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Surface Dynamics of Poly(Methy Methacrylate) Films Affected by Concentration of Casting Solution

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ABSTRACT: The effect of concentration of casting solution on the surface dynamics of corresponding spin-coated poly(methyl methacrylate) (PMMA) was investigated by measuring the surface reorganization of fluorine tracer-labeled PMMA. The onset temperature of fluorinated PMMA chain end reorganization (T_R^{onset}) was identified and is shown to depend on the PMMA concentration in the film-forming solution. It was found that the surface T_R^{onset} and relaxation activation energy E_a of the PMMA films prepared from 4.2 wt% PMMA cyclohexanone solution are 70°C and 260 kJ/mol respectively, which are higher than those of the PMMA films prepared from 0.8 wt% PMMA cyclohexanone solution (55 °C and 144 kJ/mol respectively). The T_R^{onset} and E_a of PMMA films increased with increasing concentration of casting solution within the range of 1.8wt% and 4 wt%. The chain entanglement of PMMA chains is proposed as the speculative origins for this observed depressed dynamics of poly(methyl methacrylate) chains on the films surface prepared by casting solutions of various concentrations.

Keywords: surface dynamics; poly (methyl methacrylate); chain entanglement; casting solution concentration

1. INTRODUCTION

Many recent technological devices have been reduced to nanometer scales, so that the performance of thin film coatings and nano-devices are intimately correlated with the dynamic properties of the chains residing on a surface. [1-4] In addition, the dynamics of polymer chains near a surface is of significance for a broad range of practical applications, including surface coatings, lubricants, adhesives, microelectronics and biomedical engineering uses such as DNA packaging in viruses.[5-9] For the past two decades, investigations of chain dynamics on polymer surfaces have attracted much attention [4,10-14] and considerable data exits for systems such as atactic polystyrene (PS) [4,10-12] and poly（methyl methylacrylate） (PMMA) [13,15-18] in particular. In these situations, the polymer chains were homogeneously distributed on the surface without any chain association or preferred interactions. The results showed that the quasi-equilibrated homopolymer chains on free surfaces exhibit faster relaxation and lower T_g compared with the molecules in bulk. [10-14] These enhanced surface dynamics of quasi-equilibrated homopolymer chains are very representative of the general behavior for macromolecular motions on a surface. However, it was reported previously[19] that chain aggregative structures significantly influence the surface dynamics of PMMA, in which the relaxation activation energy (E_a) and the onset temperature of surface rearrangement (T_R^{onset}) of the micellized PMMA are much higher than those of the non-associated free chains.

For ultrathin polymer films, some factors have been reported to influence the observed dynamics of chains, including measurement ambients,[20,21] molecular weight,[22,23] tacticity and conformation of the polymer, [24-26] the nature or properties of the substrate surface[17,24,27-30] and interchain interactions.[31-38] Fundamentally different from the features of small molecules, the interactions of polymer chains are inherently complicated, and for which the influence of chain entanglement has most commonly been reported. The effect of entanglement on chain motion was reported to be induced by different molecular weights (MW) and concentrations of the solution.[28,33,34] Polymers with low MW are considered to exist as separate, discrete entities that form close-packed and sphere-like structures, in which the only interactions between the chains arise from van der Waals forces. Conversely, polymers with high MW may form large systems of entangled chains,[36,37] resulting in restrained chain motions.[31,39] At the same time, it was observed that the chain mobility of PS films prepared from the concentrated solution was weakened, since the density of chain entanglement increased with increasing solution concentration. [33] The chain entanglement was also influenced by the solvent quality and annealing temperature. In a good solvent, the interaction between the chain segments and solvent molecules is more favorable than that between the chain segments, resulting in swelling of the chains. [26] For a solvent of poor quality, the case is contrary to that above, with the chain coil size becoming smaller and individual polymer chains would be more compact, so that the interchain entanglement is further reduced.[40] It is documented that chain conformations in spin-coated films are in nonequilibrium and in a partially disentangled state.[41,42] Due to the rapid drying of the solvent, the resultant dried film may retain a memory of the chain conformations in the original solution, resulting in a lower entanglement density in the films, which has been confirmed in recent experiments studying the viscosity of freshly spin-coated polystyrene films supported by silicon.[43,44] Moreover, the entanglement recovery process occurs spontaneously above the glass transition temperature (T_g) of the sample[38,45,46] as verified by Teng et al.,[38] who monitored the reentanglement kinetics of freeze-dried polystyrene (PS) above T_g.

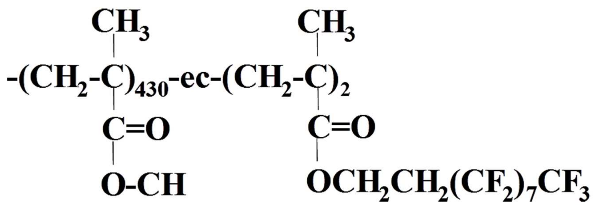
Generally speaking, the chains near a thin film surface are not geometrically confined and have lower entanglement density and greater mobility relative to those in the bulk.[32] Using more direct methods to characterize surface dynamics in polymers, Boiko et al. [10,12,47-51] found that the temperature dependence of surface relaxation rates above the apparent $T_{g,s}$ corresponds to Arrhenius behavior, suggesting that surface mobility can be ascribed on the segmental length scale. The elementary unit involved in segmental motion has been postulated to be the Kuhn segment,[47] typically several nanometers in length and comprising about 8−10 monomers.[52] At the present time, the effect of chain entanglement on the molecular motion on film surfaces is not clearly understood. In our previous reports,[19,53] the segmental mobility distribution at the poly(methyl methacrylate) film surface within the depth of 9.0 nm was investigated by measuring the surface reorganization of fluorinated tracer-labeled PMMA using different surface-sensitive techniques with various analytical depth capabilities. An approximately 2.4 nm surface layer with depth-independent T^{onset} was found, below which the T^{onset} increased with increasing depth. [53] At the same time, the constraint of conformational freedom, reduction of free volume and increment of chain packing density were proposed as the origins for this depressed dynamics of poly (methyl methacrylate) chains in the corona of collapsed dry micelles tethered by a fluorinated block core.[19]

There has been enormous interest in the question how size and surface affects the glass transition temperature of thin polymer films. Different groups of researchers have reached conflicting conclusions during the last 20 years, even when studying the same type of polymer. In the last years, there has been some evidence that this controversy is due to the fact that the equilibration of thin polymeric films on substrates is not well enough controlled (and not well understood). Therefore, there is need for a careful examination of the factors which control the establishment of thermal equilibrium in such polymer films near the glass transition temperature when spin casting techniques are applied. At the same time, it was also necessary to understand the knowledge about effect of chain entanglement on the polymer motion on film surfaces. In the present work, poly(methyl methacrylate) polymers end-capped with two 2-perfluorooctylethyl methacrylate (FMA) units was used as a model system, and the effect of concentration of casting solution on the surface mobility of PMMA films was investigated. It was found that chain entanglement may be main factor affecting the surface onset temperature of chain rearrangement (T_R^{onset}) and surface relaxation activation energy (E_a).

2. EXPERIMENTAL SECTION

Materials

The poly(methyl methacrylate) polymers end-capped with two 2-perfluorooctylethyl methacrylate (FMA) units (PMMA$_{430}$-ec-FMA$_2$, PDI=1.05, where the subscript is the degree of polymerization) was synthesized in our lab using atom transfer radical polymerization (ATRP), as described in our previous work. [19,54,55] The chemical structure of the fluorinated moiety end-capped PMMA is shown in Fig 1. The 2-perfluorooctylethyl methacrylate was purchased from Sigma-Aldrich Inc. The bulk T_g of the PMMA$_{430}$-ec-PFMA$_2$ was 110°C as measured by DSC, which was the same as the T_g of PMMA$_{430}$ homopolymer. This indicates that the fluorinated units at the PMMA$_{430}$ chain end in this study do not affect the T_g of PMMA. Cyclohexanone (Shanghai Reagent Co.) was distilled twice under reduced pressure in the presence of CaH_2. Other reagent grade chemicals were purchased from Shanghai Reagent Co. and used without further purification. Silicon wafers were used as substrates. The substrates were cleaned before use in a piranha solution (a mixture of H_2SO_4 and H_2O_2 in 3:1 by volume) at 130°C for 20min and then thoroughly rinsed in deionized water and dried in pure nitrogen gas. The thickness of SiO_2 on the Si substrates was ~2.2nm as measured by ellipsometry EP3 SW (Accurion Co., Germany).



$$-(CH_2-\overset{CH_3}{\underset{\underset{O-CH}{C=O}}{C}})_{430}-ec-(CH_2-\overset{CH_3}{\underset{\underset{OCH_2CH_2(CF_2)_7CF_3}{C=O}}{C}})_2$$

Fig. 1 Chemical structure of $PMMA_{430}$-ec-$PFMA_2$

Film formation

Thin films of the polymer were spin-coated at 3600 rpm onto silicon wafers from solutions of $PMMA_{430}$-ec-$PFMA_2$ in cyclohexanone with concentrations ranging from 0.8 wt% to 8.0 wt%. The films were dried under vacuum (45°C) for 48 h to remove the residual solvent, then subjected to a subsequent annealing process in air for various times and temperatures for elucidating the surface dynamics. The thicknesses of the resulting films, evaluated by ellipsometry, ranged from about 20 nm to 250 nm. More than four samples at each concentration were prepared to ascertain the reproducibility of the contact angle measurements.

Characterization

Water contact angle measurements were used to investigate the temperature-dependent changes in surface structure of the polymer films as a function of annealing treatment as previously reported.[19,56] Contact angles (θ) of water were measured by the sessile drop method (Kruss DSA-10, Hamburg, Germany) at room temperature and ambient humidity. Samples which had been heated in air were slowly cooled to room temperature before θ measurement. The volume of the water drops used in the measurements was always 3μL. In order to ascertain the reproducibility of the results of the measurements, the experimental errors in measuring the θ values were evaluated to be less than ±2°.

X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA system) was employed to characterize the films with a Mg Ka X-ray source (1253.6 eV). The X-ray anode was operated at 250 W and the voltage was maintained at 14.0 kV. Spectra were acquired at a detection angle of 15°(θ=15°， sampling depth about 2.3 nm). Calibration was conducted on the C 1s peak of the C-C bond at 284.6 eV. The data analysis was carried out using the PHI-MATLAB software provided by PHI Corporation.

Atomic force microscopy (XEI-100， SPM, PSIA Co.) was used to investigate the morphology of the top surface of the samples. SPM measurements were performed in air with an etched silicon probe having a length of 125 μm. Scanning was carried out in the tapping mode at a frequency of approximately 300 Hz.

Shear viscosities (η) of solutions of $PMMA_{430}$-ec-$PFMA_2$ from various mixing solvents at 25°C were measured at different shear rates by viscometer (Antonpaar, MCR301, Austria). Zero-shear viscosities (η_0) were obtained by extrapolating the obtained η values to the zero-shear rate.

3. RESULTS AND DISCISSION

Surface relaxation behavior of fluorinated PMMA films prepared from casting solutions with different concentrations

Due to the rapid drying of the solvent, the spin-coated films may retain a memory of the chain conformations in the original solution and are in non-equilibrium state.[41,42] Surface reorganization of the PMMA$_{430}$-ec-PFMA$_2$ films, which refer to motion of the fluorinated units along with its neighboring PMMA segments in order to attain an equilibrium state corresponding to a minimal interfacial free energy, occurred as a result of the annealing. Contact angle measurement is an effective method for detecting the surface rearrangement of the fluorinated PMMA films by tracing the enrichment of PFMA on the film surface.[19,56-58]The surface reorganization behavior of the end-functional PMMA was characterized by measuring the temperature-dependent changes in water contact angles of the polymer films as a function of annealing treatment temperature. The results of the dynamic water contact angle measurements are presented in Fig.2(A). The water contact angles remained at a constant value of 87° in the low temperatures region, which demonstrates a characteristic of the glassy surface. After this plateau region, the contact angles increased with increasing annealing temperature. When the annealing temperature approached the bulk T_g of PMMA(~110°C), the surface chains' mobility was extremely high and the contact angle remained at a corresponding constant value of 105°. The temperature dependence of the rearrangement process of the surface chains can be fitted by three straight lines, as shown in Fig. 2. We can

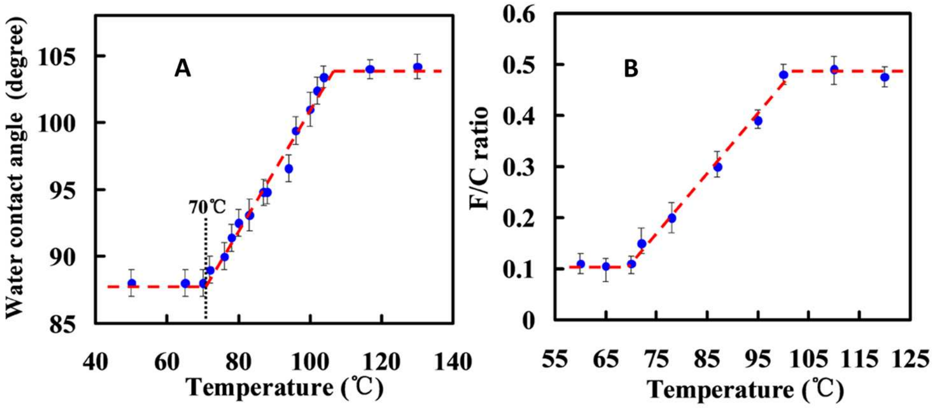


Fig. 2 (A) Water contact angle of spin-coated $PMMA_{430}$-ec-$PFMA_2$ film as a function of annealing temperature and (B) F/C ratios of corresponding film as a function of the annealing temperature. The annealing time: 24h. Solution concentration: 4.2%. The photoelectron emission angle (θ) was 15°. The dotted line is a visual guide.

define the intersection point of the two straight lines in the low temperature region as the onset temperature for the surface chain rearrangement (T_R^{onset}). For the film prepared from the solution with a concentration of 4.2% as shown in Fig.2(A), its corresponding surface T_R^{onset} was 70°C.

Under normal conditions, the main reasons accounting for the variation of contact angles are the changes of the surface roughness or chemical structures of a film. [58-60] AFM was accordingly employed to investigate the surface roughness of $PMMA_{430}$-ec-$PFMA_2$ films before and after annealing. It was observed that the change of surface roughness was within 2 nm, as shown in Fig. S1 (**ESI†**), for which values it was proposed that the effect of surface roughness on contact angle is negligible.[19] X-ray photoelectron spectroscopy (XPS) was used to detect the variation of chemical composition of the topmost surface region of the samples. Fig. 2(B) shows the variation of the F/C ratios for $PMMA_{430}$-ec-$PFMA_2$ film surfaces during the annealing process. As evident in Fig. 2(B), the onset temperature for F/C ratio incrementation at a photoelectron emission angle of 15° is also 70 °C, above which the F/C ratio increases with increasing annealing temperature. These results correlate well with the contact angle measurements and confirm that the increment of water contact angle for the fluorinated PMMA films after annealing is due to segregation of the end-capped fluorinated components.

In the following section, we focus on the surface T_R^{onset} of the $PMMA_{430}$-ec-$PFMA_2$ films prepared from various concentrations of casting solution. Fig. S2 (**ESI†**) illustrates the water contact angle on $PMMA_{430}$-ec-$PFMA_2$ films prepared from different concentrations of polymer solutions as a function of annealing temperature. The onset temperature of chain rearrangement T_R^{onset} for $PMMA_{430}$-ec-$PFMA_2$ film surfaces obtained from Fig. S2 (**ESI†**) as a function of concentration of casting solution is plotted in Fig. 3. The results show that the surface T_R^{onset} increased from 55°C to 70°C with increasing concentration from

0.8 wt % to 4.2 wt % and maintained an almost constant value of 70°C when the concentration of casting solution was up to 8 wt%.

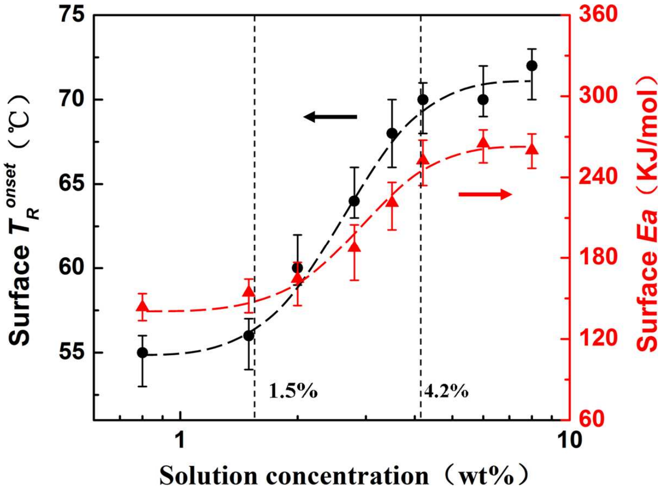


Fig. 3 Surface chain rearrangement temperature T_R^{onset} and apparent activation energy (Ea) for $PMMA_{430}$-ec-$PFMA_2$ films prepared from solutions with different concentration.

The thickness of the films was affected by the concentration of casting solution. Fig.S3 **(ESI†)** shows the relationship between the concentration of casting solution and the thickness of the resulting films. The thickness of the films increased from 20 nm to 250 nm with increase of solution concentration from 0.8 wt% to 8.0 wt%. According to a three-layer model [61-63], chain mobility of the surface layer may be affected by the interaction between the polymer film and the substrate when the thickness of the supported film was sufficiently thin [64-66]. Therefore, it is necessary to determine whether the concentration dependence of the surface T_R^{onset} of the resulting film was related to the thickness of the PMMA film. Fig.S4 **(ESI†)** shows the thickness dependence of the glass transition temperature of both PMMA and fluorinated end-capped PMMA (PMMA$_{430}$-ec-PFMA$_2$) thin films. It was found that the fluorinated end group did not affect the glass transition temperature of thin PMMA films. At the same time, the glass transition temperature of thin PMMA films did not change when the film thickness was above 20 nm. Fig.S4 **(ESI†)** indicates that the glass transition temperature of thin PMMA films was the same regardless of the SiO$_2$ and Si-H substrates, when the thickness of the thin PMMA films was above 20 nm.

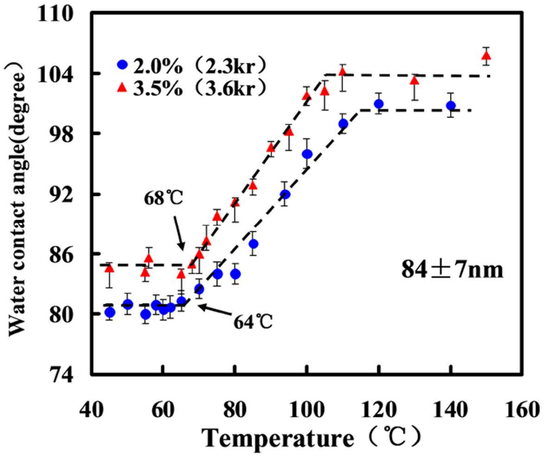


Fig. 4 Water contact angle of PMMA$_{430}$-ec-PFMA$_2$ spin-coated films vs annealing temperature. The films were prepared from casting solutions with different concentration, but their thickness was almost the same. "▲" the concentration of casting solution was 3.5wt%, spinning rate 3600 rpm; "●"the concentration of casting solution was 2.0 wt%, spinning rate 2300 rpm.

Fig. 4 shows the surface T_R^{onset} of PMMA$_{430}$-ec-PFMA$_2$ spin-coated films with almost the same thickness prepared from casting solutions with different concentrations. It is apparent that the surface T_R^{onset} of PMMA$_{430}$-ec-PFMA$_2$ spin-coated films is related to the concentration of the corresponding film-formation solution. When the thickness of the films was the same, the surface T_R^{onset} of the film prepared from higher concentration of casting solution was higher than that of the film prepared from lower concentration of casting solution. The results above indicate that the surface T_R^{onset} change with concentration of casting solution shown in Fig. 3 was not caused by the thickness of the films. Since the glass transition temperature (T_g) of PFMA chains is near room temperature,[67] and X-ray diffraction (XRD) illustrates an amorphous PFMA state,[19] the migration of PFMA to the film surface is kinetically controlled by the mobility of the PMMA chains. Therefore, the surface T_R^{onset} reflects to a certain extent the surface T_g of PMMA and the PFMA segment did not influence the mobility of the PMMA chains. The surface T_R^{onset} of PMMA$_{430}$-ec-PFMA$_2$ films is 70°C and it is close to the surface T_R^{onset} of PMMA (67°C) measured by polarization- rotating sum frequency generation vibrational spectroscopy,[68] in which the film was prepared from a casting solution of similar concentration. The results above indicate that the surface T_R^{onset} on PMMA surface is affected by the concentration of casting solution.

Effect of solvent quality on the surface T_R^{onset} of PMMA films

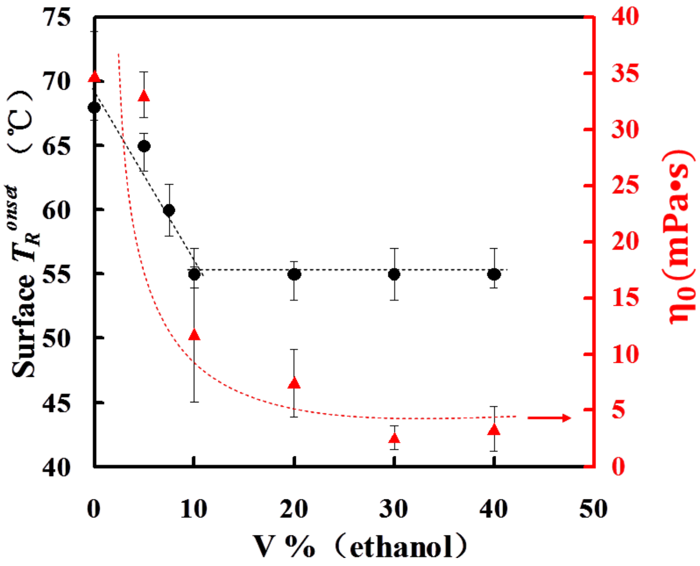


Fig. 5 Surface T_R^{onset} for corresponding spin-coated PMMA$_{430}$-ec-PFMA$_2$ films and the zero-shear viscosity η_0 of casting solution (at 25°C) as a function of the volume ratio of ethanol in cyclohexanone solution. PMMA$_{430}$-ec-PFMA$_2$ concentration: 3.5%. The dotted line is a visual guide.

In order to further understand the effect of concentration of casting solution, the mixed solvent system consisting of cyclohexanone (a good solvent for PMMA) and ethanol (a poor solvent) was used to prepare casting solutions for spin coating. The solvent quality can be changed from good to poor by controlling the volume ratio of ethanol in the mixed solvent, so that the effect of solvent quality on the surface T_R^{onset} of spin-coated PMMA films could be investigated, in which chain structure in the thin film was changed. As shown in the Fig. 5, the surface T_R^{onset} for fluorine-labeled PMMA films decreased linearly from 70°C to 55°C with increasing volume ratio of ethanol in the mixed solvent and then remained at 55°C when the volume ratio of ethanol exceed 10%, which was almost same as that of the film prepared by 0.8 wt% PMMA cyclohexanone solution. It is well known that the wetting behavior of polymer film surfaces is determined by their chemical structures and physical roughness. [55,60] The surface roughness of the spin-coated films before and after annealing was investigated by AFM. The results, given in Fig. S1 (**ESI†**) show that the film surfaces are smooth and flat, with the RMS roughness less than 30.0 nm, indicating that the effect of physical roughness is negligible. [55,60] Therefore, the variation in contact angles

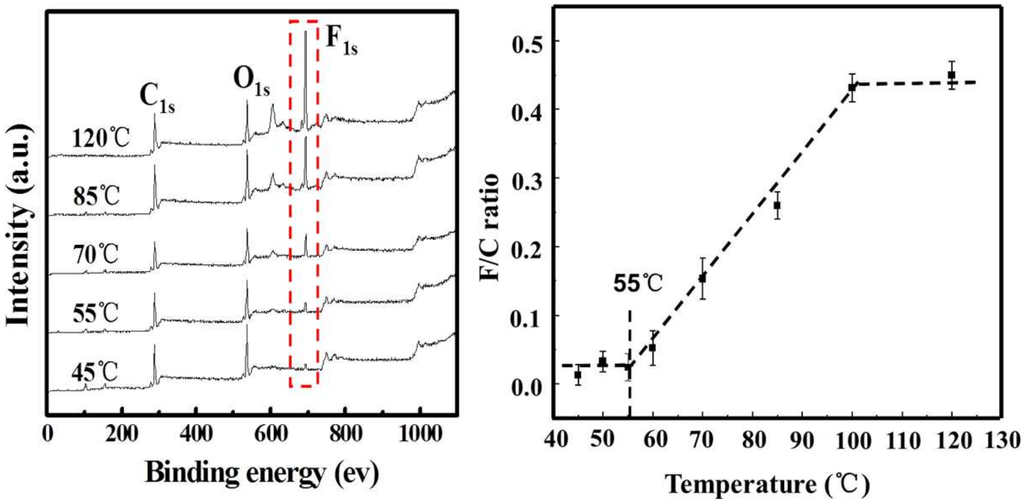


Fig. 6 XPS spectra (left) and F/C ratios (right) of PMMA$_{430}$-ec-FMA$_2$ spin-coated films as a function of annealing temperature (24 h). The photoelectron emission angle (*θ*) was 15°. The concentration of casting solution: 3.5wt%. The volume ratio of ethanol in cyclohexanone solution was 40%.

shown above should be solely associated with the surface chemical structures of the films, due to surface chain rearrangement. The chemical composition of the topmost surface region was quantitatively analyzed by XPS. Fig. 6 shows the F/C ratios for $PMMA_{430}$-ec-$PFMA_2$ films prepared by 40% volume ratio of ethanol in cyclohexanone solution after annealing at various temperatures. As evident in Fig. 6, the onset temperature for F/C ratio incrementation at a photoelectron emission angle of 15° is about 55°C, above which the F/C ratio increases with increasing annealing temperature. These results correlate well with the contact angle measurements and confirm that the increment of water contact angle for the fluorinated PMMA films prepared with ethanol/cyclohexanone mixed solution after annealing is due to segregation of the end-capped fluorinated components. These results indicate that the mobility of the polymer chains on the film surface is gradually enhanced with increasing volume ratio of ethanol in the mixed solvent.

Effect of the concentration of casting solution on surface dynamics of corresponding spin-coated PMMA films

Contact angle measurement is one of the most effective and sensitive methods for studying surface reconstruction and chain relaxation.[19,57,58,69,70] The apparent activation energy (E_a) for the surface relaxation of fluorine-labeled PMMA films prepared from various concentrations of casting solutions was examined on the basis of the time-temperature superposition principle for chain dynamics. The results above showed that variation in contact angle on PMMA films after being annealed was attributed to changes in chemical components on the film surface. Therefore, water contact angle measurement of the films was employed to evaluate their surface relaxation. Fig. 7 displays the time dependence of the measured contact angle for $PMMA_{430}$-ec-$PFMA_2$ film at different temperatures. The water contact angles exhibit an exponential increment with increasing annealing time. The relaxation rate is highly dependent on the temperature: a higher temperature results in a shorter time necessary to attain a meta-stable contact angle. We re-scaled the abscissa of each curve in Fig. 7 with a temperature- dependent shift factor, $\alpha_{T,}$

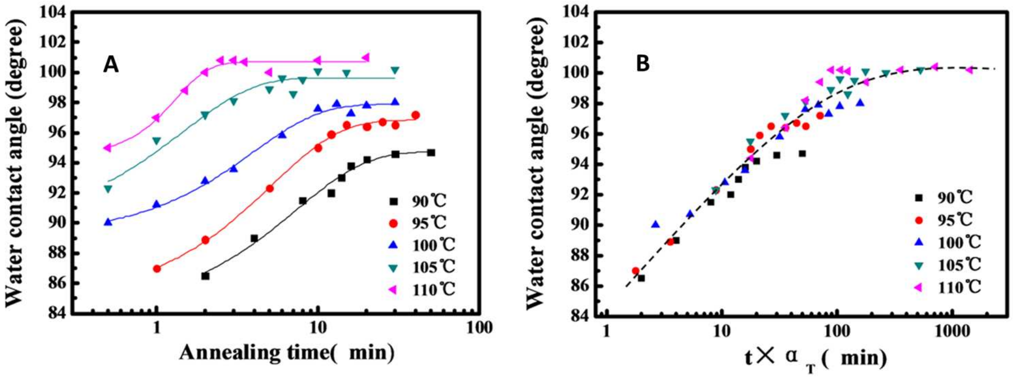


Fig. 7 (A) Time evolution of water contact angles of $PMMA_{430}$-ec-$PFMA_2$ films annealed at various temperatures. (B) Master curve of the annealing time-contact angle relationship for $PMMA_{430}$-ec-$PFMA_2$ films drawn from each curve in **Fig. 5(A)** with the abscissa re-scaled by a temperature-dependent shift factor, $\alpha_{T,}$ (reference temperature (T_s): 90 °C). The dashed line in panel b is a visual aid. The concentration of casting solution: 2.8 wt%.

using 90°C as the reference temperature (T_s), to qualitatively describe the time and temperature dependence of the surface relaxation (a vertical shift is also conducted). The curves in Fig. 7(A) are super-imposed into a master curve shown in Fig. 7(B). This clearly demonstrates that a time-temperature equivalence property, which is characteristic of the bulk viscoelastic properties of polymeric materials, can be also applied to the surface relaxation of the PMMA film.

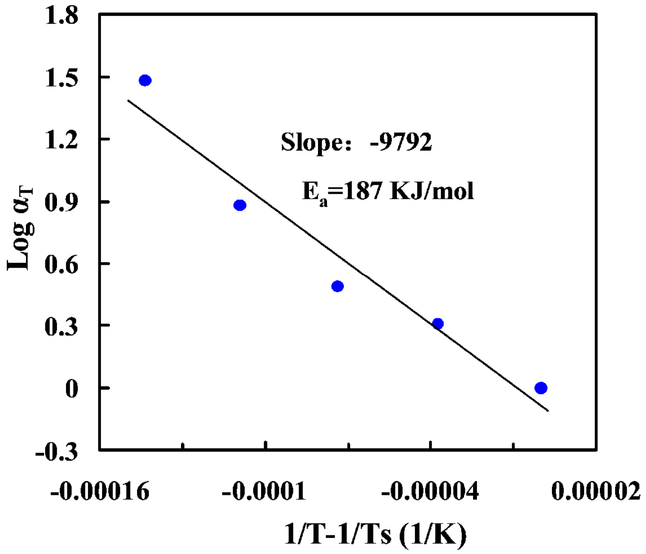


Fig. 8 Arrhenius plots of α_T vs. temperature for PMMA$_{430}$-ec-PFMA$_2$ films. The solid line is a linear least-squares fit to the data by Eq.1 with a slope for elucidating the activation energy. The concentration of casting solution: 2.8 wt%

Fig. 8 shows the relationship between α_T and annealing temperature, which corresponds to a linear Arrhenius plot. The appearance of an Arrhenius-related linear superposition suggests that the surface chains have a temperature-independent activation energy for relaxation, which is different from the WLF-like chain relaxation present in bulk, with the activation energy increasing with decreasing temperature. Similar Arrhenius-related polymer surface dynamics have previously been observed in the literature. [12,57,70] The apparent activation energy for surface relaxation can be obtained by fitting the data in Fig 8 with the modified Arrhenius equation described by the following:

$$Log\alpha_{\mathrm{T}} = -\frac{E_a}{2.303R}\left(\frac{1}{T}-\frac{1}{T_s}\right) \qquad (1)$$

where R is the gas constant, and E_a is the apparent activation energy for surface relaxation. The apparent activation energy (E_a) for surface relaxation of the PMMA film prepared from the 2.8 wt% solution is estimated from the slope in Fig 8 to be 187 kJ/mol, which is lower than the E_a for α relaxation of bulk PMMA (460KJ/mol). [71] This lower activation energy for the film indicates that the mobility of the polymer chains on the film surface is substantially enhanced compared to that in the bulk, which is in accordance with the results determined by scanning probe microscopy [72,73].

The E_a values of PMMA films prepared from casting solutions of various concentrations are determined by the same time-temperature equivalent shift of the contact angle vs. annealing time curves, and the linear correlations between the logarithmic α_T and $1/T$-$1/T_s$ values are shown in Fig. S5 **(ESI†)**. The E_a for surface dynamics of the PMMA films prepared by 0.8 wt% and 1.8wt% casting solutions are very similar, with values of 144 and 152 KJ/mol, respectively. The E_a data for surface dynamics of PMMA films prepared by various concentration of casting solutions were presented in Fig. 3. For the PMMA films prepared from casting solutions with concentration above 4.2 wt% casting solution, the E_a is measured to be about 260 KJ/mol, which was lower than that for the micellized PMMA on the surface (about 310 KJ/mol) reported previously.[19] The E_a for the PMMA film prepared from casting solution with concentrations above 4.2 wt% solution are about twice as high as those of the films prepared from casting solutions with concentrations below 1.8 wt%. The E_a for the PMMA films increased from 152 KJ/mol to about 260 KJ/mol when the concentration of the corresponding film-formation solution increased from 1.8wt% to 4.2wt%. Thus, it can be predicted from the magnitude of the activation energy that the energy barrier of thermal molecular motion for the chains in the films prepared from the solution with lower concentration may be increased in comparison with those for the chains in the films prepared from the solutions with higher concentrations.

The cause of casting solution concentration dependence of the surface dynamics of PMMA films

It is commonly observed that polymer chains tend to form aggregates in polymer solutions of sufficiently high concentration.[74] The origin of the aggregation is the interchain attraction forces. From this point of view, one would expect that these interactions are maximized in the solid state when the polymer chains are densely packed. In fact, the formation of aggregates in thin films is well-documented for various polymers. Therefore, one would expect that the morphology of a spin-cast film depends on the relative strengths of the cohesive force of the solution and the centrifugal force asserted by the spinning. When the centrifugal force is comparable to the cohesive force of the solution, one would expect to see a spin speed dependence of the film morphology. In this regard, the viscosity of the polymer solution can, to a certain extent, reflect the intermolecular interactions. In other words, a higher solution viscosity suggests higher intermolecular forces, and *vice versa*. [74,75] The zero-shear viscosity η_0 is a basic quantity in the global-motion dynamics of polymer chains in solution, which is an important parameter that suggests the effect of chain entanglement on polymer dynamics.[75] The concentration regimes for the fluorine-labeled PMMA solutions were determined using solution rheology measurements. Shear rate sweeps from 80 to > 1000 s^{-1} were performed on polymer solutions ranging from 2 to 10% in cyclohexanone solution at 25 ± 0.2°C. All the solutions investigated in this study displayed shear thinning behavior at high shear rates (viscosity-shear rate curves not shown). The initial slope of the plot of the shear stress-shear rate data where Newtonian behavior was observed gives the zero shear viscosity, η_{0}. The η_0 values are plotted as a

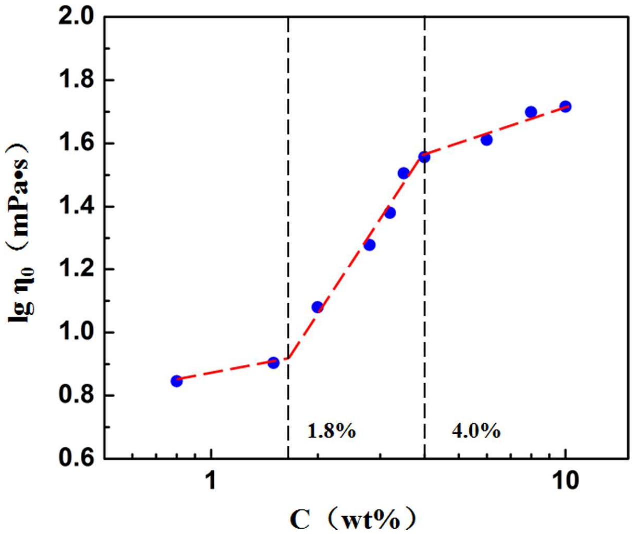


Fig. 9 Fluorine-labeled PMMA concentration dependence of the zero-shear viscosity of cyclohexanone solutions at 25 ± 0.2□.

function of concentration in Fig. 9 for the fluorine labeled PMMA. It is apparent that the dependence of the zero shear viscosity of the solution on the concentration (C_s) can be divided into three regions. Based on the literature, [76,77] for $C_s < 1.8\%$, the solutions are dilute, the macromolecular chains are separated and can not contact with each other; thus the change of η_0 with the concentration is small. For $1.8\ \% < C_s < 4.0\%$ (semi-dilute solutions), the dimensions of the macromolecular chains decrease and they contact each other due to the thermal motion. The quantity of isolated chains is reduced and a certain amount of entanglement occurs, so that the degree of chain entanglement increases and large systems of entangled chains are formed, resulting in η_0 increasing sharply with the increasing concentration. For C_s > 4.0 wt% (concentrated solutions), the density of chain entanglement still increases but the variation in the degree of entanglement is small, resulting in η_0 increasing slowly. By comparison, it is obvious that in these three concentration regions, the observed change in η_0 is identical to that of the surface T_R^{onset} of the films shown in Fig. 3. This result suggests that surface T_R^{onset} of the resulting film is related to entanglement of the PMMA chains on the film surface.

Fig. 5 shows the zero-shear viscosity η_0 of 3.5 wt% fluorine labeled PMMA solutions vs the volume ratio of ethanol in the cyclohexanone solvent. It is observed that the zero-shear viscosity η_0 decreases with increasing volume ratio of ethanol in cyclohexanone and it will be less than 10 mPa.s and decrease slightly when the volume ratio of ethanol in the solvent is more than 10%. At the same time, it is apparent from both concentration of casting solution and solvent quality-dependent surface T_R^{onset} that it almost reaches minimum value at 55°C when the zero-shear viscosity of casting solution was below 10 mPa.s.

When a polymer solution is subjected to rapid drying, as in spin-coating, the polymer chains in the solution may not have enough time to attain equilibrium before vitrifying. As a result, some memory of the chain conformations in the solution may carry over to the resulting dry film. Such an effect has been confirmed by investigating the relationship between the surface structures of spin-coated fluorinated polymer films and their corresponding film-formation solution/air interface structures. [54,78,79] When a polymer solution is dried, the sample volume decreases consequently, the interpenetration between neighboring chains increases. Rapid drying can, however, preclude the chains from achieving full interpenetration before vitrification, resulting in the final, dried film having a smaller degree of entanglement than would be the case at equilibrium. The notion that spin-coated polymer films possess less entanglement than at equilibrium has been confirmed in recent experiments studying the viscosity of freshly spin-coated polystyrene

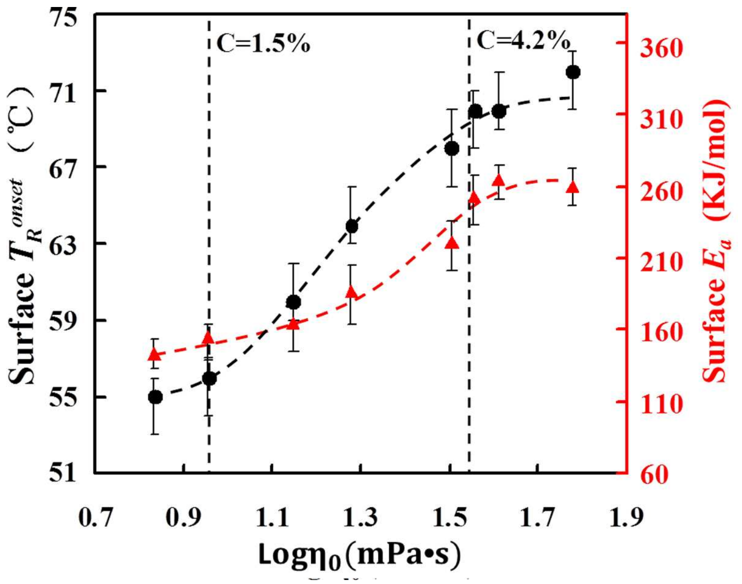


Fig.10 Relationship between surface T_R^{onset} , apparent activation energy (E_a) of PMMA films and the corresponding zero-shear viscosity of casting solutions.

films supported by silicon.[43,44] At the same time, a more detailed analysis of the data by Steiner [80] suggested the formation of a surface-near region with more strongly deformed chains during spin coating.

Fig. 10 shows the onset temperature of chain rearrangement T_R^{onset} and its corresponding energy barrier (E_a) for PMMA film surfaces as a function of the corresponding zero-shear viscosity of their casting solutions. The results show that both T_R^{onset} and E_a increase linearly with increasing η_0 of the corresponding solution within the range of 10 to 36 mPa.s, which corresponds to the concentration range of 1.8 wt% to 4.2 wt%. Both surface T_R^{onset} and E_a for the PMMA film surfaces did not change when the corresponding η_0 of the casting solution was below 10 mPa.s and above 36 mPa.s. Therefore, the cause of casting solution concentration-dependent surface dynamics of the resulting spin-coated films may be explained as follows. When the concentration of the fluorine-labeled PMMA solutions is below 1.8 wt%, the macromolecular chains are separated and do not have direct contact with each other. Since spin-coated films are formed by the very rapid evaporation of solvent under a high rate of spinning of the substrate, the chain conformations in the corresponding casting solution are frozen in a non-equilibrium state, resulting in formation of a film surface with a smaller degree of entanglement, which promotes the mobility of the segments at the film surface. Thus, the surface T_R^{onset} of the resulting spin-coated films with casting solution concentration of below 1.8 wt% was almost 55°C and changes little as the concentration increases within this range (as shown in Fig. 3). For 1.8 % < C_s < 4.2% (semidilute solutions), the dimensions of the macromolecular chains decrease and they impact each other due to the thermal motion. Thus, the quantity of isolated chains is reduced and a certain amount of entanglement occurs; the degree of chain entanglement increases and large systems of entangled chains are formed, resulting in a sharp increase of η_0 with increasing concentration. Thus, the degree of chain entanglement on the resulting spin-coated film surface increases with increasing concentration of the corresponding casting solution. Intrachain entanglements are effective in restricting the mobility of the chain segments in polymer condensed matter materials.[5,32] It is clear that high concentrations can result in heavy entanglement of the polymer chains and the mobility of the molecules is correspondingly lessened. [33] It is found that both the surface T_R^{onset} and surface relaxation activation energy E_a of the PMMA films increased with increasing concentration of casting solution. For C_s > 4.2 wt% (concentrated solutions), the density of chain entanglement still increases but variation in the degree of entanglement is small, resulting in a slow increase in η_0. Consequently, it was demonstrated that high concentrations of solution result in heavy entanglement of chains in the films, resulting in a gradually lessening of the mobility of the surface segments of the chains. The surface T_R^{onset} of corresponding PMMA films reached about 70°C and was almost constant when the concentration was above 4.2 wt%.

The solvent quality can influence the conformation of polymer chains to a large extent.[26] By the use of solvents of different qualities, the degree of entanglement can be further fine-tuned. Specifically, when solvents with poorer quality are used, individual polymer chains would be more compact, and so the interchain entanglement would accordingly be further reduced. It is apparent from Fig. 5 that the macromolecular chains are separated and can not contact with each other when the volume ratio of ethanol in the solvent was more than 10%. Therefore, it is obvious that the decrease in the surface T_R^{onset} with increasing ethanol content in the casting solutions shown in Fig. 5 can be attributed to a decrease in interchain entanglement. From the results above, it is evident that the surface T_R^{onset} increases with increasing the degree of chain entanglement on the PMMA film surface, which was accomplished using various values of the zero-shear viscosity of the casting solutions.

4. CONCLUSIONS

In this paper, the effect of concentration of casting solution and solvent quality on the surface dynamics of corresponding spin-coated fluorine-labeled PMMA thin films were investigated. The results showed that the surface chain rearrangement temperature T_R^{onset} and the apparent activation energy (E_a) for surface relaxation increased from 55°C to about 70°C, from 144 KJ/mol to about 260 KJ/mol, respectively, with increasing concentrations of fluorine-labeled PMMA in the casting solutions from 1.8wt% to about 3.8 wt%. However, when the concentration of the casting solution was below 1.8wt% and above 3.8 wt%, both surface T_R^{onset} and E_a remained at a constant value. It was found by investigating the relationship between the zero-shear viscosity η_0 and concentration of casting solution that the surface dynamics of spin-coated PMMA films was related to the zero-shear viscosity of the corresponding polymer solution. Therefore, the enhanced surface T_R^{onset} and higher E_a for the PMMA suggest that the entanglement of PMMA chains substantially reduces their chain dynamics on the surface. It was also evident that the mobility of the polymer chains on the film surface was gradually enhanced with increasing volume ratio of a poor solvent (ethanol) in the solvent system. The surface dynamics of PMMA are well correlated to the entanglement of the PMMA chains: a higher degree of PMMA chain entanglement results in larger depression of PMMA segment mobility on the surface. In conclusion, chain entanglement not only influences the chain mobility in the films but also has a pronounced inhibiting effect on surface segmental motion. This work will help increase the understanding of the effect of chain entanglement on the surface dynamics of polymer thin films.

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Notes

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Supplementary Information

† Electronic Supplementary Information (ESI) available: AFM topographies of various PMMA films before and after annealing; water contact angle of various spin-coated $PMMA_{430}$-ec-$PFMA_2$ films as a function of annealing temperature, the thickness of various spin-coated $PMMA_{430}$-ec-$PFMA_2$ films; glass transition temperature of the PMMA and fluorine-labeled PMMA films on Si-SiO_2 and Si-H substrates with different thickness; apparent activation energy determination for

surface dynamic of PMMA$_{430}$-ec-PFMA$_2$ films prepared from various concentrations of casting solutions. See DOI: 10.1039/b000000x/

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Table of contents entry：

Surface Dynamics of Poly(Methy methacrylate) Films Affected by Concentration of Casting Solution

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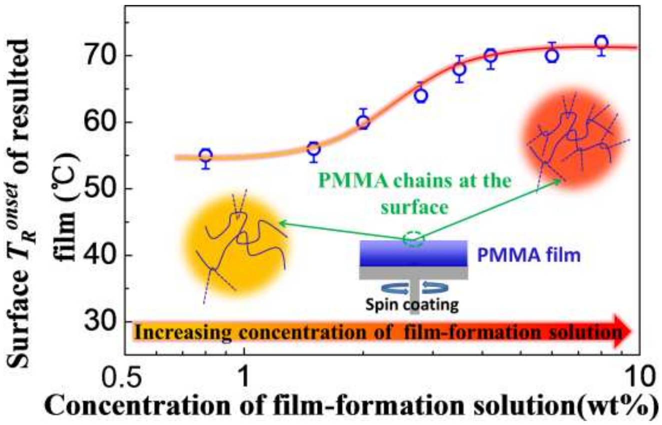

Suppressed surface dynamics of poly (methyl methacrylate) chains on the surface of spin-coated film prepared from concentrated casting solution.