

## Detection of Site-dependent Segmental Mobility of Polymer by Fluorescent Defocused Imaging\*

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**Abstract** Polymer chain ends play an important role in the glassy dynamics of polymeric materials. In this study, a combination of single molecule defocus fluorescence microscopy and well-controlled atom transfer radical polymerization was used to investigate site-dependent segmental mobility of poly(*n*-butyl methacrylate). As the temperature increased, the rotation of fluorophores, which were selectively labelled in chain end and chain middle, was gradually activated. The power spectra of rotation trajectories, the distribution of angular displacement as well as the population of rotating fluorophores demonstrated that the local dynamics was more activated at the chain ends than the middles, showing the unique contribution of the chain end to the dynamics of the system.

**Keywords** Glass transition; Segmental mobility; Chain end effect; Fluorescent defocused imaging

**Electronic Supplementary Material** Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1976-8>.

## INTRODUCTION

Though holding just very low proportion in weight, polymer chain ends affect the dynamics of polymeric materials remarkably. Unique location of chain end along the chain gives its specificity in dynamics. Many processes of polymer chain, such as reaction with surrounding molecules<sup>[1]</sup>, translocation through a micro-pore<sup>[2–5]</sup>, reptation in melts<sup>[6]</sup> or diffusion at interfaces<sup>[7]</sup> are initiated by chain ends. For glass transition<sup>[8–10]</sup>, in which the dynamics of a chain segment is very much involved, dynamics around a chain end has been receiving lots of attention. Based on the assumption that polymer chain ends have excess free volume, the relationship between glass transition temperature ( $T_g$ ) and number-average molecular weight ( $M_n$ ) was derived, *i.e.* the Fox-Flory relation<sup>[11]</sup>. It is also discovered that the fragility index of polystyrene decreased with a reduction of the molecular weight, interpreted as the result of an increase in any configurational freedom conferred by chain ends<sup>[12, 13]</sup>. Besides bulk materials, the effects of chain ends on the dynamic behaviors of polymer thin films are often more emphasized, relative to the bulk, since chain ends tend to segregate at the surfaces and interfaces easily<sup>[14, 15]</sup>. Chain ends with different chemical structures can significantly change the property of bulk polymer materials and thin films<sup>[14, 16–18]</sup>. Understanding dynamic properties around the chain ends is important not only for basic theory developments but also for advanced polymeric material manufacturing.

Though attempts to elucidate specific contributions to the segmental dynamics have been made by several techniques such as electron spin resonance spectroscopy<sup>[19, 20]</sup>, broadband dielectric spectroscopy<sup>[21]</sup>, nuclear

\* This work was financially supported by National Basic Research Program of China (No. 2014CB643601).

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Received April 8, 2017; Revised May 9, 2017; Accepted May 10, 2017

doi: 10.1007/s10118-017-1976-8

magnetic resonance spectroscopy<sup>[22]</sup>, getting a better understanding of chain end dynamics and quantitative information of the local environment is still a challenge. The technical challenge of doing this research is the capability to achieve the combination of well-controlled site sensitivity and detection with high sensitivity.

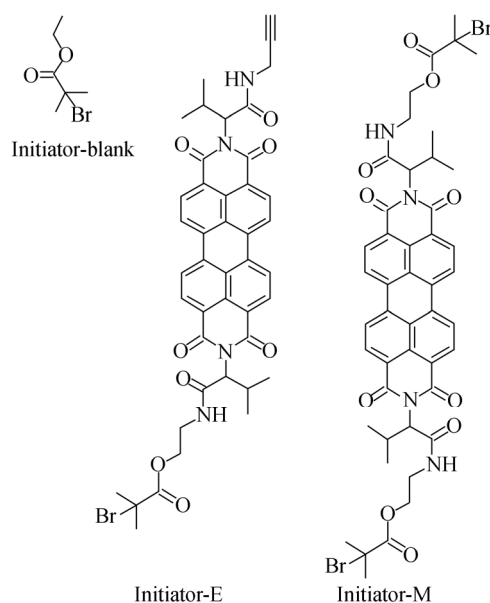
Single molecule defocus fluorescence microscopy has the potential to provide a deeper insight. It has been demonstrated to be very powerful in studying glassy polymer systems<sup>[23–26]</sup>. By recording and analyzing the diffraction patterns of the fluorescence emission of single dye molecule, the three-dimensional orientation of fluorescence emission dipoles can be explicitly determined and the rotational motion of individual molecules can be monitored<sup>[27]</sup>. With its high sensitivity and good spatial resolution, this technique allows monitoring individual molecules separately, thus avoiding ensemble averaging. With the combination of the precisely controlled polymerization and fluorescence-labelling technique, this approach can be promising to access the dynamics of polymer in a site-sensitive manner, and to access the local dynamics at polymer chain ends.

In this study, single molecule defocused fluorescence microscopy is adopted to track the rotational motion of fluorescent molecules, which are precisely labelled to different positions of a model polymer, poly(*n*-butyl methacrylate) (P*n*BMA). The precise labelling is performed by well-controlled atom transfer radical polymerization (ATRP) using fluorescent molecule with the active group either at one side or at both sides of the molecule. Site-dependent segmental dynamics is investigated by comparing probes' rotational behavior of different positions.

## EXPERIMENTAL

### Materials

P*n*BMA is synthesized *via* ATRP<sup>[28]</sup>. Three different initiators are used to synthesize fluorescence labelled P*n*BMA and non-labelled polymer. For fluorescence labelled polymers, functionalized fluorescent molecules are synthesized as initiators so that the fluorophore can be positioned at either the end or the middle of the polymer chain. The chemical structures of the initiators are provided in Scheme 1, in which the Initiator-E and Initiator-M are for end-labelling and middle-labelling P*n*BMA, respectively, while Initiator-blank is for the polymer without fluorescence labelling. Perylene diimide (PDI) is chosen as the fluorescence molecule for labelling due to its large absorption coefficient, high emission quantum yield and durability against photo-bleaching<sup>[29–31]</sup>. Methodology for the synthesis of PDI-labelled initiator and the general process of ATRP are shown in the supporting information (SI). By using Initiator-E, the ATRP reaction results in the linear P*n*BMA with its chain



**Scheme 1** Chemical structure of initiators used for synthesizing fluorescence-labelled P*n*BMA as well as that without fluorescence labelling

end labelled with PDI (denoted as Linear-E), while by using Initiator-M, polymer chains grow from both sides of the fluorescent initiator, resulting in the PDI positioned at the middle of the chain, *i.e.* at the half way of the contour length of the polymer (denoted as Linear-M).

The parameters of the polymer samples are listed in Table 1. The labelled and unlabeled polymers have similar molecular weights. “Linear-blank” denotes PnBMA without fluorescence labelling while “Linear-E” and “Linear-M” denote PnBMA labelled with PDI fluorophore at the end and the middle of the chain, respectively. Differential scanning calorimetry (DSC) measurements were conducted to characterize the  $T_g$  values of the bulk sample and spectroscopic ellipsometry was used to characterize the  $T_g$  values of the thin films. Secondary ion mass spectroscopy (SIMS) was employed to investigate the distribution of fluorescence probes along the direction normal to the film’s plane and no obvious segregation to the polymer-air or polymer-substrate interfaces was found. DSC measurement was carried out using Q2000 differential scanning calorimeter (TA Instruments) and the details of measurements are provided in SI.

**Table 1** A few parameters of the polymer synthesized

| Polymer               | $M_w \times 10^{-3}$ (g·mol <sup>-1</sup> ) | $M_w/M_n$ | $T_g$ -DSC (°C) | $T_g$ -Ell <sup>a, c</sup> (°C) |
|-----------------------|---------------------------------------------|-----------|-----------------|---------------------------------|
| Linear-blank          | 210                                         | 1.09      | 37.0            | 34.5                            |
| Linear-E <sup>b</sup> | 205                                         | 1.15      | 36.5            | 34.5                            |
| Linear-M <sup>b</sup> | 220                                         | 1.19      | 37.0            | 35.0                            |

<sup>a</sup>  $T_g$  determined by ellipsometry measurements of thermos-expansion coefficient of thin film sample; <sup>b</sup> The fluorescence labelling ratio is 100% due to the use of fluorescent initiator for polymerization; <sup>c</sup> Due to the lower cooling rate of ellipsometry measurements (1.0 K·min<sup>-1</sup>) than that of DSC measurement (10.0 K·min<sup>-1</sup>), the  $T_g$ -Ell value is constantly lower than the  $T_g$ -DSC value. Also, due to the relatively large film thickness, the possible effect of polymer-substrate attraction is not observed.

Fluorescence-labelled PnBMA was dissolved together with the blank (un-labelled) PnBMA. The concentration of the fluorescence-labelled polymer was approximately 10<sup>-10</sup> mol·L<sup>-1</sup>. By spin-casting, sample films were fabricated on 0.17 mm-thick glass coverslips (Thermo Fisher) at a spin rate of 4000 r·min<sup>-1</sup>. Afterwards, the samples were annealed in vacuum at 100 °C for 12 h to remove possible residual solvent and stress. Film thickness was approximately 75.0 nm, measured by ellipsometry on films prepared on silicon wafers under identical condition.

### Fluorescence Microscopy

Fluorescence defocus microscopic measurements were carried out on an Olympus IX-71 inverted microscope equipped with an Andor 887 EMCCD camera, as described previously<sup>[23, 24]</sup>. Excitation laser (532 nm) was beam-expanded, collimated and introduced into the microscope. Reflected by a dichroic mirror, the excitation was introduced into the sample through an oil-immersion objective lens. The optical setup was configured so that the laser beam was focused on the focal plane at the back aperture of the objective and optimum incident angle was adjusted so that total internal reflection condition was reached. The excitation light was adjusted to be circularly polarized in order to guarantee equal excitation probability for fluorophores with all spatial orientations. The optimal defocus distance was set to about 0.6 μm to generate the well-defined diffraction patterns. The samples were housed inside a commercial hot-cold stage for inverted microscopes (HCS60, INSTEC). In order to guarantee uniform distribution of temperature, the temperature of the objective lens was also controlled by a commercial lens heater (Bioscience Tools). After calibration, the temperature of the sample was well stabilized with a fluctuation less than 0.5 °C. Image analysis was conducted using commercial software, Image J.

## RESULTS AND DISCUSSION

A typical single molecule defocus fluorescence image of the sample is displayed in Fig. 1. In the image, the fluorescence emission patterns of individual fluorophores are clearly visible and most of them are of double-lobed shape. As demonstrated in previous literatures<sup>[23, 26]</sup>, such well-defined emission patterns with symmetrical double-lobed shape indicate the dipole moments of the fluorophores are oriented parallel to the film’s surface.

Beside, a few fluorophores having out-of-plane orientation are also visualized. Under the temperature studied, no translational diffusion was observed. Instead, rotation of individual fluorophore was clearly observed. A typical video of defocus fluorescence microscopy is provided in SI.

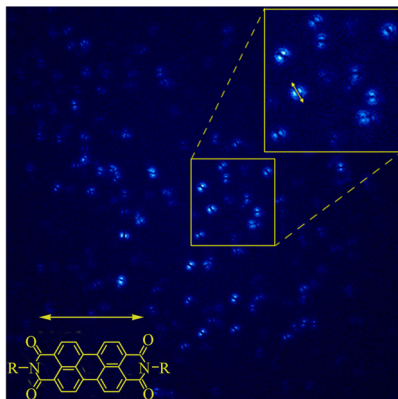


**Fig. 1** A typical single molecule defocus fluorescence image of Linear-M in PnBMA thin film with the thickness of 75.0 nm at 27.4 °C. The image size is 50  $\mu\text{m}$   $\times$  50  $\mu\text{m}$ . The chemical structure of the fluorophore is provided in the image together with the direction of its transition dipole moment. Inset: the magnified portion of the image, in which the fluorescence emission pattern of one fluorophore and the direction of its dipole moment are displayed. The online version is colorful.

At relatively low temperatures, most of the emission patterns are stationary and only a small portion of the patterns exhibits orientation changes with time, demonstrating that most of the probes' motion is frozen. As expected, rotation of more fluorophores is observed when temperature rises. Another key feature is that the rotational motion of activated fluorophores becomes more and more "violent", *i.e.* rotation angle amplitude gets bigger.

Just as demonstrated previously<sup>[24]</sup>, due to the existence of dynamical heterogeneity inside the glassy systems, it is quite helpful to characterize the rotations of the fluorophore in frequency domain, other than time domain. After recording the rotation trajectories of individual fluorophores, their power spectra are generated by fast Fourier transformation. In the current study, more than 150 fluorophores are investigated under each experimental condition and their average power spectra are displayed in Fig. 2.

These power spectra demonstrate the major contribution of local vibrations in the low frequency range, represented by a decay from  $10^{-2}$  Hz to  $10^0$  Hz, indicating the frequency range where the major dynamics with the length scale related to size of the fluorophore, *i.e.* a van der Waals volume of 0.51 nm<sup>3</sup> <sup>[24]</sup>. The existence of discrete vibration modes inside the rotational motion of the fluorophores is also observed. The effect of increasing temperature is shown as the vast amplitude increase in the higher frequency region for both end- and middle-labelling samples. The amplitude's increase shown in Fig. 2(a) is higher than that in Fig. 2(b), especially for the high frequency region, indicating that with the increasing temperature, the motion at the chain end is much more activated than that at the middle. A previous study has shown that the elevation of temperature results in the change of dimension of the region with cooperative motion (the cooperatively rearranging region), as expressed by the much bigger increase of amplitude in higher frequency region than those in lower frequency region<sup>[24]</sup>. This experimental fact shows that the motion of the fluorophore at the chain end is much more sensitive to temperature change than that at the middle of chain. Direct comparison between the rotation of fluorophore at the end and the middle of the chain clearly demonstrates more activated motion at the chain end than the middle across the frequency window, especially below  $2 \times 10^{-1}$  Hz. It is noted that such a difference is not obvious at the low temperature (Fig. 2c) while it is very remarkable at the higher temperatures (Figs. 2d and 2e). A major vibration mode is observed, located around  $7 \times 10^{-2}$  Hz, whose amplitude is much larger for the end than the middle of the polymer chain.

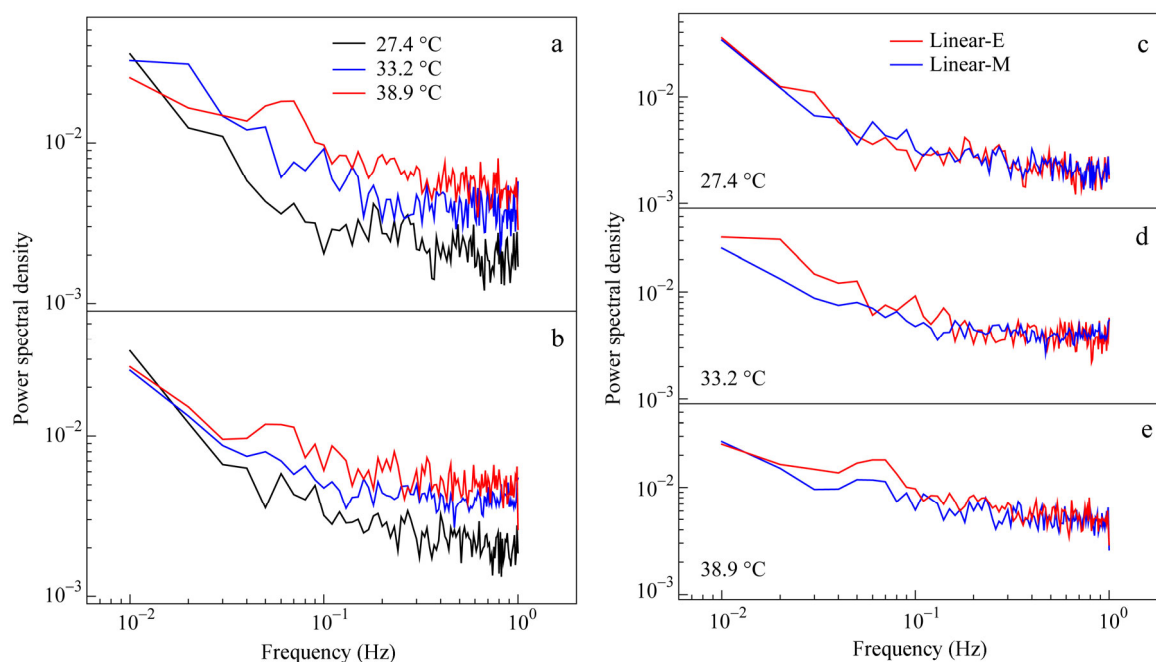


**Fig. 2** The averaged power spectra of more than 150 fluorophores recorded in the film sample of 75 nm thickness under different temperatures (The temperatures are displayed in the figure): (a) end-labelled PnBMA and (b) middle-labelled PnBMA; (c–e) comparison of power spectra between the end-labelled (Linear-E) and middle-labelled (Linear-M) sample at each temperature, *i.e.* 27.4, 33.2 and 38.9 °C, respectively (The online version is colorful.)

The activation of vibration modes of the high frequency at elevated temperature indicates more intensive absorption of thermal energy by the system, expressed by the more vigorous rotation of the fluorophores<sup>[24]</sup>. As an alternative indication of the activation energy, the variable of the fraction of rotating molecules ( $f_R$ ) is adopted, *i.e.* the ratio of number of rotating fluorophores over the total number of fluorophores in the field of view ( $f_R = N_{\text{rotating}}/N_{\text{total}}$ ), where  $N_{\text{rotating}}$  is the number of rotating fluorophores and  $N_{\text{total}}$  is the total number of the fluorophores in the images. The data are displayed in Fig. 3.

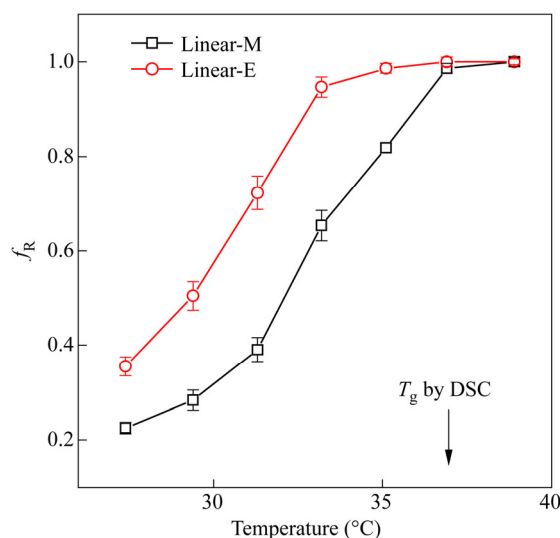


**Fig. 3** The ratio of the number of rotating fluorescent molecules to the total number of molecules ( $f_R$ ) as a function of the temperature, for fluorophore attached to the chain end (Linear-E) and the middle (Linear-M)

For both samples with fluorophore attached at the chain end and the middle, the  $f_R$  value increases monotonically with temperature, demonstrating the activation of rotation of more fluorophores. But, vast difference is observed—the  $f_R$  value of the end-labelled sample is constantly higher than that of the middle-labelled one, before both values reach unity at a high enough temperature ( $\sim 37^\circ\text{C}$ ). The results show that the fluorophore at the chain end has, in general, a lower activation energy than the middle. This is fairly understandable as it is believed that the chain end should have larger free space than the middle due to the topological reason, and therefore molecular motion at the chain end is much easier to activate than that at the middle. It is noted that the above observation is only for the identical time window ( $10^{-2}$ – $10^0$  Hz, as determined by the time resolution of the microscopy and the overall length of the rotation trajectory).

Rotation trajectories of fluorophores are inspected. Two typical examples are provided in Fig. 4(a), in which a “frozen” and a “rotating” trajectory are displayed. For the frozen fluorophore, its in-plane angle ( $\varphi$ ) fluctuation is very small, less than 0.2 rad, while for the rotating one, large orientation fluctuation is clearly demonstrated—during the observation time of 100 s, the difference in  $\varphi$  value within a time interval of 2.5 s is as big as 2.0 rad. Large “jumps” (angle change larger than 2.0 rad within 0.5 s) are also observed, demonstrating the vast and sudden change of the micro-environment surrounding the fluorophore in the polymer film.

The distribution of angle displacement (increment) should provide information on amplitude of the rotational motion, as the inspection of the single molecule video shows more “violent” motion at elevated temperature. Data in Fig. 4(b) clearly show the distribution as the superposition of two families of motions—a narrow distribution for the smaller displacements and a much wider distribution for the bigger displacements, just as the general conclusion drawn from the trajectory inspection. The larger displacement part of the distribution cannot be fitted with Gaussian distribution while the smaller displacement part is tentatively fitted by the Gaussian function (Fig. 4b). Apparently, the exponential distribution of the larger displacements demonstrates the dynamical heterogeneity<sup>[32, 33]</sup>. For smaller displacements, tentative fitting by Gaussian distribution does not provide satisfactory results and an exponential distribution can also be applied (detailed in SI), and therefore dynamical heterogeneity is exposed for motion with both small and large angle displacements.

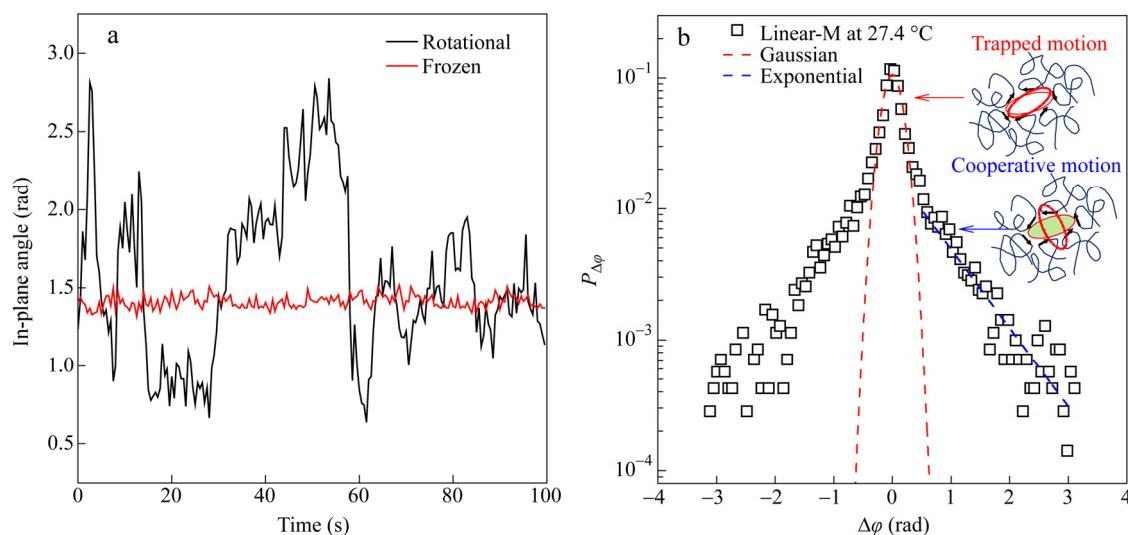


**Fig. 4** (a) Two typical examples of rotation trajectory (temporal variation of in-plane orientation angle) of sample Linear-M recorded at  $27.4^\circ\text{C}$  inside 75 nm thick film; (b) Angle displacement distribution ( $P_{\Delta\varphi}$ ) of Linear-M labelled fluorophore at  $27.4^\circ\text{C}$  (The red dashed line demonstrates the Gaussian fit and the blue dashed line is for the exponential fit. Inset: schematic pictures explaining the physical mechanism of probe’s trapped and cooperative motion.) (The online version is colorful.)

Rotations with both small and large displacements exhibit non-Gaussian distribution, indicating their inhomogeneous nature of dynamics. The smaller displacement is considered to be trapped motion, representing a

state under a certain constrain or environment while the larger displacement indicates the transition process from a state with one extent of constrain to another. None of them is dynamically homogeneous and it is believed that the fluorophore probes the dynamical heterogeneity under its own length scale. If the glassy system consists of multiple regions with its own constrain or environment, from a small to a large scale, depending on the time scale at which the dynamics is probed, the current investigation is probing dynamics with length scale larger than the dimension of the fluorophore ( $0.51 \text{ nm}^3$ )<sup>[24]</sup> and within the observation time window, *i.e.* 100 s. Being much larger than the polymer segments, the fluorophore's motion can be the result of cooperative motion of multiple segments. Therefore, any motion with large placement is attributed to the noticeable motion of much more cooperatively moving segments while the small displacement is the result of local rearrangement of smaller cooperative moving domains, just as described by the well-known cooperatively rearranging region (CRR)<sup>[34, 35]</sup>. A schematic picture is provided as the inset of Fig. 4.

What is the situation when temperature is raised? The displacement distributions of Linear-E and Linear-M under 27.4, 33.2 and 38.9 °C are compared in Fig. 5. For both samples, with the increase of temperature, the distribution of the small displacement broadens while the broadening for the large displacement is less obvious. The data demonstrate the much higher activation of the rotational motion at elevated temperature. At temperature higher than  $T_g$ , the distribution of the small displacement “merges” into that of the big ones (Figs. 5a and 5b). This is an indication of the release of previously restricted motions. Taking the picture of CCR model, this process is equivalent to the shrinking of CRR domains—the previously constrained domains with cooperative motion get smaller and the displacement of the rotation becomes larger. The values of non-Gaussian parameter  $\zeta = \langle (\Delta\phi)^4 \rangle / 3 \left( \langle (\Delta\phi)^2 \rangle \right)^2 - 1$  are discovered to decrease from 1.7 and 2.2 at 27.4 °C to 0.33 and 0.35 at 38.9 °C respectively, showing a decrease in dynamical heterogeneity when the temperature is elevated.

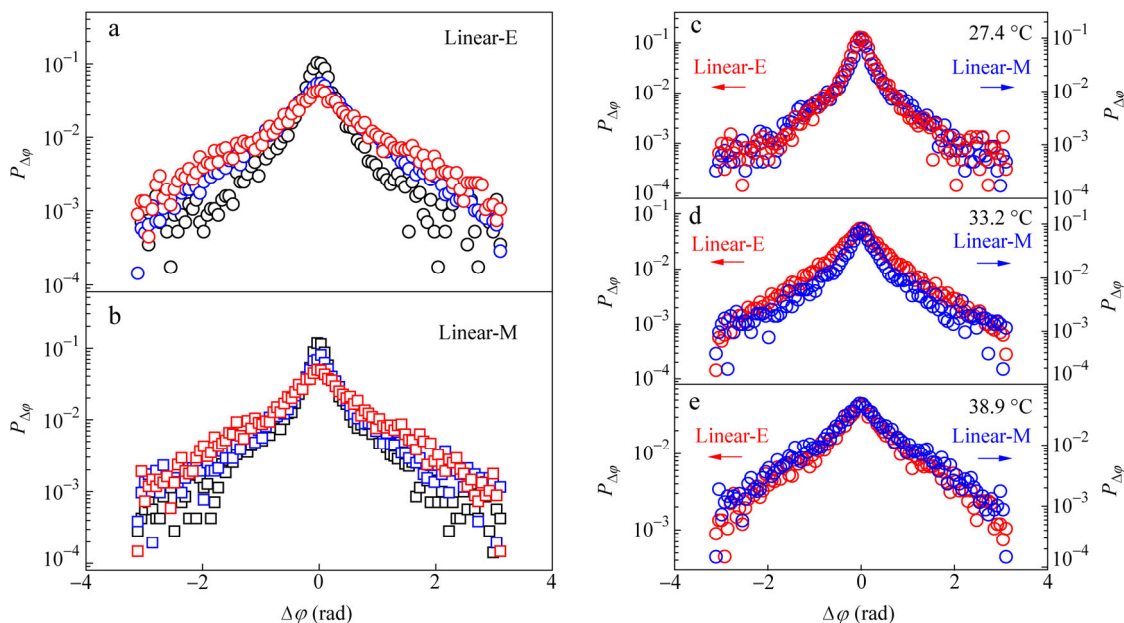


**Fig. 5** Distribution of in-plane orientation angle displacement (increment,  $P_{\Delta\phi}$ ) of fluorophore labelled at (a) chain end (Linear-E) and (b) the middle (Linear-M) under different temperatures, *i.e.* 27.4 °C (black), 33.2 °C (blue) and 38.9 °C (red); Direct comparison between Linear-E and Linear-M at (c) 27.4 °C, (d) 33.2 °C and (e) 38.9 °C with both data rescaled in display (normalization) (The online version is colorful.)

The difference between the end and middle of the chain is not obvious at temperatures well below and above  $T_g$  (Figs. 5c and 5e) while the distribution for the end is wider at temperature near  $T_g$ , according to the direct comparison between the normalized data of the two samples under identical experimental condition

(Figs. 5c–5e). This result is really surprising because the difference is supposed to be larger at lower temperature and smaller at higher temperature, due to the vast activation of the local dynamics when the temperature is raised. The indistinguishable difference at low temperature is attributed to the small chance of activation of the local vibration mode, for both the end and the middle of the polymer chain. The difference in distribution of angular displacement is noticeable only near  $T_g$ , indicating the vast difference between the micro-environment of the chain end and the middle, within the observation time window of 100 s. Within this period of 100 s, the dynamics around the volume of  $0.51 \text{ nm}^3$  at the chain end is much more activated than that at the middle of the chain. This is a clear distinction observed on local dynamics at different locations of the linear polymer chain.

## CONCLUSIONS

The high sensitivity of single molecule defocus microscopy enables detection of local dynamics at different location of a polymer chain, taking the advantage of precise fluorescence labelling. The power spectra of the rotation trajectories, the population of rotating molecules as well as the distribution of angular displacement of the rotation demonstrate that the local dynamics at the chain end is far more activated than that in the middle of the chain. It is discovered that the local dynamics within the optimum time window for glass transition is more activated at the chain end, exhibiting the contribution of chain ends to the variation of glass transition temperature.

**ACKNOWLEDGMENTS** Experimental help in Secondary Ion Mass Spectroscopy by Prof. Fuyi Wang and Prof. Kui Wu is appreciated.

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