Supplementary information for:

Relaxation of single polymer chain in binary molecular weight blends observed by scanning near-field optical microscopy

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1 Analysis of SNOM images

The SNOM image of a PMMA chain is the result of the convolution of the chain conformation and the point spread function (PSF) of the apparatus. As mentioned in the text, the apparent square chain dimension $\langle {R_{xx}}^2 \rangle$ is mathematically given by the sum of the second moment of the chain conformation $\langle {R^*_{xx}}^2 \rangle$ and the PSF of the apparatus. Now we show that this relationship can be applied to the current SNOM data. In a bulk state, the mean square dimension of chains is proportional to the molecular weight:

$$\langle {R^*_{xx}}^2 \rangle = kM, \tag{S1}$$

where k is a constant. The fluorescence intensity I from a labeled chain is proportional to the number of fluorescence dye molecules in the chain. Since the fluorescent moiety is randomly introduced to the polymer chain, I is proportional to the molecular weight. Therefore,

$$\langle {R^*_{xx}}^2 \rangle = k' \langle I \rangle, \tag{S2}$$

where k' is a constant. From eqn (10) and (S2),

$$\langle R^2_{xx} \rangle = k' \langle I \rangle + a^2, \tag{S3}$$

where a^2 is the variance of the PSF. This indicates that $\langle R^2_{xx} \rangle$ is linearly dependent on the fluorescence intensity. In order to compare the experimental data with eqn (S3), the values of R^2_{xx} and I were averaged over $\sim$10 chains, which have similar I values. Fig. S1 shows the relationship between $\langle R^2_{xx} \rangle$ and I for the PMMA chain in the films before stretching. $\langle R^2_{xx} \rangle$ increased linearly with $\langle I \rangle$, which is consistent with eqn (S3). The value of a^2 can be determined to be ca. 4500 nm^2 as the extrapolated value of $\langle R^2_{xx} \rangle$ at $I = 0$.

The value of a^2 was independently evaluated from the measurement of the PSF of the apparatus. The PSF can be observed as the image of an infinitely small object. We used quantum dots as the sample because of

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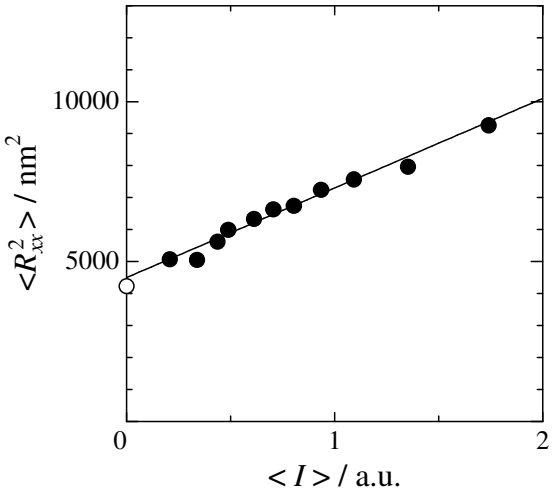

Fig. S1 Square chain dimension plotted against the fluorescence intensity, which were averaged over ~ 10 chains with near I, in the film before stretching. The open circle at $I = 0$ indicates the value of a^2 evaluated from the observation of a quantum dot.

their bright fluorescence and infinitely small size compared to the SNOM aperture.[1] Commercially available quantum dots (Qdot 655 ITK, Invitrogen) were dispersed in a poly(vinyl alcohol) film with a thickness of 80 nm and observed by SNOM. The intensity profile along the x axis was fitted to a Gaussian function. The fluorescence intensity distribution of the quantum dot was well fitted by the Gauss function with a standard deviation of 65 nm and the variance of 4225 nm^2. This is in good agreement with the value of a evaluated from the extrapolation of $\langle R_{xx}^2 \rangle$ at $I = 0$ as is shown in Fig. S1. Thus, the actual chain dimension $\langle R_{xx}^{*\,2} \rangle$ can be analyzed from the SNOM image and the extension ratio of single chain λ_c can be evaluated as follows:

$$\lambda_c^2 = \frac{\langle R_{xx}^{*\,2} \rangle}{\langle R_{xx}^{*\,2} \rangle_0}. \tag{S4}$$

References

1 J. Yang, R. Sekine, H. Aoki and S. Ito, *Macromolecules*, 2007, **40**, 7573–7580.