFM scanner which is integrated in an optical microscope (ULTRAobjectiv*) is used in non-contact mode.

Results and discussion

Fig. 1 shows the LV-SEM photograph of a thin HDPE film (a) crystallized on a gold substrate that was patterned with a PDMS stamp with hexagonal periodic motifs (b). Inside the hexagonal areas the gold surface was polar modified with the 11-mercaptopoundecanoic acid. Obviously, the texture of the crystallized material represents the same periodic features as the original stamp. The size of the hexagonal structures in the crystalline film corresponds to the motif size of the PDMS stamp used for surface heterogenization (within the experimental error of ±3%).

A closer look at the different structural features of the film demonstrates remarkable differences in the spherulite size grown in contact with the hexagonal areas and the unmodified gold surface (Fig. 2). The bright thin lines in the micrograph (Fig. 2) represent the boundaries of individual spherulites within the spherulitic texture.

Two different populations of spherulite sizes can be distinguished in Fig. 2. The larger ones generally appear inside the hexagonal hydrophilic modified areas, while the smaller ones cover the hydrophobic parts of the surface. Micrographs taken by AFM (Fig. 3 a, b) show the morphological features characteristic for both species in more detail. The average film thickness of the films imaged in Fig. 3 a, b is about 60 nm and 25 nm, respectively. While in Fig. 3 a typical spherulite structures are formed inside the hexagonal pattern (A/hydrophilic), only central sheaf like elements of spherulite nuclei are visible in the hydrophobic areas (B). Thin films show the same principal features with more pronounced dendritic structures (Fig. 3 b).

The internal structure of the spherulites in thin films can be regarded as a result of a dendritic growth process. The highly branched features are commonly explained in terms of a diffusion-limited aggregation (DLA) model\textsuperscript{6} which also describes morphological features of other diffusion-controlled growth processes such as bacteria growth on substrates, dendritic morphologies formed during electrocrystallization or the formation of ice crystals\textsuperscript{7,8}. In a solidification or crystallization process, the DLA model assumes that the velocity of the growth or solidification front is proportional to the concentration gradient of the material which solidifies\textsuperscript{9}.

In our experiments the dendritic growth process is influenced by the dewetting process of the polymer solution on
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The hydrophilic stamped domains. We assume that the mass transport during the dewetting process increases the concentration gradient in front of the solidification boundary, which results in a higher growth velocity of the solidifying structure and therefore in larger spherulite sizes. Differences in spherulite size can also be caused by different nucleation densities on heterogenized areas.

At low evaporation rate of the polymer solvent and low supercooling of the crystallizing species, the dewetting process becomes dominant in the hydrophilic domains and the nucleation density decreases in the hydrophobic domains, favouring larger spherulites. The morphology of such films (Fig. 4) shows typical dewetting structures on the hydrophilic domains and large spherulites on the hydrophobic areas.

In the previous context, dewetting and crystallization in thin films can be regarded as interacting processes. Areas of higher surface free energy increase the growth velocity of a proceeding crystallization front within a thin liquid layer. Rapid crystallization on the other hand suppresses the proceeding dewetting. A complementary example in which the morphology of spherulites in thin films determines the dewetting structures upon remelting has recently been demonstrated by Kressler et al. [11]

The experiments clearly demonstrate the successful use of molecularly imprinted surfaces to study the influence of chemically heterogeneous surfaces on crystalline morphology. From an analytical point of view, microstructured surfaces are well-defined models for the investigation of strongly parameter-sensitive structure-forming processes such as surface-induced phase segregation of polymer blend systems [12] or, as shown in this paper, for competitive processes on surfaces.

Fig. 3 a, b. AFM micrograph of dendritic features grown on a hydrophilic (A) or hydrophobic (B) area in films of 60 nm (3a) and 25 nm (3b)

Fig. 4. Dewetting structures inside polar modified areas and large spherulites grown outside the hexagons (LVSEM micrograph)

7) E. Ben-Jacob, Contemp. Phys. 34, 247 (1993)
8) E. Ben-Jacob, Contemp. Phys. 38, 205 (1997)