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Influence of Linkage Type between Polymer Backbone and Side Groups on Surface Segregation of Methyl Groups During Film Formation

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Abstract: Although poly(vinyl acetate) (PVAc) differs from poly(methyl acrylate) (PMA) only in the reversed position of the ester group, a large difference in the concentration dependence of the casting solution on the corresponding surface structure of the cast films of PVAc, PMA and poly(methyl methacrylate) (PMMA) was observed. The hydrophobicity of both PMA and PMMA films increased with increasing concentration of the corresponding polymer solution, whereas cast PVAc films showed the reverse trend. The surface structure of the cast films prepared with different concentration of the casting solution, characterized by sum frequency generation (SFG) vibrational spectra, showed that the order of the methylene groups increased while that of the acetyl methyl group decreased on the surface of cast PVAc film with increasing concentration of casting solution. However, the order of the ester methyl group increased and that of methylene groups did not change for cast PMA films with increasing concentration of casting solution. The cast PMMA film showed a reverse trend compared with the corresponding PMA film. It is apparent that well-ordered ester or acetyl methyl groups on the surface which are oriented away from the polymer film, rather than methylene groups, play an important role in determining surface hydrophobicity, as the latter shield the OC=O groups of PVAc, PMA and PMMA film surfaces from being exposed, resulting in low surface free energy. The reason for this difference is attributed to the relative lower energy for ester methyl group reorientation, an ester group structure nearer to the *trans* state and more regular local configuration of segments in concentrated solutions of PMA and PMMA compared to that of PVAc.

Keywords: surface structure; concentration dependence; reorientation; methyl group; linkage of side group

1. Introduction

The composition and the structure on a surface, which are distinct from the bulk of the corresponding material, play an important role in those applications where properties such as wettability, adhesion, biocompatibility, permeability and friction are concerned. [1-4] The control of the surface composition is of paramount importance in many applications of materials. The preferential segregation at polymer surfaces is an important factor affecting surface structure of materials when there are differences in the surface free energy of the components within a polymer or a polymer system. [5-9] Due to the complexity of the film-forming process, the relationship between the surface structures of polymer thin films and the corresponding molecular structure of the polymer have been little studied and are accordingly not clearly understood.[10-17, 18-26] In general, the surface structure formation is governed by thermodynamics, but the kinetics for the segregation and array processes also play an important role in the ultimate surface structure formation which is mainly determined by fixed process methods and conditions. The free surface or, in other words, the polymer-air interface, is usually enriched by the component with the lower surface energy, in order to satisfy the thermodynamic requirements for a minimal surface free energy. The extent of such a preferential surface segregation depends on the nature of the system and the conditions of sample preparation. [21,26-31] It was reported [5,21,28,29] that the segregation of the fluorinated moieties was affected greatly by micelle stability in the corresponding casting solution and by the evaporation rate of the solvent, when a methyl methacrylate (MMA) and 2-perfluorooctylethyl methacrylate (FMA) block copolymer (PMMA-b-PFMA) film was prepared from its micelle solution with a PMMA block as the micelle corona and PFMA block as the micelle core. The rapid solvent evaporation rate together with the good micelle stability resulted in the formation of a micelle-like aggregate structure at the film surface, on which the PMMA coronas were partly exposed to the surface. [21,28,29] The nature of the solvent also affects the surface segregation and packing of the functional groups at the uppermost surface.[30,32] A result contrary to that observed for perfluorinated block polymers as described above, was observed when random copolymers composed of methacrylate and fluorinated methylacrylate were investigated.[25,26] As entropic forces dominated the solution–air interfacial structure, film preparation by spin-coating weakened the entropy effect of the polymer chains due to centrifugal force, resulting in the segregation of the fluorinated moieties on the film surface. When the migration of perfluoroalkyl groups at the solution–air interface was controlled by enthalpic forces, the segregation extent of the perfluoroalkyl groups at the surface of the film was determined by the solidification time of the polymer solution. It has been reported that the free surfaces of as-cast [33] or annealed [34,35] films of SI diblock copolymers obey the thermodynamic requirements: the component in the block with the lower surface energy covers the external surface, independently of copolymer composition, molecular weight and casting solvent. Similar results were reported by treating triblock copolymer SBS and SIS films under toluene vapor.[36,37] However, opposite results have also been observed. Turturro[38] showed that for a given evaporation rate range, microdomains of 1,4-PB and PS blocks were present together on the free surface, independent of copolymer composition and molecular weight. A similar phenomenon was observed for SBS film surfaces prepared by casting toluene solution, [39] and for other systems such as PS/PEO [27] and BAPC/PDMS. [40] The tuning of appropriate chemical-physical properties at the molecular level may lead to novel developments in a number of fields where interfacial interactions are important. In such cases, operating within a few nanometers of a surface is often critical. However, knowledge of the formation mechanism of surface structures and their affecting factors is still limited.

To date, considerable research has focused on the surface structure of polymers at equilibrium free surfaces. [13,32-36,38,39] Such equilibrium surfaces however, are not often achieved during the casting process, clearly indicating the presence of kinetic and thermodynamic effects related to the specific characteristics and evaporation conditions of the casting solvent. Solution casting is a preparation method of practical importance, and is used in many industrial applications. The non-equilibrium states obtained by this method can be reproducible and metastable over relatively long time periods, while true thermodynamic equilibrium states in polymers are difficult to reach because of the large polymer molecular weights.[41] Therefore, it is of practical importance to study the surface structures which are easily formed under common conditions.

Most studies about the formation of surface structures have focused on multicomponent polymer systems. The aim of these studies was primarily surface modification by preferential surface segregation of the component in the polymer system with the lower surface energy. Few studies have been performed on homopolymers. However, the orientations of the groups in homopolymers on the film surface also affect the surface properties of the resultant film. [10,42] Tanaka[16] found that the chains adopted an elongated conformation in the substrate plane induced by the spinning torque or the centrifugal force during the spin-coating process, while no interfacial orientation of chains was observed for the PS films when prepared by the solution-casting method.

In this paper, PVAc, PMA and PMMA were used as model polymers to investigate the effect of type of linkage between the polymer backbone and the side groups on surface segregation of methyl groups during film formation. The surface structures of thin PVAc, PMA and PMMA films prepared by various casting solution concentrations were investigated by contact angle goniometry and sum frequency spectroscopy (SFG), which can provide abundant information about the molecular structure on the film surfaces. Furthermore, we found in this study that there is a clear difference in surface structure dependence on concentration of casting solution between cast PVAc, PMA and PMMA films, despite their similar molecular structures. To elucidate the effect on surface structure caused by this small structural difference in the polymer chains, the corresponding surface pressure dependent SFG spectra were employed.

2. Experimental section

2.1 Materials

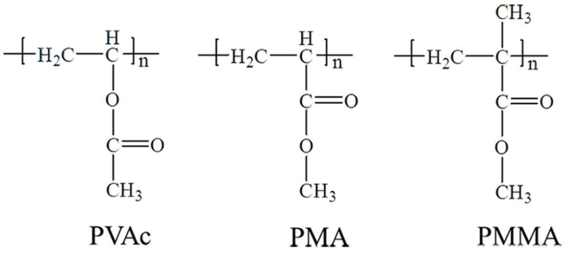

Fig.1 Schematic representation of the chemical structures of PVAc, PMA and PMMA.

Poly (vinyl acetate) (PVAc) (M_w=100 kg/mol, PDI=1.18) and poly (methyl methacrylate) (PMMA) (M_w=120 kg/mol, PDI=1.15) (shown in Figure 1) were purchased from Aldrich Co. (USA), and used without further purification. The PVAc sample is a linear polymer confirmed by its ^{13}C NMR spectrum. Poly(methyl acrylate) (PMA) (M_w=68 kg/mol, PDI=1.08) was synthesized by the ATRP technique as reported previously.[30,43]The molecular weights and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) using a Waters 1500 GPC apparatus (with THF as the eluent at a flow rate of 1.0mL/min). The GPC chromatograms were calibrated against polystyrene standards. Water used in the experiments was purified by a Milli-Q Plus (Millipore Inc.), and its resistivity was measured to be higher than 18 MΩ. Toluene (AR) and benzene (AR) were purchased from Shanghai Reagent Co. and used without further purification. Fused silica substrates were used, which were cleaned before use in a piranha solution (a mixture of H_2SO_4 and H_2O_2 in 3:1 by volume) at 90°C for 20 min and then thoroughly rinsed in deionized water and dried in pure nitrogen gas.

2.2 **Film Preparation**

The PVAc, PMA and PMMA solutions of various concentrations were prepared by dissolving different amounts of polymer in toluene, which were then filtered through a porous sand core filter with pore size of 0.25 μm in diameter. The solution-casting method was employed to prepare thin polymer films on the clean fused silica. The films were first dried in air for 24 h and then in vacuum at room temperature for another 48h.

2.3 Preparation of Monolayers

PVAc, PMA and PMMA were separately dissolved into benzene to prepare stock solutions with the concentration of 0.15 mg/mL. The monolayers at the air-water interface were prepared by spreading the stock solution delivered by microsyringe in a trough (a MiniMicro trough of KSV Instruments Ltd.), which allows us to measure monolayer compression (π-A) isotherms and to keep the pressure at a constant value by using a PC control system. A sample spread on pure water was compressed to a certain surface pressure for at least 15 min to stabilize the monolayer, and also served for SFG spectral measurements.

2.4 Characterization

Sum frequency generation (SFG) vibrational spectra were collected by a custom-designed EKSPLA SFG spectrometer, which has been described in detail by various researchers.[42,44,45] Briefly, the visible input beam at 0.532 μm was generated by frequency doubling of part of the fundamental output from an EKSPLA Nd: YAG laser. The IR beam, tunable between 1000 and 4300cm^{-1} (with a line width <6cm^{-1}), was obtained from an optical parametric generation/amplification/difference frequency generation (OPG/OPA/ DFG) system based on LBO and $AgGaS_2$ crystals. Both beams were pumped by the second harmonic and the fundamental output of the laser and had a pulse width of ~30 ps, a repetition rate of 50 Hz, and a typical beam diameter of 0.5 mm at the sample surface or interface. The incident angles of the visible beam and the IR beam were 60° and 55°, respectively, with respective energies at the sample surface of ~230 and ~130 μJ. The measurements were carried out at room temperature using two types of polarization combinations, namely *ssp* and *ppp* (SF output, visible input, and infrared input). In the SFG spectra presented below, each data point represents an average of 500 laser pulses of five individual experiments, and the standard deviation for each data point is less than ± 3%.

The intensity of the sum frequency signal can be expressed as follows: [46]

$$I_{SFG} \propto \left|\chi_{eff}^{(2)}\right|^2 \bullet I_{vis} \bullet I_{IR} \qquad (1)$$

Where I_{vis} and I_{IR} are the intensities of the two input lasers (visible and infrared, respectively), and $\chi_{\mathrm{eff}}^{(2)}$ is the effective nonlinear susceptibility, which can be expressed in the form:

$$\chi_{eff}^{(2)} = \chi_{NR}^{(2)} + \chi_{R}^{(2)} = \chi_{NR}^{(2)} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \qquad (2)$$

where $\chi_{\mathrm{NR}}^{(2)}$ is the nonresonant contribution and $\chi_{\mathrm{R}}^{(2)}$ is the resonant contribution. $\chi_{\mathrm{R}}^{(2)}$ consists of A_q, ω_{IR}, ω_q, and Γ_q, which are the strength, the frequency of the incoming IR beam, the resonant frequency, and damping coefficient of the *q*th resonant vibrational mode, respectively. A_q was determined from equations (1) and (2) by performing Lorentzian fits to the experimental data.

The high-resolution XPS spectra of the C_{1s} region for the PVAc, PMA and PMMA films were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al*Kα* radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C_{1s} at 284.6 eV from adventitious carbon. The film thickness was determined using an ellipsometer (Accurion Co., Germany) at a fixed angle of incidence of 60°.

3. Results and discussion

3.1 Effect of the concentration of casting solution on the surface structures of

cast PVAc, PMA and PMMA films

Fig. 2 shows the solution concentration dependence of water contact angle of the cast PVAc, PMA and PMMA films. It is observed that the water contact angle decreases sharply from 71° to 61° with concentration of PVAc casting solution increasing from 0.5% to 2%. The water contact angle reaches a constant value of 61° when its corresponding concentration of casting solution is above 2%. However，the reverse trend is exhibited for cast PMA and PMMA films. The water contact angle increases from 77° to 91° with concentration of PMA casting increasing solution from 0.5wt% to 4wt%. The contact angle reaches a constant value of 91° , when the concentration of casting solution is above 4wt%. Similar results are presented for the cast PMMA films as shown in Fig.2. It is very interesting that a large difference in the concentration-dependent surface properties of the cast films was observed although poly(vinyl acetate) differs from poly(methyl acrylate) only in the reversed position of the ester group.

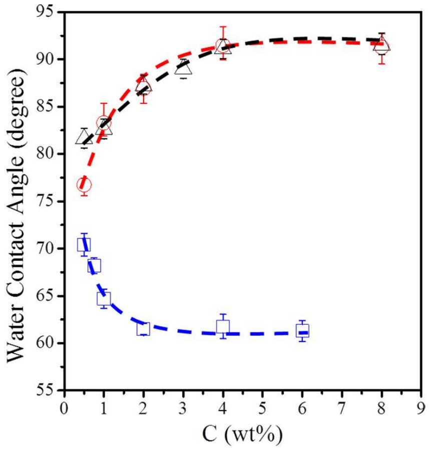

Fig. 2 Concentration dependence of water contact angles of PVAc（□）, PMA （○）and PMMA （Δ）films prepared by solution casting. The dashed line is a visual guide.

Fig.3 shows SFG spectra of cast PVAc films prepared by various concentrations of casting solution in the infrared frequency range of 2800 cm^{-1}- 3050 cm^{-1}, corresponding to the C-H stretching vibrations. The *ssp* spectrum of cast PVAc film prepared by 0.5% concentration is dominated by a strong peak at 2942 cm^{-1} and a weak shoulder peak at 2910 cm^{-1} which are assigned to the Fermi modes of the methyl groups from acetoxy groups and symmetric stretching vibrations of the backbone methylene groups, respectively. [45,47-49] The *ppp* spectrum of PVAc is dominated by a strong peak at 2965 cm^{-1} which is assigned to the antisymmetric stretching (*as*) mode of the methyl groups. [45,47-50] The appearance of the dominating peaks of the methyl Fermi (*ssp* spectrum) and *as* modes (*ppp* spectrum) on the surface of the PVAc film cast from 0.5% solution indicates that the side methyl groups of the VAc units preferentially protrude towards the air, with few backbone methylene groups pointing outwards (as shown in Fig.4).

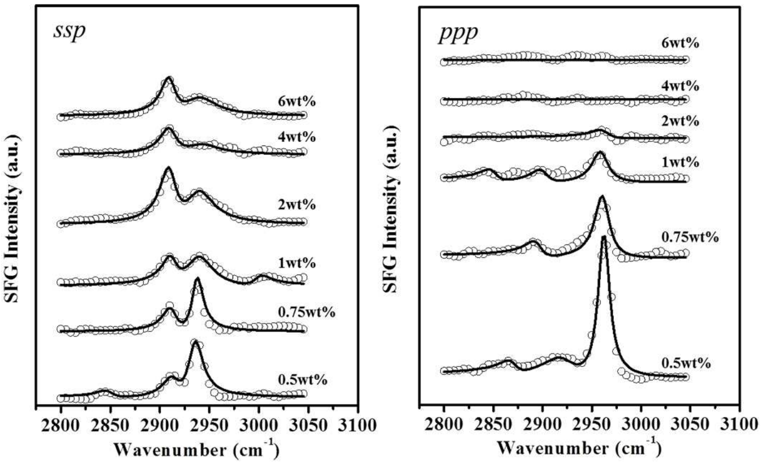

Fig. 3 SFG spectra of cast PVAc films prepared by various concentrations of casting solution.

With increasing concentration of casting solution, it is apparent that for the *ssp* spectra, the intensity of the peak at 2910 cm^{-1} increase while that of the peak at 2942 cm^{-1} decrease for the corresponding cast PVAc films. For the *ppp* spectra, the intensities of the peaks at 2965 cm^{-1} decrease and these peaks disappear when the concentration of the casting solution is above 2 wt%. These results indicate that the side methyl groups in the acetyl group preferentially protrude towards the air only when the concentration of casting solution is low, which is in agreement with the contact angle measurements.

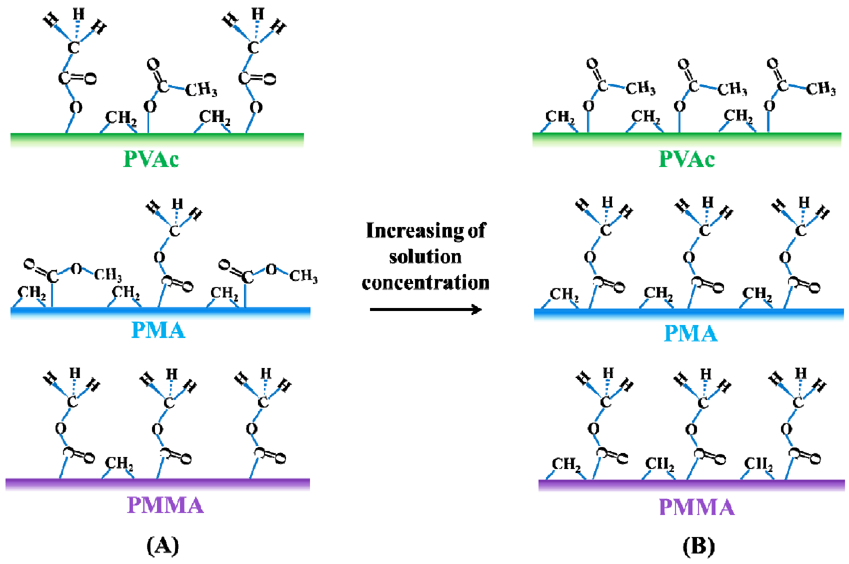

Fig.4. Schematic representation of the surface structure of PVAc, PMA and PMMA films cast from (A) low and (B) relative high concentration of casting solutions.

Fig.5a shows SFG spectra of cast PMA films prepared by various concentrations of casting solution. Two peaks at 2960 cm^{-1} and 2910 cm^{-1} are observed in the *ssp* spectra, for which the intensity of the peak at 2960 cm^{-1} increases and that of the peak at 2910 cm^{-1} remains almost constant with increasing concentration of the film-formation solution from 0.5wt% to 4.0wt%. However, for the *ppp* spectra, the intensity of the peak at 2960 cm^{-1} of cast PMA film was not sensitive to the corresponding concentration of the casting solution. For the cast PMMA films shown in Fig.5b, both the peak at 2955 cm^{-1} in the *ssp* spectra and the peak at 2965 cm^{-1} in the *ppp* spectra remain almost unchanged and only the peak at 2910 cm^{-1} in the *ssp* spectra increases with increasing concentration of corresponding casting solution. The peak assignments for vibrational signals of PMMA and PMA have been extensively studied. As detailed in the literature[51-55] with regard to the *ssp* SFG spectra of cast PMMA and PMA films, there are two major bands at 2910 and 2955 cm^{-1}, which can be assigned to the C-H symmetric stretching vibrations of the methylene groups (CH_2) in the main chain and the ester methyl groups (OCH_3), respectively. In the *ppp* SFG spectra of PMMA and PMA, the major band at around 2960cm^{-1} is attributed to the C-H symmetric stretching vibrations of the ester methyl groups. Similar to

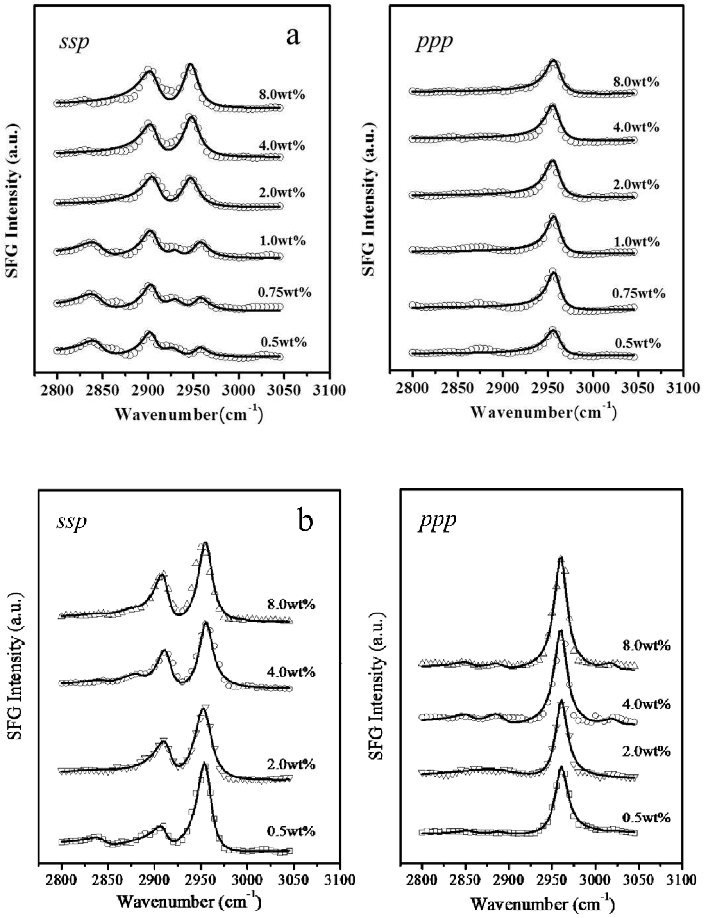

Fig. 5 SFG spectra of cast PMA (a) and PMMA (b) films prepared by various concentrations of casting solution.

observations reported by Tanaka[55] for cast PMMA film surfaces, hydrophobic functional moieties such as methylene groups, were also present. For the PMMA film, while the α methyl group was oriented along the direction parallel to the interface, the ester methyl and methylene groups were oriented normal to the interface; this indicates that the methylene groups became randomly oriented at the surface of cast films prepared with low concentration of casting solution or, in part, migrated into the internal region. For cast PMMA film prepared with relatively high concentration of casting solution, hydrophobic methylene groups in the main chain can be more ordered and partially oriented in the plane of the surface (as shown in Fig.4), which is favorable for decreasing the free energy. These observations are also in good agreement with both the contact angles and surface free energies of the PMMA films. However, for cast PMA films, the concentration-dependent surface structure was different from that of the cast PMMA films. The ester methyl groups were randomly oriented at the surface when the cast film was prepared with low concentration of casting solution or, in part, migrated into the internal region. As the concentration of casting solution increases, the ester methyl groups in the main chain on the corresponding cast PMA film surface could be more ordered and partially orient in the plane of the surface, while the structure of the methylene groups in the main chain on the surface remains almost unchanged, partially oriented in the plane of the surface with a relatively close-packed structure (as shown in Fig.4). The results above indicate that the well-ordered methyl groups of ester side chains on the film surface, oriented away from the polymer film, play a more important role in determining the surface free energy than the methylene groups in the backbone of the polymers, since only this structure could shield the neighboring OC=O polar component from contacting the air, resulting in a hydrophobic surface. At the same time, it is obvious that there is a pronounced difference in the change in surface structures of the PVAc, PMA and PMMA films with corresponding change in concentration of casting solution, although the differences in their molecular structures are very slight.

The water contact angles of PVAc film prepared by casting 2wt% PVAc solution and those of the annealed corresponding cast film are presented in Fig. 6. The results show that after annealing the cast PVAc film, its water contact angle increased from 61° to 72°, the same as that of the cast film prepared by 0.5 wt% casting solution. The SFG spectra show that for the annealed cast film, the band at 2910cm^{-1} became smaller in the *ssp* SFG spectra, while the peaks at 2942cm^{-1} in the *ssp* SFG spectra and 2965cm^{-1} in the *ppp* SFG spectra became larger compared to those of the corresponding cast film, which were similar to the cast PVAc film prepared by 0.5wt% casting solution. The results above indicate that the PVAc molecular chains at the surface of its films cast from concentrated solution adopt a more thermodynamic

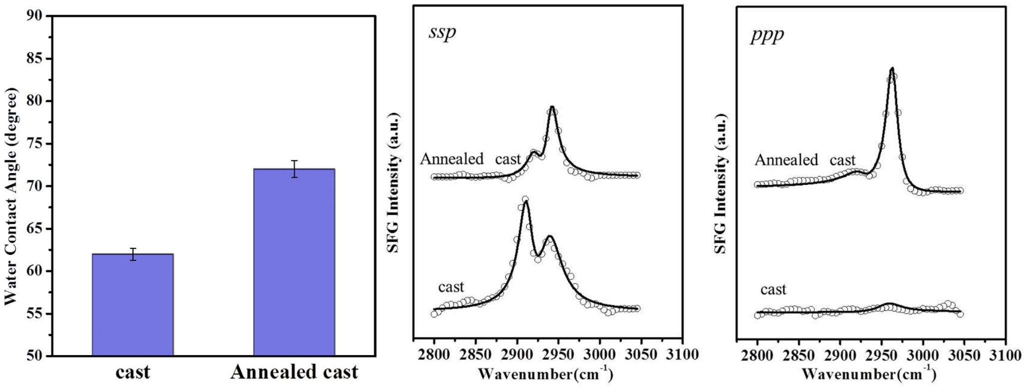

Fig.6 Water contact angles and SFG spectra of PVAc films prepared by solution casting and corresponding annealed cast film. The solution concentration was 2.0wt%. Annealing at 70 ºC for 12 h.

nonequilibrium conformation relative to those of the films cast from dilute solution. However, both PMA and PMMA films cast from concentrated solution have higher water contact angles, suggesting that their molecular chains adopt a more thermodynamic equilibrium conformation relative to that of films cast from dilute solution. Once the solution concentration reaches 4.0wt%, the chain conformation on the resulting film surface is at a relative equilibrium state under such conditions.

3.2 π-A isotherms and SFG spectra of PVAc, PMA and PMMA at the air/water interface

Fig. 7 shows the surface pressure-area (π-A) isotherms of PVAc, PMA and PMMA monolayers at the air/water interface. It is observed that the shapes of both PMA and PVAc isotherms belong to a typical expanded-type isotherm in which changes in the surface pressure are detected at a large surface area, i.e. low surface concentration, similar to that reported by Kawaguchi[56] and Crisp[57]. The surface pressure gradually increases with decreasing surface area and attains a plateau value. However, the shape of the PMMA isotherm corresponds to a typical condensed-type isotherm. π is first observed at a smaller surface area than the expanded π-A isotherm, then shows a steep increase, and the monolayer then shows a collapse, similar to that previously reported [56,57].

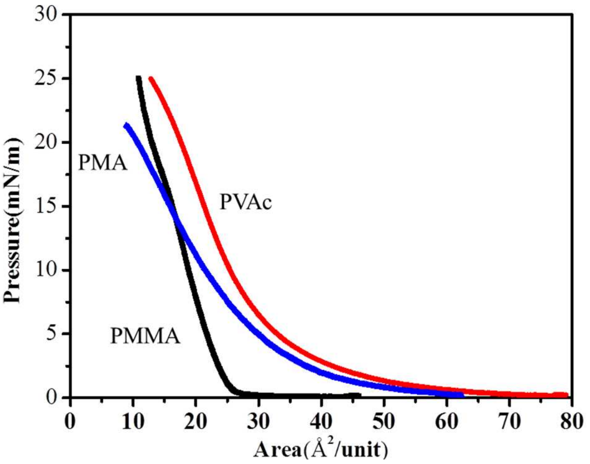

Fig. 7 Surface pressure-area (π-A) isotherms of PVAc, PMA and PMMA monolayers spread on water at 20ºC.

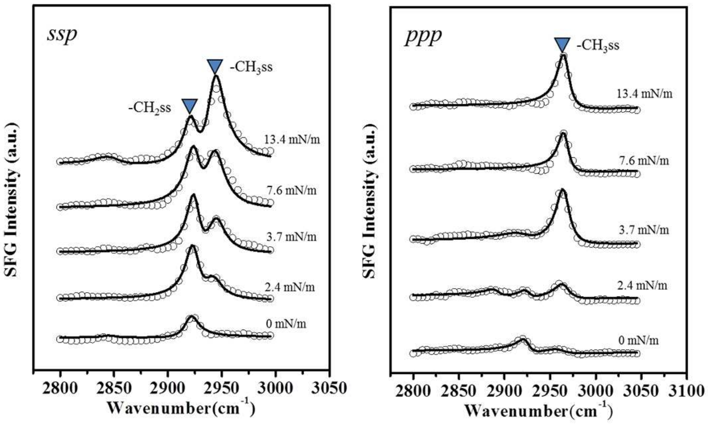

Fig. 8 Surface pressure dependence of the SFG spectra for 2800-3050 cm^{-1} region measured under the *ssp* and *ppp* polarization for PVAc monolayer (at 25ºC).

Fig.8 exhibits the surface pressure dependence of the SFG spectra in the 2800-3100 cm^{-1} region observed for the PVAc monolayer with *ssp* and *ppp* polarization combinations, respectively, spread on pure water. It is apparent that only a peak at 2920 cm^{-1} in the SFG spectra of PVAc is observed in both *ssp* and *ppp* polarization combination when the surface pressure is 0. With increasing surface pressure, the peak at 2945 cm^{-1} increases sharply and the peak at 2920 cm^{-1} decreases in the *ssp* spectra, while the peak at 2965 cm^{-1} increases sharply and the peak at 2920

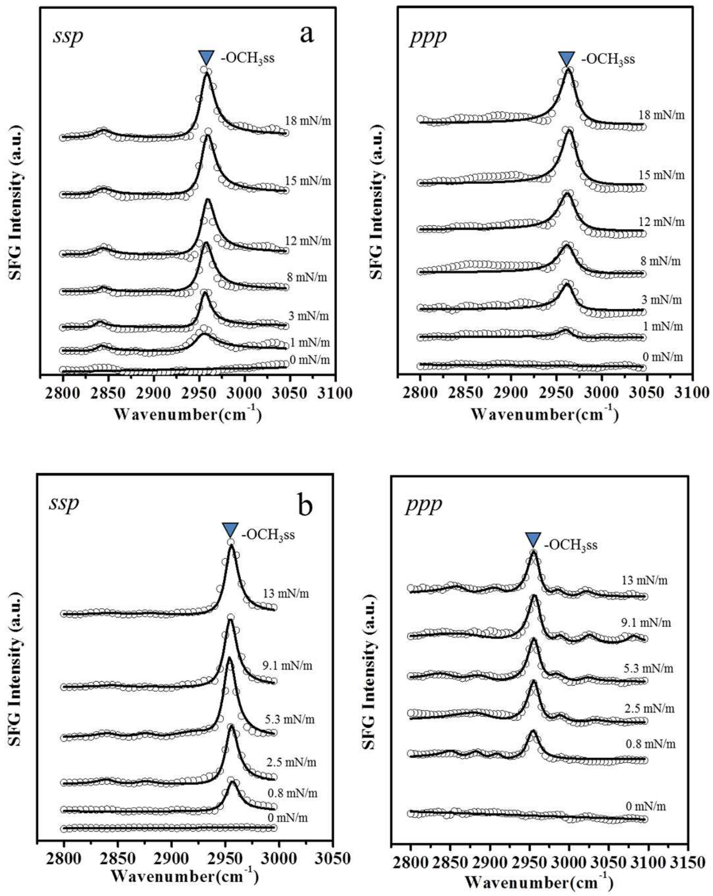

Fig. 9 Surface pressure dependence of the SFG spectra for 2800-3100 cm-1 region measured under *ssp* and *ppp* polarization for PMA (a) and PMMA (b) monolayers (at 25ºC).

cm^{-1} disappears in the *ppp* spectra. The two peaks at 2920 cm^{-1} and 2945 cm^{-1} in the *ssp* spectra were assigned to the symmetric stretching mode of the backbone methylene and the methyl groups from the side chains, respectively, while the peak at 2965 cm^{-1} originates from the antisymmetric stretching mode of the acetyl methyl groups of the side chains.[45] This indicates that the backbone methylene groups in PVAc dominate the PVAc monolayer at lower surface pressures, but when surface pressure increases, the surface is dominated by acetyl methyl groups.

Fig. 9a and 9b show the SFG spectra of PMA and PMMA monolayers at various surface pressures with *ssp* and *ppp* polarization combinations in the range of 2800~3050 cm^{-1}, corresponding to the C−H stretching vibrations. It is apparent that no peaks are observed when the surface pressure is 0 mN/m. The peaks at 2955 cm^{-1} in the *ssp* spectra and at 2960 cm^{-1} in the *ppp* spectra of PMMA monolayer appear with only a small surface pressure, and then a slight change occurs with increasing surface pressure. However, for PMA, these two peaks increase sharply when the surface pressure increases from 0 to 3 mN/m, and then change slightly as the surface pressure exceeds 3 mN/m. These peaks are assigned to the stretching mode of the ester methyl groups in PMA and PMMA. [51, 58]

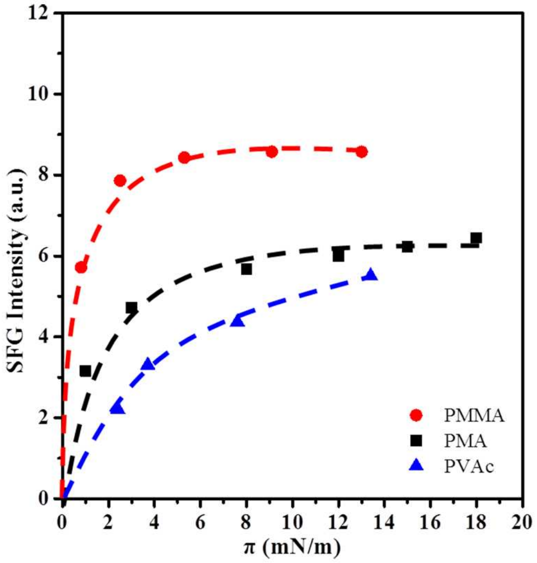

Fig.10 The *ssp* intensity of the methyl stretching peak as a function of surface pressure of PVAc, PMA and PMMA monolayer spreading on water at 25 ºC.

The intensities of the methyl stretching peaks of PVAc, PMA and PMMA in their corresponding *ssp* spectra are plotted in Fig.10 as a function of surface pressure. The error of the peak intensities is estimated to be <10%. The strength of the methyl symmetric stretch mode in the *ssp* spectra increases as the average tilt angle of the methyl groups decreases and also as the number density of the methyl groups in the adsorbed layer increases. [59-61] The changes observed in the intensity of this peak can be interpreted in terms of the changes of the segregation amount accompanied by the orientation changes of the side chain methyl groups of the polymers. As seen from Fig.

10, the behavior of PVAc is different from that of PMA and PMMA. With increasing surface pressure, the sum-frequency intensity first increases and then above 2.5mN/m for PMMA and 8mN/m for PMA appears to approach a limiting value. On the other hand, the values for PVAc steadily increase with increasing surface pressure although the intensities are significantly lower at any given surface pressure compared to those of PMA and PMMA, indicating the presence of a smaller amount of oriented methyl groups in the adsorbed layer for PVAc.

In order to get further information about the structure of PVAc, PMA and PMMA monolayers at air/water interface, we calculate the average tilt angle of the ester methyl groups in PMMA and the acetyl methyl groups in PVAc under every surface pressure, base on Chen and Tanaka's work.[51, 55] The results showed that the average tile angle of the ester methyl groups in PMMA and PMA change slightly from 36º to 30º , 40º to 36º respectively relative to the surface normal with increasing surface pressure at air/water interface, while the orientation of acetyl methyl groups in the PVAc monolayer changes greatly from 71º to 45º under the compression. It was reported[62] that a higher probability of the *cis* state of side group in PVAc chain should help the carbonyl groups to be more exposed and result in a higher surface area of the carbonyl moiety since the carbonyl group of PVAc is more distant from the polymer chain backbone compared to those in PMMA chains. The results from molecular models and force area curves reveal [57] that steric hindrance will prevent all the acetyl groups in PVAc arranging themselves simultaneously into the *trans* form with the resultant moment vertical. Since the electric force on the dipoles is balanced by repulsion between the methyl groups and the main chain, external compression of the film might cause further re-orientation towards the *trans* position. For PMA and PMMA, only the *trans* orientation of ester methyl groups is compatible with a really close-packed condition of the main chains. This is in agreement with the surface pressure dependence of the SFG spectra for PVAc, PMA and PMMA monolayers.

Therefore, we believe that the reason for PVAc debasing surface tension is caused by both the synergetic effects of concentration and the orientation of the PVAc molecules, which is analogous to the phenomena of cis-6Az10-PVA monolayers in

Itoh's paper.[63] Since the carbonyl groups in PVAc chains have more conformational freedom than those in PMMA chains due to the longer distance from the chain backbone, polyvinyl acetate shows a structure nearer to the *cis* than *trans* state when the surface pressure is low. With increasing surface pressure, external compression of the film might cause further re-orientation towards the *trans* position. Therefore, the peak at 2960 cm^{-1} attributed to the acetyl methyl group increased and the peak at 2910 cm^{-1} attributed to the methylene group in the PVAC main chain decreased with increasing surface pressure on the PVAc monolayer, as shown in Fig.8.

For PMMA and PMA, the ester methyl group is connected to an oxygen atom located between the carbonyl and ester methyl groups. Being far from the "anchor point", the ester methyl groups in PMMA and PMA posess more degree of freedom compared to the methyl group in PVAc. Only the *trans* orientation is compatible with a really close-packed condition of the main chains, the main chain being somewhat below the side chains. In other words, the ester methyl groups in PMMA and PMA more easily form an oriented structure when the surface pressure stays quite low at the air/water interface. Further compression does not change the orientation of the ester methyl groups, which is also similar to the discovery in the thesis of Itoh[63] and also as observed by Yu.[64] Therefore, only the peak at 2960 cm^{-1} was observed and changes little with increasing surface pressure. However, the ester methyl group on the PMMA monolayer surface easily adopts a *trans* orientation compared with that on the PMA surface due to steric hindrance of the α-methyl group in the PMMA main chains. This results in much higher surface pressure for PMA than that for PMMA, as the sum-frequency intensity seems to approach a limiting value. This result is in agreement with the observations from the surface pressure-area (π-A) isotherms.

3.3 The cause of solution concentration dependence of surface structure of PVAc, PMA and PMMA films

The SFG spectra for PVAc, PMA and PMMA films after immersion in water for the *ssp* polarization combination were presented in Fig.11. Broad peaks were observed around 3200 and 3600 cm^{-1}. However, the peak around 3600 cm^{-1} for PVAc was much stronger that that for PMA and PMMA. The peak around 3200 and 3600 cm^{-1} were specifically assigned to ice-like water and free O-H, respectively. It was reported that the peak around 3600 cm^{-1} at water/PMMA interface was related to water molecules hydrogen bonded to the carbonyl groups located in a confined geometry and this peak could be used to analyze H-bonding ability between carbonyl group and water.[55,65] The SFG spectra in Fig.11 indicated that hydrogen-bond ability of PVAc was stronger that that of PMMA and PMA. This was also confirmed by water adsorption in thin PVAc, PMA and PMMA films with about 200 nm. After immersion in water at 25 ºC for 1h, a 1.78% increase in the thickness of thin PVAc film was observed, which was much higher than these of thin PMA and PMMA films (about 0.32%).

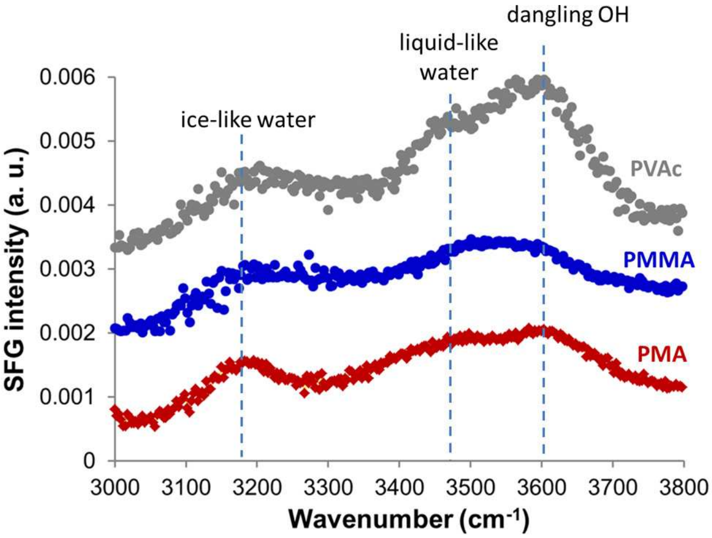

Fig.11 SFG spectra (*ssp*) in the OH stretching region of PVAc, PMA and PMMA films cast from 6 wt% solution after immersion in water at 25 ºC for 30 min.

Further characterization of the surface of PVAc, PMA and PMMA films prepared with various concentrations of casting solutions was conducted by X-ray photoelectron spectroscopy (XPS). Fig.12 presents the high-resolution XPS spectra of the C_{1s} region for the PVAc, PMA and PMMA films. In each case, three spectral components at 284.6, 286.2 and 289.0 eV were observed, which correspond to C-H, C-O and O-C=O groups, respectively.[45] It was observed that the composition of the O-C=O groups on the surfaces of PMA and PMMA films decreased with increasing the concentration of casting solution, while the cast PVAc film showed a reverse trend. It is obvious that the composition of the O-C=O groups on the PMA and PMMA surfaces are only 2.9% and 2.7 %, respectively, which is much lower than that on the PVAc surfaces (12.0%) when the films was cast from 6% polymer solution. It was evident that the composition of the O-C=O groups shown in Fig.12 was related to the exposed surface area of carbonyl group on corresponding film surface, since these data were

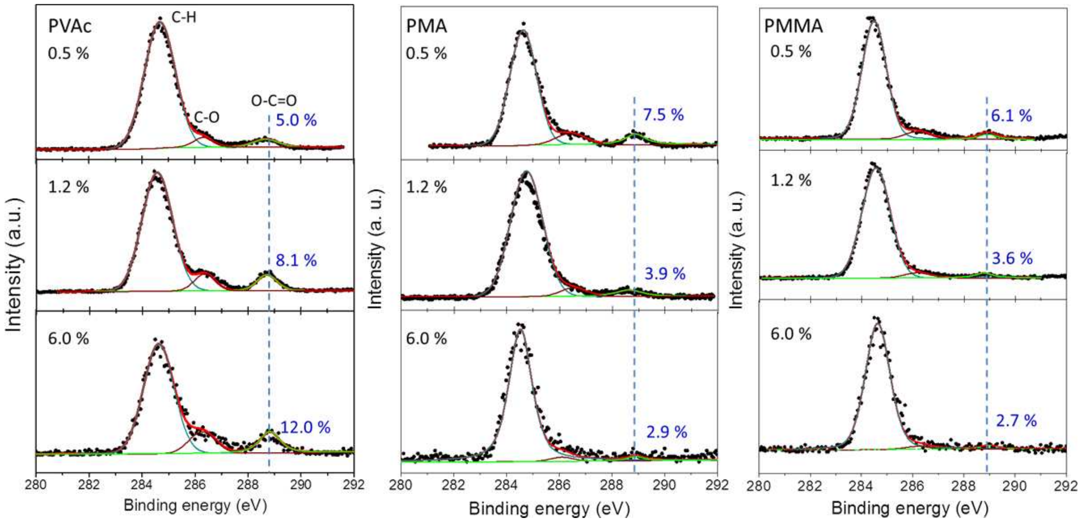

Fig. 12 High-resolution XPS spectra in the C_{1s} region for the surfaces of PVAc, PMA and PMMA films cast from 0.5wt%,1.2wt% and 6.0wt% polymer solutions. The photoelectron emission angle was 5°, corresponding to the effective sampling depth of about 0.9 nm.

obtained from the effective sampling depth of about 0.9 nm. Chang et. al [62] constructed a model of their chains and calculated the Connolly surface area, which is the surface area of the carbonyl moiety accessible for a small molecule to interact with. The average Connolly surface area of carbonyl groups of PMMA and PVAc with 150 of the repeat units were 1388±75 $Å^2$ and 1935±108 $Å^2$, respectively. This simulation study was consistent with our results obtained by XPS analysis, SFG spectra and contact angle measurements.

In general, the formation of surface structure is governed by thermodynamics, but the kinetics for the segregation and array processes, determined by fixed process methods and conditions, also play an important role in the ultimate surface structure formation. It is commonly observed that polymer chains tend to form aggregates in polymer solutions of sufficiently high concentration.[66] The origin of the aggregation is the interchain attraction forces. Since these interactions are short-range forces, the polymer chains are isolated in dilute solution, thus these intermolecular forces can be neglected. It is expected that the probability for the coiled polymer chains to penetrate each other is small. As the concentration increases and the distance between the polymer chains decreases, these interchain forces become more significant. As a result, the polymer coils start to entangle with each other to form “loose aggregates”. It is predicated that further increases in the concentration will eventually result in heavy interpenetration of the polymer chains, or the formation of “strong aggregation”. 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.

It is clear that water contact angle is high when both the acetyl methyl group and methylene groups are oriented outward at the surface of PVAc from SFG spectra. These observations are in agreement with Helfand’s speculations regarding results from studies of poly(vinyl alcohol-co-vinyl acetate) copolymer by XPS and Tof-SIMS. [67] Results from the annealing experiments indicate that the observed surface structure formation at the PVAc film cast by dilute solution is dominated by thermodynamic requirements. However, the domination is by kinetic hindrance when the concentration of casting solution is relatively high. From surface pressure dependent SFG spectra of the PVAc monolayers, it is apparent that the methylene groups in the PVAc backbone can be more ordered than the acetyl methyl groups which usually exhibit *cis* state. At the same time, it is already known that the homopolymers poly(methyl acrylate) and poly(vinyl acetate) differ significantly in their subglass relaxation behavior.[68,69] The relaxation process is much weaker in the latter. The reason for this relaxation difference was attributed to the site energy difference for side-group reorientation in PVAc being greater than that in PMA.[70] It was also found that the local configuration of PVAc segments presented more irregularity in concentrated solution compared to those in the dilute solution[71], while the local configuration of the PMA segments presented more regularity in concentrated solution compared to those in the dilute solution. [72,73] Thus, when the concentration of casting solution is low, the PVAc chains have enough mobility to change their conformation and the acetyl methyl groups will orient easily towards the *trans* position to form a well-ordered arrangement, associated with well-ordered methylene groups during solvent evaporation, resulting in a relatively high water contact angle and low surface free energy for the cast PVAc films, due to thermodynamic requirements. When the concentration of casting solution is relatively high, the mobility of the PVAc chains is hindered due to chain entanglement and local configurations of the PVAc segments having more irregularity in concentrated solution. It is difficult for the PVAc chains to change side group conformation from *cis* to *trans* state in order for the acetyl methyl groups to form regularity of alignment to meet the requirement of minimum surface free energy during film formation, due to the relatively higher energy required for acetyl methyl group reorientation. Thus, the resulting random arrangement of acetyl methyl groups on PVAc film surfaces should help the carbonyl groups to be more exposed, resulting in a decrease in water contact angle and an increase in surface free energy.

For the PMMA and PMA systems, the ester methyl group easily adopts a *trans* orientation. At the same time, it is easier for the ester methyl groups to form well-ordered structures due to the relative lower energy for ester methyl group reorientation. This was confirmed by the surface pressure dependent SFG spectra of their monolayers. In addition, it is much easier for the ester methyl groups in PMMA to form regularity of alignment than in PMA due to steric hindrance of the α-methyl groups in the main chains. Based on the literature[74,75], it may be inferred that the surface structures of the resulting PMA and PMMA films are related to the entanglement of the PMA and PMMA chains in the corresponding casting solutions. It has been accepted that when a film was prepared by polymer solution casting, the polymer concentration in the film increased as the solvent evaporated during film formation.[76,77] In thermal equilibrium, the number of entanglements per chain with surrounding chains increases with polymer concentration. The entanglement density will be enhanced further by annealing of the polymer film. The re-entanglement of the chains in the film by annealing was found to be substantially longer than the reptation time.[76] As a result, some memory of the chain conformations in the solution may carry over to the resulting dry film, including that of its surface structure.

Higher degrees of PMA and PMMA chain entanglements on the film surfaces were obtained when the films were prepared using a relatively high concentration of casting solution.[78] Solution casting is a relatively mild process during which the solvent evaporates slowly, allowing enough time for the polymer chains to minimize free energy by adjusting their chain conformations. As the solution concentration increases, the polymer chains will penetrate and entangle with each other, contributing to achieve an equilibrium state, in which the methylene groups in the PMMA backbone became well-ordered on the surface while the ester methyl group adopts a *trans* orientation and remains well-oriented toward the surface. Therefore, a relative equilibrium state on a film surface is easily achieved when casting solution with relatively high viscosity is employed to prepare PMMA film by solution casting. However, for PMA, since there is a lack of α-methyl groups in the main chain, the ester methyl groups in the PMA chains have relatively high freedom to orient in comparison with PMMA, which also results in the methylene groups in the backbone easily forming a well-oriented structure. When the concentration of PMA casting solution is low, similar to PVAc, a well-oriented methylene group structure is easily formed during film formation. As the solution concentration increases, the polymer chains will penetrate and entangle with each other, contributing to achieve an equilibrium state. At the same time, the local configuration of the PMA segments present more regularity in concentrated solution, resulting in well-oriented both ester methyl groups and methylene groups in the backbone on the surface of the PMA film prepared by concentrated solution. Therefore, a relative equilibrium state on a film surface is easily achieved when casting solution with relatively high viscosity is employed to prepare PMA film by solution casting.

4. Conclusions

The effects of type of linkage between the polymer backbone and the chain side groups on the surface segregation of methyl groups during film formation were investigated using poly(vinyl acetate)(PVAc), poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) as model polymers. The hydrophobicity of both PMA and PMMA films increased with increasing concentration of the corresponding polymer solution, whereas cast PVAc film gave the reverse trend with respect to concentration of casting solution. The film surface structures were characterized by sum frequency generation (SFG) vibrational spectra. The results showed that the methylene groups can be more ordered while the acetyl methyl group became more random on the surface of cast PVAc film with increasing concentration of casting solution. However, the regularity of alignment of the ester methyl group increased and that of methylene groups did not change for cast PMA films with increasing concentration of casting solution. The cast PMMA film showed a reverse trend compared with the corresponding PMA film. The SFG results indicated that only when both the methyl and methylene groups are oriented outward at the surface with regularity of alignment, does the surface present a relatively high water contact angle and low surface free energy. Significantly, well-oriented methyl groups on the surface, rather than methylene groups, play an important role in determining surface hydrophobicity. The observed surface structural differences in the concentration dependence of the casting solution on the corresponding cast films can be attributed to the relative lower energy for ester methyl group orientation, an ester group structure that is nearer to the *trans* state, and more regularity of the local configuration of segments in concentrated solutions of PMA and PMMA compared to that of PVAc.

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Notes

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References

1 W. R. Dreher, A. Singh and M. W. Urban, *Macromolecules*, 2005, **38**, 4666−4672.

2 H. Yang, U. Sa, M. Kang, H. S. Ryu, C. Y. Ryu and K. Cho, *Polymer* , 2006, **47**, 3889−3895.

3 S.Wu, *Polymer Interface and Adhesion*, Marcell Dekker, New York,1982.

4 F. Carbassi, M. Morra and E.Occhiello, *Polymer Surface: From Physics to Technology*, John Wiley and Sons, New York, 1994.

5 H. G. Ni, D. W. Xue, X. F. Wang, W. Zhang, X. P. Wang and Z. Q. Shen, *Sci. China, Ser. B: Chem.*, 2009, **52**, 203−211.

6 C. Neto, M. James and A. M. Telford, *Macromolecules*, 2009, **42**, 4801-4808.

7 D. Alexander, P. Yana and W. Norbert, *Appl. Mater. Interfaces*, 2010, **2**, 2060−2068.

8 J. A. Mielczarski, E. Mielczarski, G. Galli, and A. Morelli , *Langmuir*, 2010, **26**, 2871−2876.

9 Y. Y. Lua, X. P. Cao, B.R. Rohrs and D.S. Aldrich, *Langmuir*, 2007, **23**, 4286−4292.

10 H. G. Ni, X. H. Li, Y. Y. Hu, B. Zuo, Z. L. Zhao, J. P. Yang, D. X. Yuan, X. Y. Ye and X. P. Wang, *J. Phys. Chem. C*, 2012, **116**, 24151−24160.

11 A. F. Boue, A. Menelle and J. P. Cotton, *Macromolecules*, 2000, **33**, 997−1001.

12 Z. H. Yan, R. P. Zhang, Y. R. Zhao, B. Zuo, F. F. Zheng, T. Y. Chen X. P. Wang and Z. Q. Shen, *Sci. China. Ser. B-Chem.*, 2012, **55**, 1263−1273.

13 Y. L. Hei, M. Deng, X. Y. Ye, H. G. Ni, P. Ye, X. P. Wang and Z. Q. Shen, *Sci. China. Ser. B-Chem.*, 2009, **39**, 1627−1637.

14 X. H. Zhang, J. F. Douglas and R. L. Jones, *Soft Matter*, 2012, **8**, 4980−4987.

15 X. L. Lu and Y. L. Mi, *Macromolecules*, 2005, **38**, 839−843.

16 H. Tsuruta, Y. Fujii, N. Kai, H. Kataoka, T. Ishizone, M. Doi, H. Morita and K. Tanaka. *Macromolecules*, 2012, 45, 4643−4649.

17 X. L. Lu, I. Cheng and Y. L. Mi, *Polymer*, 2007, **48**, 682−686.

18 M. Kobashi and H. Takeuchi, *Macromolecules,* 1998, **31**, 7273−7278.

19 L. Y. Wong, R. Q. Png, F. B. Shanjeera Silva, L. L. Chua, D. V. Maheswar Repaka, S. Chen, X. Gao, L. Ke, S. J. Chua, A. T. S. Wee and P. K. H. Ho, *Langmuir*, 2010, **26**, 15494−15507.

20 A. M. Botelho do Rego, O. Pellegrino, J. M. G. Martinho and J. Lopes da Silva, *Langmuir*, 2000, **16**, 2385−2388.

21 Y. Urushihara and T. Nishino, *Langmuir*, 2005, **21**, 2614−2618.

22 B. Zuo, W. L. Liu, H. Fan, Y. Z. Zhang, T. T. He and X. P. Wang, *Soft Matter*, 2013, **9**, 5428−5437.

23 K. Shuto, Y. Oishi, T. Kajiyama and C. C. Han, *Macromolecules*, 1993, **26**, 6589−6594.

24 R. L. Jones, S. K. Kumar, D. L. Ho, R. M. Briber and T. P. Russell, *Nature*, 1999, **400**, 146−149.

25 X. Y. Ye, B. Zuo, M. Deng, Y. L. Hei, H. G. Ni, X. L. Lu and X. P. Wang, *J. Colloid Interface Sci.*, 2010, **349**, 205−214.

26 D. W. Xue, X. P. Wang, H. G. Ni, W. Zhang and G. Xue. *Langmuir*, 2009, **25**, 2248−2257.

27 H. R. Thomas and J. J. O'Malley, *Macromolecules*, 1979, **12**, 323−329.

28 T. Nishino, Y. Urushihara, M. Meguro and K. Nakamae, *J Colloid Interface Sci*, 2005, **283**, 533−538.

29 A. Synytska, D. Appelhans, Z. Wang, G. F. Simon, F. Lehmann, M. Stamm and K. Grundke, *Macromolecules*, 2007, **40**, 297−305.

30 X. F. Wang, H. G. Ni, D. W. Xue, X.P. Wang, R. R. Feng and H. F. Wang , *J Colloid Interface Sci.*, 2008, **321**, 373−383.

31 W. L. Wu, G. C. Yuan, A. H. He and C. C. Han, *Langmuir*, 2009, **25**, 3178−3183.

32 H. Y. Huang, Z. J. Hu, Y. Z. Chen, F. J. Zhang, Y. M. Gong and T. B. He, *Macromolecules*, 2004**, 37**, 6523–6530.

33 H. Hasegawa and T. Hashimoto, *Macromolecules*, 1985, **18,** 589−590.

34 K. Ishizu and T. Fukuyama, *Macromolecules*, 1989, **22**, 244−248.

35 K. Ishizu, Y. Yamada and T. Fukutomi, *Polymer*, 1990, **31**, 2047−2052.

36 F. R. Saraf, S. Niu and E. Stumb, *Appl. Phys. Lett.*, 2002, **80**, 4425−4427.

37 Z. T. Shi, M. Han, F. Q. Song, J. F. Zhou, J. G. Wan and G. H. Wang , *J. Phys. Chem. B*, 2006, **110**, 18154−18157.

38 A. Turturro, E. Gattiglia, P. Vacca, G. T. Viola, *Polymer*, 1995, **36**, 3987−3996.

39 G. Kim and W. Libera, *Macromolecules*, 1998, **31**, 2670−2672.

40 R. L. Schmitt, J. A. Gardella, J. H. Magill, L. Salvati and R. L. Chin , *Macromolecules*, 1985, **18**, 2675−2679.

41 T. P. Russell, *Science*, 2002, **297**, 964−967.

42 J. Q. Xu, Y. J. Liu, J. S. He, R. P. Zhang, B. Zuo and X. P. Wang, *Soft Matter*, 2014, **10**, 8992−9002.

43 J. P. Yang, D. X. Yuan, B. Zhou, J. Gao, H. G. Ni, L. Zhang and X. P. Wang, *J. Colloid Interface Sci.*, 2011, **359**, 269−278.

44 Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley-Interscience, New York, 1984.

45 B. Zuo, Y. Y. Hu, X. L. Lu, S. X. Zhang, H. Fan and X. P. Wang, *J. Phys. Chem. C*, 2013, **117**, 3396−3406.

46 X. Zhuang, P. B. Miranda, D. Kim and Y. R. Shen, *Phys. Rev. B*, 1999, **59**, 12632−12640.

47 A. P. Davis, G. Ma and H. C. Allen, *Analytica Chimica Acta*, 2003**, 496**, 117−131.

48 X. J. Cai and S. Baldelli, *J. Phys. Chem. C*, 2011**, 115**, 19178−19189.

49 H. Rangwalla, A. D. Schwab, B. Yurdumakan, D. G. Yablon, M. S. Yeganeh and A. Dhinojwala, *Langmuir*, 2004**, 20**, 8625−8633.

50 X. Wei, X. Zhuang, S. C. Hong, T. Goto and Y. R. Shen, *Phys. Rev. Lett.* 1999**, 82,** 4256−4259.

51 J. Wang, C. Y. Chen, S. M. Buck and Z. Chen, *J. Phys. Chem. B,* 2001, **105**, 12118−12125.

52 M. L. Clarke, C. Y. Chen, J. Wang and Z. Chen, *Langmuir*, 2006, **22**, 8800−8806.

53 K. C. Jena, P. A. Covert, S. A. Hall and D. K. Hore, *J. Phys. Chem. C*, 2011, **115**, 15570−15574.

54 A. Horinouchi, H. Atarashi, Y. Fujii and K. Tanaka, *Macromolecules*, 2012, **45**, 4638−4642.

55 Y. Tateishi, N. Kai, H. Noguchi, K. Uosaki, T. Nagamura and K. Tanaka, *Polym. Chem.*, 2010, **1**, 303−311.

56 M.Kawaguchi and K.Nagata, *Langmuir*, 1988, **4**, 407−410.

57 D. J. Crisp, *J. Colliod Sci.*, 1946, **1**, 49−70.

58 A. Rao, H. Rangwalla, V. Varshney and A. Dhinojwala, *Langmuir*, 2004, **20**, 7183−7188.

59 M. C. Henry, L. K. Wolf and M. C. Messmer, *J. Phys. Chem. B*, 2003, **107**, 2765−2770.

60 I. Varga, T. Keszthelyi, R. Mészáros, O. Hakkel and T. Gilányi, *J. Phys. Chem. B*, 2005, **109**, 872−878.

61 Ė. Kiss, T. Keszthelyi, T. Kormány and O. Hakkel, *Macromolecules*, 2006, **39**, 9375−9384.

62 H. Lee and T. Chang, *Macromolecules*, 2001, **34**, 937−941.

63 C. Ohe, H. Kamijo, M. Arai, M. Adachi, H. Miyazawa, K. Itoh and T. Seki, *J. Phys. Chem. C*, 2008, **112**, 172−181.

64 C. Kim, M. C. Gurau, P. S. Cremer and H. Yu, *Langmuir*, 2008, **24** , 10155−10160.

65 Y. Oda, A. Horinouchi, D. Kawaguchi, H. Matsuno, S. Kanaoka, S. Aoshima, K. Tanaka, *Langmuir*, 2014, **30**,1215−1219.

66 E. Wyn-Jones and J. Gormally, *Aggregation Processes in Solution*, Elsevier, Amsterdam, 1983.

67 M. A. Helfand, J. B. Mazzanti, M. Fone and R. H. Reamey, *Langmuir*, 1996, **12**, 1296−1302.

68 Y. Ishida, *Kolloid Z.*, 1961, **174**, 124−127.

69 Y. Ishida , M. Matsuo and K. Yamafuji, *Kolloid Z.*, 1962, **180**, 108−114.

70 G. D. Smith, F. Liu, R. W. Devereaux and R. H. Boyd, *Macromolecules,* 1992, **25**, 703−708.

71 M. Yada, M. Nakazawa, O. Urakawa, Y. Morishima and K. Adachi, *Macromolecules*, 2000, **33**, 3368−3374.

72 K. Adachi and Y. Ishida, *Polymer J.*, 1979, **11**, 233−239.

73 K. Adachi and T. Kotaka, *Polymer J.*, 1981, **13**, 687−692.

74 R. H. Colby, L. J. Fetters, W. G. Funk and W. W. Graessley, *Macromolecules*, 1991, **24**, 3873−3882.

75 A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, 1995, **28**, 1859−1871.

76 D. R. Barbero and U. Steiner, *Phys. Rev. Lett.*, 2009, **102**, 248303.

77 K. R. Thomas, A. Chenneviere, G. Reiter and U. Steiner, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **83**, 021804.

78 H. K. Tian, Y. H. Yang, J. Ding, W. L. Liu, B. Zuo, J. P. Yang and X. P. Wang, *Soft Matter*, 2014, **10**, 6347−6356.

Table of contents entry:

Influence of Linkage Type between Polymer Backbone and Side Groups on Surface Segregation of Methyl Groups During Film Formation

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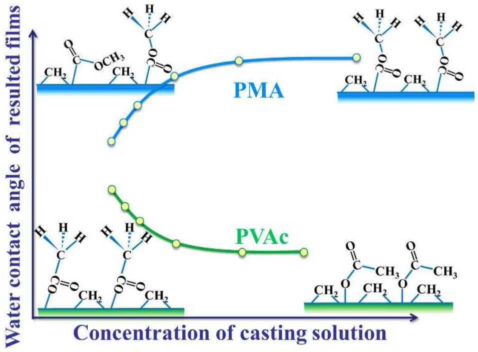

A large difference in the concentration-dependent surface structures of the cast PMA and PVAc films was caused by the reversed position of the ester group