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Conformation of single PMMA chain in uniaxially stretched film studied by scanning near-field optical microscopy

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Abstract

The conformation of the single polymer chain in uniaxially stretched poly(methyl methacrylate) (PMMA) films was studied by scanning near-field optical microscopy (SNOM), which enabled us to observe the elongated conformation of each polymer chain embedded in the film. The conformation of the individual PMMA chains was quantitatively evaluated from the fluorescence intensity distribution. Observation of films with different strains showed that the microscopic strain of the single chain was smaller than the macroscopic strain (ε) of the film. Especially at the later stage of the deformation ($\varepsilon > 1.5$), the PMMA chain was not stretched with the increase in the macroscopic elongation of the film, suggesting the presence of slipping of polymer chain on the course of stretching.

Keywords: Single polymer chain; Scanning near-field optical microscopy; Uniaxial stretching

1. Introduction

The variation of the conformation of a polymer chain is the origin of the unique physical properties of polymer materials such as the entropic elasticity. The chain morphology induced by uniaxial elongation has been extensively investigated so far from both theoretical and experimental points of view. The orientation of the polymer chain in the stretched state has been studied by various methods such as birefringence and infrared absorption dichroism. Whereas these techniques examine the average orientation of the chain segments, the conformation of the whole chain contour has been investigated by small angle neutron scattering (SANS) [1–9]. Both uncrosslinked [3–5] and crosslinked [6–9] polymer systems have been analyzed by SANS measurements. In these studies, the deformation of the deuterated polymer chains was examined in terms of the chain dimensions in the directions parallel and perpendicular to the elongation axis. In most cases, the deformation of the polymer chain differs from that expected from the affine deformation. The conformation of the single polymer chain under uniaxial deformation is complicated, and has not been completely described by the model.

The direct observation of the single polymer chain provides detailed information on the shape of each polymer chain and would be of great help to understand the rheological properties at the molecular level. Several studies on the direct observation of single polymer chains have been reported using atomic force microscopy (AFM) so far [10–12]. Since AFM probes the surface topography, it has been applied to the isolated polymer chains absorbed on a flat substrate in an extremely dilute condition. It cannot be used to observe a single polymer chain embedded in a bulk medium. Fluorescence labeling technique is an established method to distinguish such a single polymer chain from its surroundings [13,14]. However, the conventional fluorescence microscopy suffers from the diffraction-limited resolution of a half of the wavelength of light. Therefore, the application of the optical microscopy to single macromolecular imaging has been limited to the observation of huge biomacromolecules such as DNA [13,14].

Scanning near-field optical microscopy (SNOM) is an emerging scanning probe technique, which allows optical measurement with high resolution beyond the diffraction limit

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of light [15–19]. The light incidence to the sub-wavelength-sized aperture generates an optical near-field restricted in the space of the aperture size. This allows one to illuminate the specimen and to obtain the optical response from the nanometric area. Therefore, SNOM is a promising tool to directly observe the conformation of the single chain of the fluorescently labeled polymer [20,21]. Since the optical near-field illuminates the region beneath the surface by 200 nm, SNOM enables us to observe the chain conformation in the bulk system.

In the current study, we used SNOM to evaluate the conformation of the single polymer chain in the uniaxially elongated film and discuss the conformational change of poly(methyl methacrylate) (PMMA) chain by the macroscopic stretching.

2. Experiments

Perylene-labeled PMMA (PMMA-Pe) was synthesized by bulk free radical copolymerization of methyl methacrylate and 3-perylenylmethyl methacrylate initiated by azoisobutyronitrile. The fraction of the labeled unit was evaluated to be 0.77% by UV–vis absorption (U3500, Hitachi). The obtained polymer was purified by the fractional precipitation in methanol from toluene solution to achieve a relatively narrow molecular weight distribution. The weight- and number-averaged molecular weights, M_w and M_n, were determined by gel permeation chromatography (GPC) (D-7000G, Hitachi) using a column with the exclusion limit of 2×10^7 (Shodex KF806 M) with the eluent THF, which was calibrated by the PMMA standards (Scientific Polymer Products, Inc.): $M_w = 1.95 \times 10^6$, $M_n = 1.25 \times 10^6$, and $M_w/M_n = 1.56$.

In order to observe the isolated single labeled chains in the PMMA bulk, the PMMA thin film containing a trace amount of PMMA-Pe was prepared by the spin-coating method. The mixed toluene solution of the unlabeled PMMA ($M_w = 2.09 \times 10^6$) and PMMA-Pe (0.005 wt.% to the unlabeled polymer) was spin-coated onto a glass substrate to form a film with a thickness of 80 nm. The thin film was floated onto a water surface and picked up on a self-standing film of the unlabeled PMMA (the size was 25 mm × 7 mm, and the thickness was 300 μm), which was prepared by the solution casting of the unlabeled PMMA. The conformation of PMMA-Pe may be affected by the shear flow in the spin-coating process and the confinement effect of the thin film [22]. Therefore the sample film was annealed for 48 h at 180 °C in vacuum to reach the equilibrium. The later discussion was not affected by the further annealing at 200 °C, which indicates that the annealing time was sufficient. The GPC measurement of the film after annealing confirmed that the thermal cleavage of the polymer chains did not occur.

A tensile tester (RTM-500, Orientec) with a 10 kg load cell was used for stretching of the films. The length between the clamps was 20 mm. The stretching was carried out at 140 °C with a crosshead speed of 50 mm/min. The force and displacement were monitored on a chart recorder. After the stretching, the film was rapidly quenched to room temperature in the stretched state. The strain ε was calculated as $(l - l_0)/l_0$, where l_0 and l are the lengths of the film along the stretching direction before and after the elongation, respectively. The true stress σ was evaluated as follows assuming the constant volume of the film.

$$\sigma = \frac{F}{A} = \frac{F}{A_0}(\varepsilon + 1)$$

where F is the force applied to the sample, A is the sample cross-section at the strain of ε, A_0 is the cross-section at $\varepsilon = 0$. The photoelasticity measurement was carried out by a polarization microscope equipped with a Berek compensator.

The SNOM measurement was performed by a commercially available instrument (α-SNOM, WITec) with the hollow cantilever probe with a sub-wavelength aperture of 60 nm. The laser beam at a wavelength of 438 nm was focused onto the backside of the aperture to generate the optical near-field. The perylene fluorescence was collected by a microscope objective (0.80NA, 60×, Nikon) from the backside of the substrate and guided to a photomultiplier (H8631, Hamamatsu Photonics). The SNOM measurement was carried out at an ambient condition.

3. Results and discussion

Fig. 1a shows the stress–strain curve of the PMMA film. This indicates the stress yielding at $\varepsilon = 0.1$ followed by the necking of the film. The necking spread over the whole specimen at the range of $\varepsilon = 0.1-1.5$, and the stress increased again until the film fracture at $\varepsilon = 2.3$. Fig. 1b shows the result of the photoelasticity measurement. The birefringence Δn increased with the macroscopic strain of the film. The birefringence was proportional to the stress according to the linear stress-optical rule, indicating that the stress arises from the orientation of the PMMA chain [23].

Fig. 2a shows the fluorescence SNOM image of the initial PMMA film before stretching. The perylene-labeled PMMA chains embedded in the unlabeled PMMA bulk film were observed as bright spots in the fluorescence image. Each fluorescence spot was confirmed to be corresponding to the individual PMMA-Pe chain from the statistical analysis [18]. Since the optical near-field penetrates into the sample film by a few hundred nanometers, the shape of the PMMA chain observed in the SNOM image corresponds to the two-dimensional projection of the chain conformation. The ratio of the fluorescent monomer unit in PMMA-Pe was very small (0.77%); therefore, the effect of the dyes on the chain conformation is considered to be negligible. The single PMMA-Pe chains with the same molecular weight were observed in various forms, indicating the flexibility of the PMMA chain. Fig. 2b and c depicts the SNOM images of the films after stretching to the strain of 1.0 and 2.0, respectively. These images clearly show the polymer chains in the elongated conformation along the macroscopic stretching direction. In the same stretched film 1 h, 6 h, and 24 h after stretching, no conformational change was observed. Therefore the effect of the relaxation at room temperature is negligible because of the resolution of SNOM in the order of 10 nm.

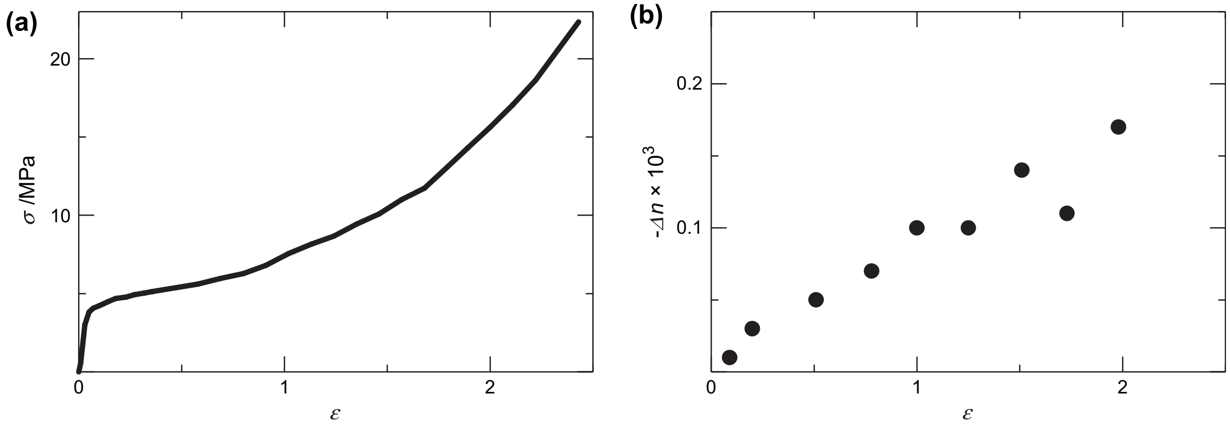

Fig. 1. (a) Stress–strain curve for the PMMA film stretched at 140 °C with a crosshead speed of 50 mm/min. (b) Birefringence of the stretched PMMA films plotted against the strain.

The conformation of the single PMMA chain was quantitatively evaluated from the fluorescence intensity distribution [14]. The fluorescence intensity is proportional to the number of fluorescent dye molecules randomly introduced along the PMMA-Pe main chain; therefore, the intensity at each pixel corresponds to the number of the chain segment therein. The first moment of the fluorescence intensity distribution denotes the position of the center of mass.

$$\mathbf{r}_0 = \frac{\sum_i \mathbf{r}_i I_i}{I}$$

where I_i is the fluorescent intensity at the i-th pixel, $\mathbf{r}_i$ is the position vector, and I is the total fluorescence intensity from the single chain. The second moment of the fluorescence intensity distribution is calculated as

$$R_{xx}^2 = \frac{1}{I}\sum_i (x_i - x_0)^2 I_i$$

$$R_{yy}^2 = \frac{1}{I}\sum_i (y_i - y_0)^2 I_i$$

$$R_{xy}^2 = R_{yx}^2 = \frac{1}{I}\sum_i (x_i - x_0)(y_i - y_0) I_i$$

where (x_i, y_i) and (x_0, y_0) are the positions of the i-th pixel and the center of mass in the orthogonal coordinate system. The tensor **R** is a parameter related to the polymer conformation [24].

$$\mathbf{R} = \begin{pmatrix} R_{xx}^2 & R_{xy}^2 \\ R_{yx}^2 & R_{yy}^2 \end{pmatrix}$$

The eigenvalues λ_1 and λ_2 ($\lambda_1 > \lambda_2$) are corresponding to the squared lengths of the long and short axes of the most appropriate ellipsoid considering the segmental distribution. When we let the x axis to be the macroscopic elongation axis, the angle, θ, between the stretching direction and the long axis of the ellipsoid is given by

$$\theta = \arctan\left(\frac{\lambda_1 - R_{xx}^2}{R_{xy}^2}\right)$$

The dimension of the optical near-field depends on the shape of the aperture of the cantilever. We eliminated this effect by the data correction considering the point-spread function of the probe used here.

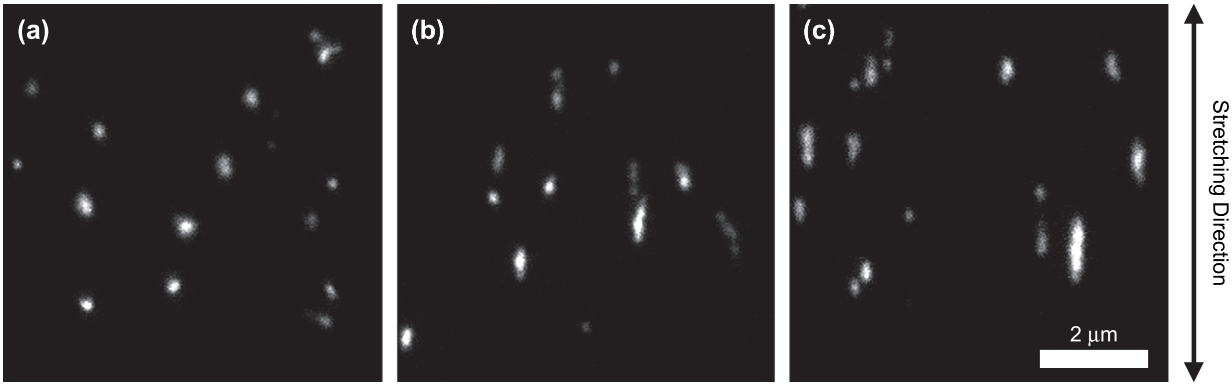

Fig. 2. Fluorescence SNOM images of single polymer chains in the PMMA films (a) before stretching, and after stretching to the strain of (b) 1.0 and (c) 2.0.

Fig. 3 shows the histogram of θ for the 150 PMMA-Pe chains. It clearly shows that before stretching each chain was randomly oriented. After stretching, the orientation angle shows the narrow distribution with a peak at $\theta \sim 0°$. This indicates that the PMMA chains in the elongated film take a stretched conformation along the elongation axis. The distribution narrowed with strain. None of the PMMA chains showed the orientation of $|\theta| > 45$ at $\varepsilon = 2.0$, indicating that all the chains deformed to the stretching direction.

Not only the direction of the orientation, the asphericity of the single chain is discussed in terms of the aspect ratio R_{xx}/R_{yy}, which is the ratio of the chain dimensions along the parallel and perpendicular axes to the stretching direction. Fig. 4 shows the distribution of R_{xx}/R_{yy} in the films before and after stretching. Before stretching, the PMMA chain did not show the circular form due to the conformational distribution. However, the orientation of the chain conformation was random, resulting in the homogeneous distribution of the orientational angle θ and the distribution of R_{xx}/R_{yy} in the range of 0.5–1.5 with the maximum probability at unity: $\langle R_{xx}/R_{yy}\rangle = 1.00 \pm 0.18$. On the other hand, the asphericity of the PMMA chains increased by the macroscopic elongation and its distribution spread: $\langle R_{xx}/R_{yy}\rangle = 1.35 \pm 0.38$ and 1.78 ± 0.63 in the films of $\varepsilon = 1.0$ and 2.0, respectively. Few chains showed the asphericity less than unity after stretching, indicating that most of the chains were deformed by the macroscopic elongation.

The deformation at the single chain level is compared with the macroscopic strain. The microscopic strain at the single chain level, ε_c, can be defined as the increment in R_{xx} to the initial value of R_{xx}. In the current experiment, the film elongation and the SNOM imaging were performed with the separate instruments; therefore, it was impossible to observe both R_{xx0} and R_{xx} for the identical single chain. Therefore, we define the average chain strain as

$$\overline{\varepsilon_c} = \frac{\langle R_{xx}\rangle}{\langle R_{xx0}\rangle} - 1$$

where R_{xx0} indicates the R_{xx} before stretching, and $\langle\ \rangle$ denotes the ensemble average. Fig. 5 shows the relationship between the microscopic and macroscopic strain. It should be noted that the macroscopic strain is not homogeneous through the whole film when the necking occurs ($0.1 < \varepsilon < 1.5$), and the thinnest region of the film was observed in the SNOM

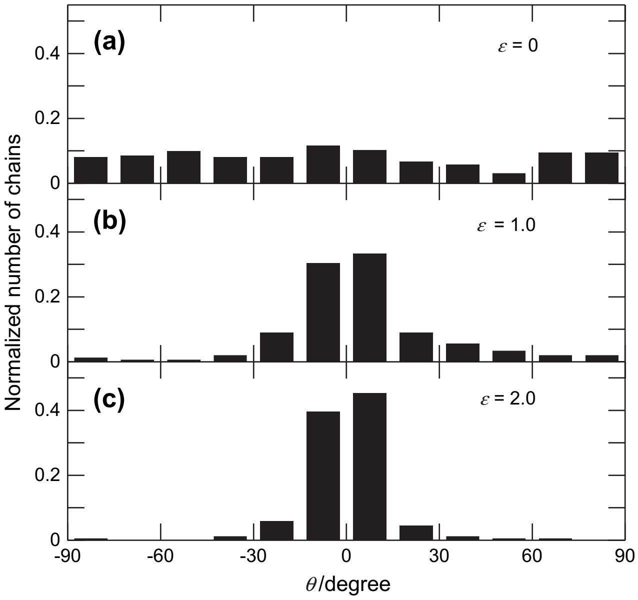

Fig. 3. Histograms of the orientation angle of the PMMA chain to the stretching direction of the film: (a) before stretching, and after stretching to the strain of (b) 1.0 and (c) 2.0.

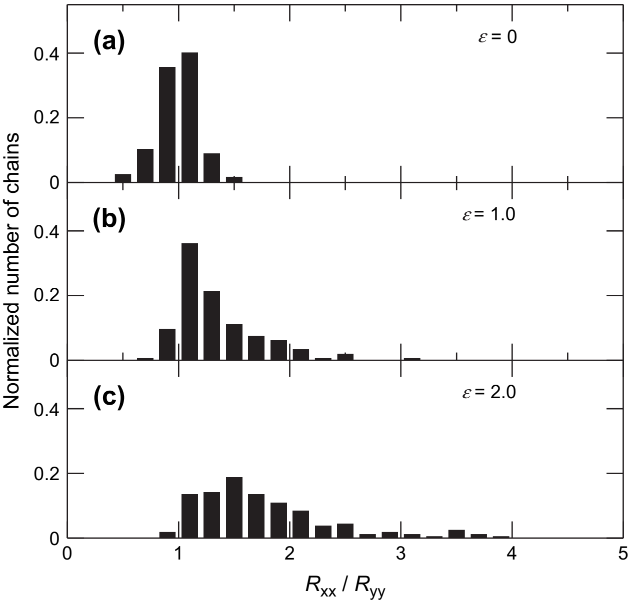

Fig. 4. Histograms of the chain aspect ratio R_{xx}/R_{yy} in the film (a) before stretching, and that after stretching to the strain of (b) 1.0 and (c) 2.0.

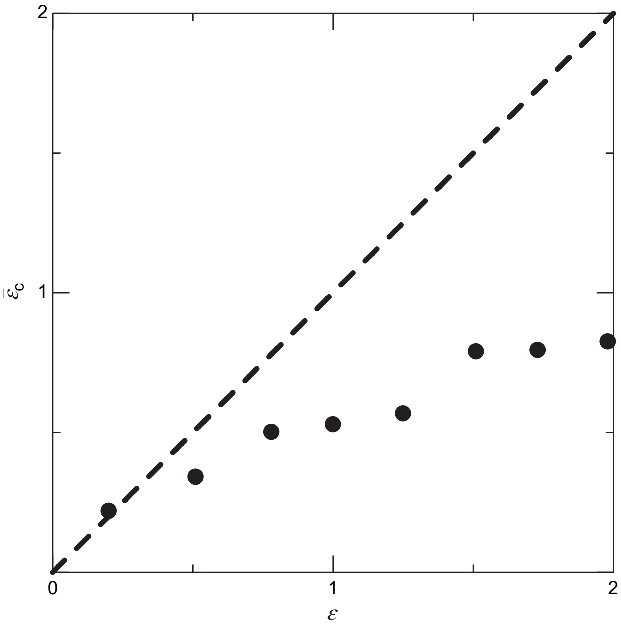

Fig. 5. Average chain strain plotted against the macroscopic strain of the film. The broken line indicates the case of the purely affine deformation ($\overline{\varepsilon}_c = \varepsilon$).

measurement. This means that we observed the locally stretched area and probably underestimated the macroscopic strain because it was evaluated from the whole length of the film. Nevertheless, in spite of the underestimated macroscopic strain, Fig. 5 indicates that the average chain strain was still smaller than the macroscopic strain, showing the deviation from affine deformation at the single chain level. Since the film used had no chemical crosslinks, the polymer network is supported only by physical entanglements. Therefore, it is suggested that the chains cannot follow the mechanical deformation and slip along the adjacent chains. Another possible process is some chain breakage, but this was not observed from the GPC measurement of the film after stretching. At the later stage of the deformation ($\varepsilon > 1.5$), where the necking had finished and the macroscopic strain was homogeneous over the whole film, $\bar{\varepsilon}_c$ hardly increased further. In this region, the film deformation is mostly caused by the intermolecular chain slip.

4. Conclusion

The conformation of the single polymer chain in uniaxially stretched PMMA was studied by SNOM. We succeeded in the direct observation of the individual elongated single polymer chain. The chain showed smaller deformation than that expected from the affine deformation. The deviation from the affine deformation increased with the macroscopic strain, suggesting the presence of chain slip in the film. The further study using SNOM is expected to reveal the mechanical property of polymer solids from the level of single polymer chain.

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