Surface Structure of Amorphous PMMA from SPM: Auto-Correlation Function and Fractal Analysis

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SUMMARY: The surface topography of amorphous poly(methyl methacrylate) has been investigated by scanning probe microscopy technique and analysed using an auto-correlation function approach. Spatial correlations in the arrangement of sub-macromolecular fragments on the surface are studied depending on preparation conditions (whether the surface was free, i.e. in contact with air, or confined with the silicon substrate). The correlation length of the roughness distribution on the surface of amorphous polymers corresponds to the internal dimensions of unperturbed polymer chains (the radius of gyration). The scaling behaviour of the roughness is analysed with the Hurst approach, and found to be different for the free surface and for the confined one. As a result of annealing at a temperature above the glass transition temperature of the bulk polymer, both surfaces converge to similar fractal dimensionalities and correlation lengths.

Introduction

The structural arrangement of polymer chains near surfaces and interfaces impacts many technological areas such as coatings, adhesion, and composite materials. Interfacial properties and behavior can be very different from those of the bulk. Study of the surface structure and properties is a challenging and difficult task particularly for amorphous polymers, which are soft and disordered objects. Even nowadays when the investigation of surface structure and molecular motion near the surface has been paid great attention, the surface structure-property relationships are still not known for many polymer materials.1)

The structure and properties of the surface of amorphous polymers are much less understood in comparison to crystalline polymers where some well-established structural techniques (such as grazing incidence X-ray diffraction, electron diffraction)

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can be applied. However, theoretical models of conformational behavior of polymer chains were originally developed for amorphous polymers (for example, scaling concept, fractals),$^{2)}$ making the structural analysis of amorphous polymers especially attractive as a point of comparison with the existing theoretical predictions.

Scanning force microscopy (SPM) techniques have become available as a powerful tool for studies not only of morphology but also of physical properties of the surface. This has stimulated a reconsideration of many physical phenomena, which occur at the surface and is giving a new impulse for critical review of some basic principles of the polymer structural organisation.$^{3)}$

The classical methods of visualisation of correlations in an arrangement of some structural units in space typically employ the Fast-Fourier Transform algorithm and are the most computationally efficient methods available. Fourier transforms, being very efficient in applications to periodical or quasi-periodical systems, are not so efficient when applied to structural characterization of poorly organized amorphous polymers.$^{4)}$

In this paper we apply an auto-correlation function (ACF) analysis of the SPM data to characterize the surface structure of two different types of amorphous polymer surfaces: the free surface (in contact with air) and the confined surface which has been restricted by a solid surface during formation of the polymer film.

Experimental

We have studied the surface structure of a model amorphous polymer poly(methyl methacrylate) (PMMA) (Aldrich, $\langle M_n \rangle$=120k). Films with a thickness of about 1 μm, as measured by SPM $^{4)}$, were solution cast from 1% PMMA solution in chloroform (Aldrich) on silicon single crystal wafers. The silicon substrates were cleaned before polymer deposition by sonification in ethanol (Aldrich). The preparation allowed formation of two surfaces: a free surface (in contact with air during the film preparation), and a "confined" surface (in contact with solid substrate and therefore restricted in molecular motions). The films were peeled off the substrate for study of the confined surface, or left on the substrate for investigation of the free surface. Films were subjected to annealing at 130°C (T_g=110°C) in a vacuum oven for structural relaxation of the polymer chain conformations. The annealing of the confined surfaces was carried out after the film was removed from the substrate. The morphology was studied at each stage of the annealing after quenching the sample to room temperature.

The samples were examined using a JEOL SPM4200 microscope operated in a tapping mode. Typical scan-sizes were between 300x300 nm^2 and 5 x 5 μm^2. An auto-correlation function analysis, described below, was applied to quantitatively characterize the polymer surface topography. Comparison of RMS roughness and its changes at different scales revealed that the effect of annealing was most pronounced on a sub-micrometer scale, and therefore surface areas of 300 x300 nm^2 have been chosen as the most suitable for the ACF analysis, which was implemented in a MAPLE-based program.

ACF analysis

Peculiarities of the distribution of matter in such complex materials as amorphous polymers can be found with ACF approach, which has been found to be a better way of the statistical description of amorphous systems.4), 5) The ACF can be defined through the faltung product, or self-convolution of a profile function (function of the surface roughness) ρ (x):

$$ACF(x) = \int \rho(x)\rho(x-x')dx' = \rho(x) * \rho(x) \qquad (1)$$

where the integral extends over the whole plane of the surface.4) Using the convolution theorem (the Fourier transform of the convolution of two functions equals the product of the Fourier transforms of these two functions) and denoting direct and reverse Fourier transforms as $F(\,)$ and $F^{1}(\,)$ respectively, we will have the following relations between Fourier transforms and ACF 4):

$$ACF(x) = \left|F^{-1}(G(u))\right|^2 \; and \quad G(u) = F(\rho(x)) \qquad (2)$$

and x and u are variables in real and reciprocal spaces respectively (*G(u)* is a Fourier image of some structural distribution function *ρ (x)* in real space). Equations 2 define the auto-correlation function through the Fourier transforms.

An alternative definition of the 2D ACF may be given by:

$$ACF(x, y) = \frac{\iint \rho(x - x', y - y') \cdot \rho(x', y')dx'\,dy'}{\iint \rho^2(x, y)dxdy} \qquad (3)$$

where *ρ(x, y)* is a profile function defined on the surface *(x, y)*, and the denominator serves for normalization.

Correlation in Height Distribution

Fig. 1 shows a typical topography of the PMMA free surface. It can be characterised as a random distribution of density inhomogenites. Two types (scales) of such inhomogenites could be observed: several nano-meters size blobs, and more smooth waves that are larger in scale. The as prepared confined surface is rough in comparison to the free surface.

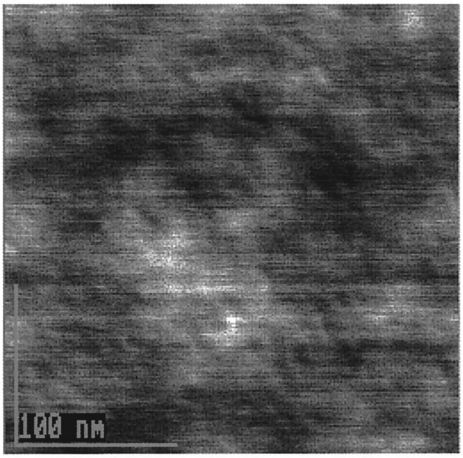


Fig. 1a: SPM tapping mode image of the PMMA free surface.

An algorithm based on equation (3) has been applied for of 2D ACF calculation. The analysis revealed an asymmetric nature of the 2D ACF in respect to X and Y directions as directions of fast and slow scans during SPM imaging.

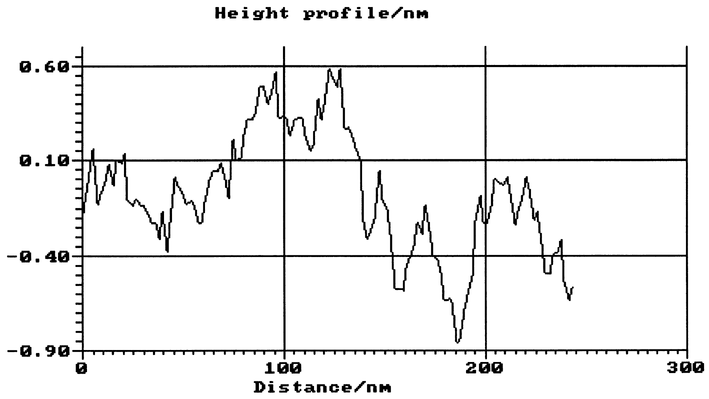


Fig. 1b. Surface profile function as recorded along a single line by SPM.

We have characterized the surface topography with 1D ACF calculation applied in X direction later on (the direction of more stable "fast" scanning to eliminate such instrumentation contribution). An example of 1D ACF is shown in Fig. 2.

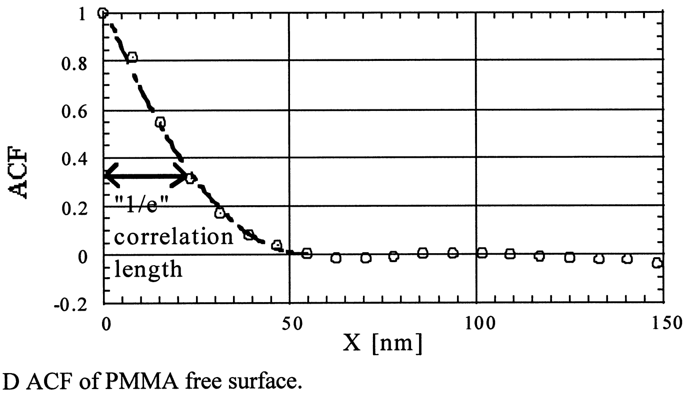


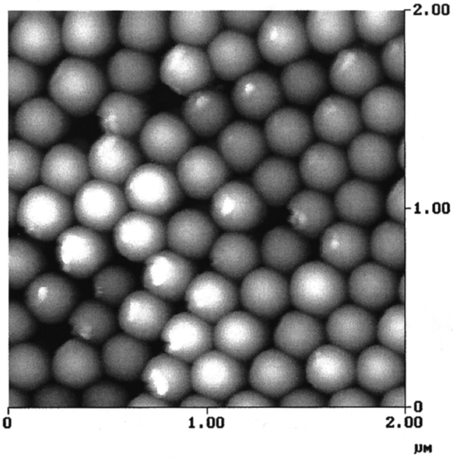
Fig. 2: 1D ACF of PMMA free surface.

The validity of the approach has been tested by applying the ACF calculation procedure to more organized closely packed latex nanospheres. Fig. 3a shows an SPM image of a polystyrene latex quasi-crystal formed by self-assembly of functionalized polystyrene latex spheres on a silicon surface.$^{6)}$ The corresponding ACF function shown in Figure 3b reveals the main features of the para-crystalline order in the system. The period of the oscillations observed corresponds to the diameter of latex nano-spheres, while the envelope curve, which display an exponential decay:

$$ACF \sim \exp(-x/\xi) \quad (4)$$

allows extraction of the characteristic correlation length ξ (as $ACF=1/e$). This structural parameter defines an average distance from an arbitrary point in the sample beyond which the correlation in arrangement of the structural units (latex spheres in this case) is lost. The decay of ACF for the latex system is equal roughly to five latex diameters, and can be visually observed from the real-space image (Fig. 3a).

a)



b)

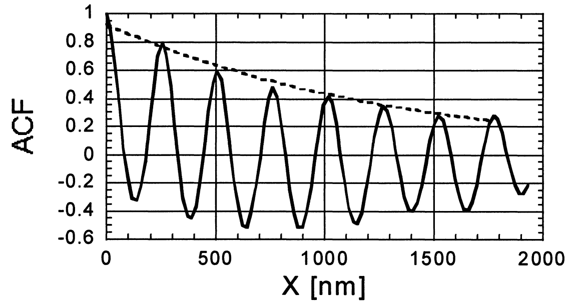


Fig. 3: SPM image (a) and corresponding ACF (b) for a PS Latex film. (image is a courtesy of V. Gorbunov and V. Tsukruk)

In this case we obtain two different structural parameters obtained from ACF: a length scale associated with the periodical arrangement of structural subunits, and a characteristic distance of the mutual coupling in such an arrangement. When applied to continuos polymer systems, constituted of long chain molecules, such distance of mutual influence in the arrangement of structural elements might correspond to the characteristic dimensions of macromolecules – the size of molecular coils or sub-coils (blobs).7) Capillary waves might add complexity to this picture if we could measure areas of the order of several mm squared on the surface.8)

A plot of the correlation length versus annealing time for the free and confined surfaces of a PMMA film is shown in Fig. 4. During annealing the confined surface becomes smoother while the free surface is roughening. It is not surprising that both surfaces would tend to the same roughness if we consider that both film surfaces are in the same condition with regard to surface tension and allowed conformations after peeling the film off the substrate. The systems do achieve equilibrium states with the same correlation lengths after sufficient annealing.

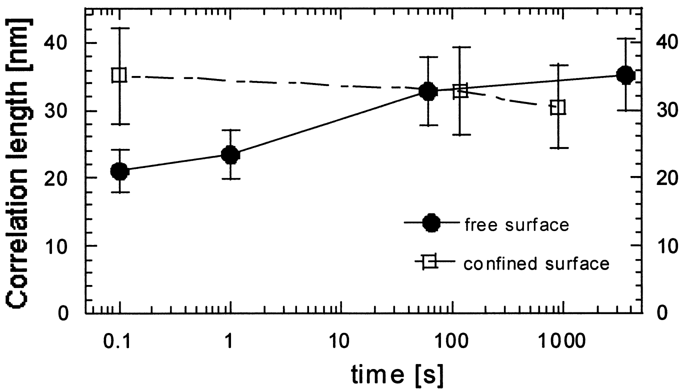


Fig. 4: Correlation length (determined from 1D ACF as shown in Fig. 2) versus time of annealing at T>T_g for PMMA free and confined surfaces.

Independently, the radius of gyration, R_g, as a parameter characterising natural dimensions of macromolecular coils in the bulk, can be calculated using geometrical dimensions of polymer chains. For the PMMA fraction used in this study (M_n=120k) one can obtain R_g=30 nm in a random coil approximation with a monomer size a=0.254 nm and free volume parameter C_∞ = 8.6 as reported in the literature.[9)] The calculated value of R_g is in a good agreement with the correlation length of hight distribution found in our experiments for the PMMA surface after annealing.

Fractal Analysis

Further insight into surface structure can be given with an analysis of the surface roughness. Among several surface roughness parameters routinely determined in SPM experiments the root mean square (RMS) roughness is the most popular as it has been demonstrated to show realistic where tapping mode is applied.[10)] The surface roughness is a function of the scale on which it has been measured and may also depend on the experimental technique used for its determination. The mathematical description corresponding to surfaces formed through random processes of diffusion or molecular motion needs application of fractal description widely used for a quantitative evaluation of random processes in nature. A fractal surface possesses a characteristic so-called fractal dimension exceeding the topographical dimension of the system. In application to surfaces it means that the fractal dimension D is in the range from 2 to 3, with higher values for relatively rough surfaces and $D = 2$ for an absolutely flat one. Fractal analysis is of growing use in polymer science, because the scaling concept simplifies significantly the characterization of the structure.11), 12) The simplest technical route for calculation of D consists of finding another characteristic exponent, H (the Hurst exponent), which is defined through the equation:

$$<|\, h(x_1) - h(x_2)|>_{|x1-x2|=x} \sim x^{H} \qquad (5)$$

where $h(x_i)$ are heights on the surface corresponding to two different points 1 and 2, and the averaging < > is performed over some designated surface area.12) Plotting the RMS roughness data obtained at different “magnifications” in SPM experiments on a double-logarithmic scale versus the scan size allows determination H and hence D through the relation:

$$H = d - D \qquad (6)$$

where d is the dimension of the embedding space ($d = 3$ in a natural case of flat surface with intrusions in the third dimension).12)

Fig. 5 shows the Hurst representation of the surface roughness data for the PMMA free and confined surfaces depending on time of annealing at 130°C (above T_g). Surprisingly, the pristine free surface does not give a stright line, which means that it cannot be described as fractal. The relaxation of the surface structure under annealing changes the nature of this surface and after 2 hours it becomes fractal with $D = 2.3$. The confined surface is fractal from the start with $D = 2.8$, but becomes less random (D decreases to a value of 2.2) under annealing. Therefore, both surfaces are merging to the same state with the $D \sim 2.3$ during structural relaxation once again proving that we have relaxed the system after long-term annealing. The values of D obtained in our experiments are in good correspondence with values extracted from computer simulations of the amorphous polymer surface (D=2.3-2.4).13)

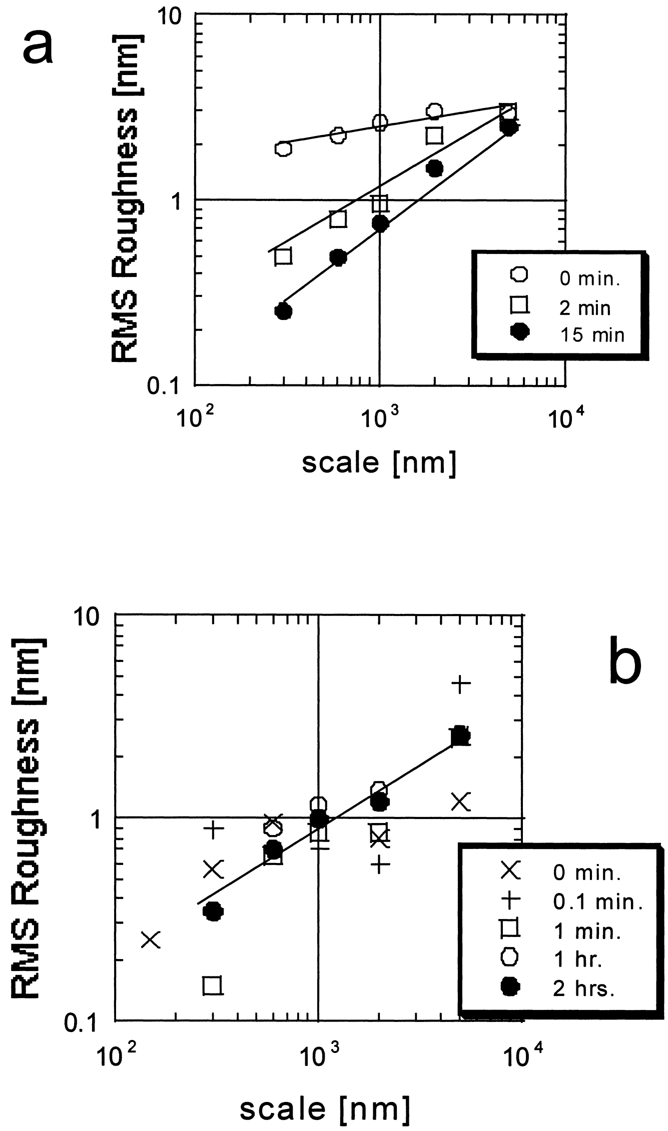


Fig. 5: Hurst plots of fractal analysis of RMS roughness determined from SPM scans of (a) confined and (b) free PMMA surfaces after different time of annealing at 130°C.

Conclusions

We have demonstrated that the auto-correlation function analysis of AFM images allows quantitative characterisation of amorphous polymer surfaces. This has been proved by application the procedure to a well characterised ordered structure: polystyrene latex quasi-crystal.

The correlation length of the height distribution of the surface of amorphous PMMA corresponds to internal dimensions of unperturbed polymer chains (radius of gyration) in the bulk state. Therefore, no special surface-driven structural behaviour has been found for this polymer in our AFM experiments.

The scaling behavior of roughness is different for the free polymer surface and for the confined surface of pristine unannealed films cast from the chloroform solution. As a result of annealing at $T > T_g$ both surfaces display similar fractal dimensionalities and correlation lengths.

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