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Stereocomplexation of Stereoregular Poly(methyl methacrylate) in Thin Film at Gold Surface

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Introduction

Thin polymer films have received more and more attention in recent years due to the wide range of applications in electronics, coating, and biomedicine. Several studies have shown that thin polymer films of submicron thickness exhibit different properties as compared with bulk material, so it becomes necessary to understand the properties, morphology, and the chain organization of polymer in thin film.

A stereocomplex of PMMA, a crystalline-like structure built of isotactic and syndiotactic PMMA (i- and s-PMMA) segments, shows a double-stranded helical structure and a high thermal stability up to around 200 °C.[1−4] Because of the special supermolecular structure and high thermal stability, the PMMA stereocomplex is expected for many potential applications. This leads the stereocomplexation of stereoregular poly(methyl methacrylate) (PMMA) to be the subject of research for more than 30 years. It was well documented that stereocomplexation can take place in the mixtures of i- and s-PMMA in suitable solvent, in high-temperature annealing, or under supercritical fluid.[5−12] Even though countless publications have appeared on dealing with the stereocomplexation of i- and s-PMMA, less attention has been paid to the stereocomplexation process and stereocomplex structures in thin films. To our knowledge, only Schouten et al. reported a procedure for producing PMMA monolayer ultrathin film with stereocomplex at the air−water interface under high surface pressure.[13] Through transferring the monolayers in stereocomplex conformation onto a solid substrate consecutively, they have built multilayers suitable for infrared (IR) study. Their IR results suggested a more or less uniaxial orientation compatible with helical structures oriented preferentially parallel to the substrate and along the transfer direction. The orientation of the helical structure in the transfer direction was attributed to the anisotropy of the rigid helical stereocomplex structures and the flow caused by transfer process. It should be pointed out that the LB thin film focuses on the structure and properties of monolayers, which are also related to the surface pressure and transfer process used in film preparation. The PMMA stereocomplex in thin film on a solid surface prepared by simple procedures, e.g., solution-casting and spin-coating, may reveal the inherent character of the stereocomplex and shed more light on the dynamic events of stereoregular PMMA molecules at a solid surface. Therefore, it may of great interesting from both practical and theoretical points of view.

Table 1. Molecular Characterization Data for PMMA[a]

	$M_w \times 10^4$	M_w/M_n	% i-	% h-	% s-
i-PMMA	13.6	2.03	97	2	1
s-PMMA	11.6	1.51	2	9	89

[a] i-, h-, and s- represent isotactic, heterotactic, and syndiotactic segments in PMMA, respectively.

In this work, thin PMMA films with PMMA stereocomplex cast from a strong complexing acetone solution of stereoregular PMMA mixture was studied by reflection−absorption infrared spectroscopy. The results show that there is some oriented structure with a thermal stability up to 195 °C in the thin film. The origin of the oriented structure was discussed on the basis of experiments.

Experimental Part

Materials. The characteristics of i-PMMA and s-PMMA are listed in Table 1. The average molecular weight was determined by means of gel permeation chromatography (PL-GP210), and their tacticity was determined by ^{1}H NMR. While acetone was used as a strong-complexing solvent, chloroform was chosen as a noncomplexing solvent.

Sample Preparation. Pure i- and s-PMMA and the mixture of i- and s-PMMA (i:s = 1:1) were dissolved in either a strong-complexing solvent, i.e., acetone, or a noncomplexing solvent, e.g., chloroform, with concentrations of 0.1 and 1 wt %. The samples for RAIR measurements were prepared by casting the 0.1 wt % solutions on glass slices, which were argon plasma sputtered with a thin layer of gold. The samples for transmission infrared (TIR) measurement were prepared by casting the 1 wt % solutions on KBr substrates. Film thickness, which was controlled by the volume of casting solution, ranges from 100 to 150 nm and 1 to 1.5 μm for RAIR and TIR measurements, respectively. The samples were annealed on a self-made temperature-controlled hot stage in the range 120−200 °C.

Infrared Spectroscopy. RAIR and TIR spectra were acquired using a Bruker EQUINOX 55 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled MCT detector at a resolution of 4 cm^{-1} with 128 scans. RAIR spectra were recorded with a p-polarized light incident at 84° with respect to the surface normal.

Results and Discussion

The orientation character of a thin film at a metal surface can be successfully studied by RAIR spectroscopy. Reflection on the metal surface results in an electrical field that is strongly elliptically polarized in RAIR measurement. With only a significant contribution of the component perpendicular to the surface, the intensity of the corresponding band would become obviously stronger in the RAIR spectrum than that in the TIR spectrum; with a component parallel to the surface, the intensity of the corresponding band would become weaker.

Figure 1 shows the TIR and RAIR spectra of thin films of an i- and s-PMMA (i:s = 1:1) mixture cast from chloroform and acetone solutions, respectively. For the thin films cast from chloroform solution (see part A of Figure 1), except for some intensity change of the band at 1148 cm^{-1}, the TIR and RAIR spectra show no obvious difference with respect to the intensities of the bands ranging from 800 to 1800 cm^{-1}. The intensity difference of the 1738 cm^{-1} band is associated with the drop of the baseline. On the contrary, great intensity changes can be identified for several bands of the TIR

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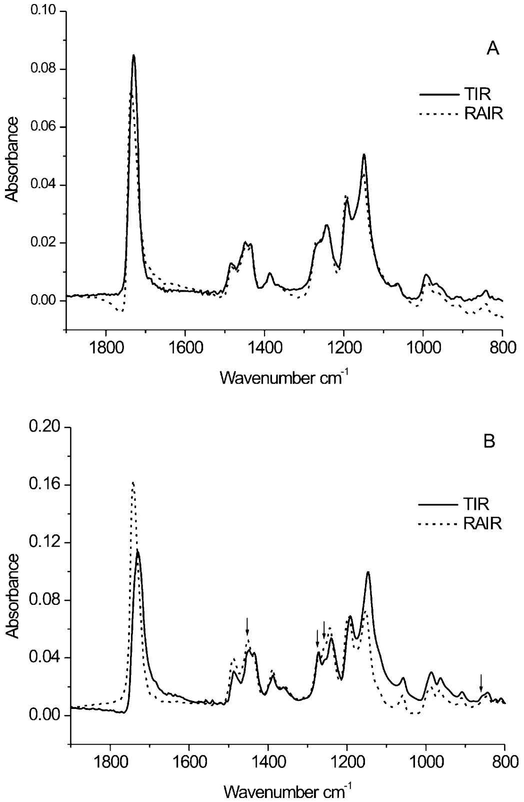

Figure 1. TIR and RAIR spectra of the thin films of i-PMMA and s-PMMA mixture (i:s = 1:1) cast on a gold surface from acetone and chloroform solutions, respectively: (A) cast from chloroform solution and (B) cast from acetone solution.

and RAIR spectra cast from acetone solution, especially those at 1450, 1273, and 1257 cm^{-1} related to the ester group and 860 cm^{-1} corresponding to the main-chain CH$_2$ rocking vibrations (see Figure 1B).[14,15] These intensity changes are mainly attributed to dichroic effect and indicate some ordered arrangement of molecular chains in thin film. It should be pointed out that (i) acetone is a strong-complexing solvent for inducing stereocomplexation of PMMAs, while chloroform is attested to be a noncomplexing solvent,[7,16,17] (ii) the stereocomplexation of PMMAs was triggered mainly by dipole−dipole interaction of i- and s-ester groups,[14,15] (iii) the changes in most bands all correspond to the energetically most favorable conformation of the PMMA ester group which are always related to the formation of stereocomplex,[14,15] and (iv) the band at 860 cm^{-1}, a character band for the formation of PMMA stereocomplex, does not appear in TIR and RAIR spectra of the films cast from chloroform, while it appears clearly in those cast from acetone. Taking all those into account, the ordered arrangement of PMMAs may originate from complexation of stereoregular PMMAs.

Since the melt temperature of PMMA stereocomplex is always in the range 160−200 °C, to confirm stereocomplex leading to the orientation of ester group, the thermal stability of the cast thin film from acetone was examined. Figure 2A shows the thermal stability of oriented structure of PMMA in the thin film at a surface. It can be seen that the intensity and position of some bands changed with the increase of annealed temperature. To see clearly, enlarged spectra in the ranges 1775−1675, 1550−1400, and 1350−1050 cm^{-1} are shown in parts B, C, and D of Figure 2, respectively. Figure 2B shows that the PMMA carbonyl bands is at around 1743 cm^{-1} when annealed at temperatures lower than 175 °C, but it shifts from 1743 to 1738 cm^{-1} when

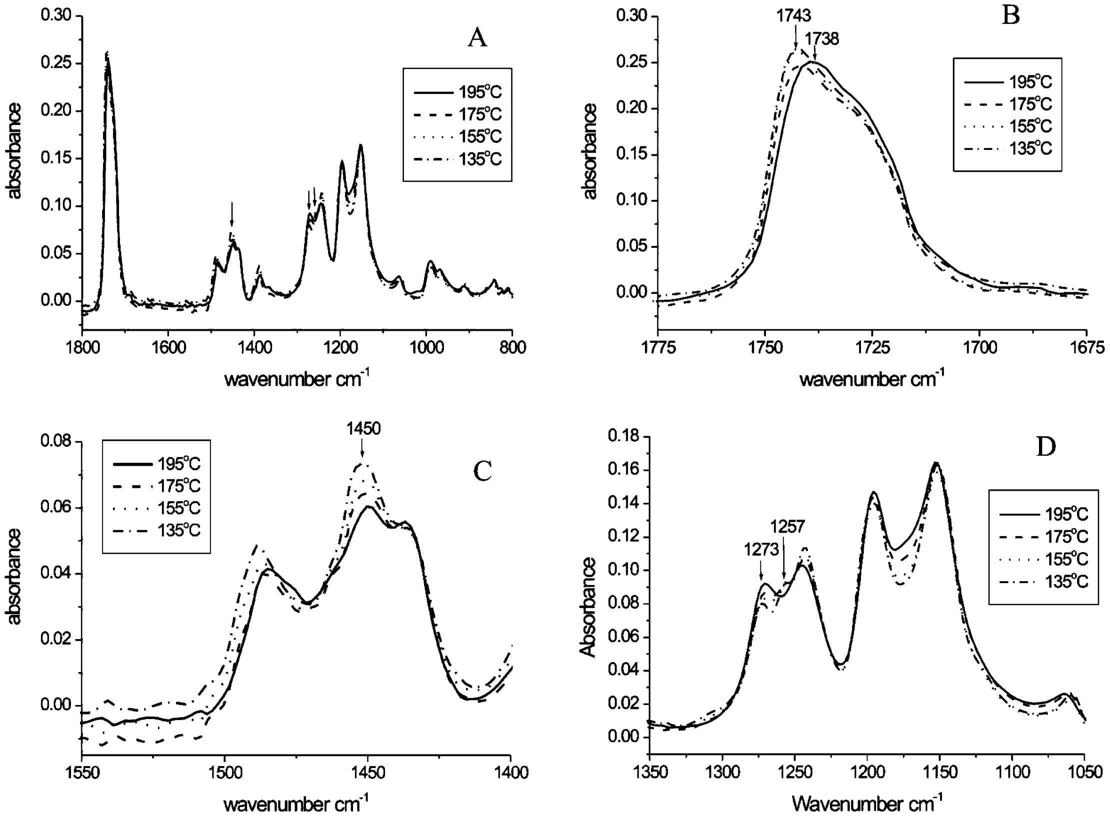

Figure 2. RAIR spectra of a stereoregular PMMA mixture thin film (i:s = 1:1) cast from an acetone solvent on a golden spattered glass slice annealed at different temperatures shown in different ranges: (A) range 1900−800 cm^{-1}; (B) range 1550−1400 cm^{-1}; (C) range 1350−1050 cm^{-1}; (D) range 1775−1675 cm^{-1}.

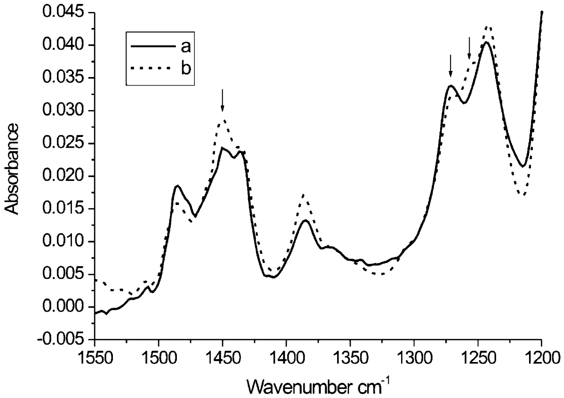

Figure 3. RAIR spectra of the thin film of i- and s-PMMA (i:s = 1:1) mixture cast from chloroform (a) and after casting a drop of acetone solvent on it (b).

annealed at 195 °C. It was supposed that the PMMA carbonyl band (1738 cm^{-1}) would shift to higher wavenumber of 1742 cm^{-1} for the formation of stereocomplex in RAIR spectra.[13,18−21] Taking this into account, the changes of carbonyl bands with temperature indicate that there exist PMMA stereocomplex in the thin films annealed at temperatures lower than 175 °C, and the PMMA stereocomplexes discompose completely at about 195 °C. In Figure 2C,D, it is recognized that the intensities of bands at 1450 and 1273 cm^{-1}, which responded to the energetically most favorable conformation of the s-PMMA ester group in the PMMA stereocomplex, change with the increase of annealing temperature. It can be also seen that the dichroism of these bands in RAIR spectra as well as the 1257 cm^{-1} one, which responded to the energetically most favorable conformation of the i-PMMA ester group in the PMMA stereocomplex, decreased with the increase of annealing temperature and was similar to that in TIR spectra when annealed up to 195 °C. These data indicate that the stereocomplexes gradually decompose with the increase of annealing temperature and decompose completely when the temperature is elevated up to 195 °C.

According to above discussion, it is clear that PMMA stereocomplexes in thin films cast from acetone solution on the gold surface adopt spontaneously an oriented structure. The dichroic character reflects a more or less orientation of PMMA stereocomplexes with a helical structure aligned preferentially in the plane of substrate. And the intensity increase of the ester group relating bands indicates that the ester groups are more or less oriented perpendicular to the plane of the substrate.

Now questions may be raised about the preferred orientation of PMMA stereocomplexes. To find an answer, we have performed another experiment. Adroplet of acetone solvent, which would lead to the occurrence interaction between i- and s-PMMA segments, was spread onto the film surface of mixed stereoregular PMMA without stereocomplex, as used in Figure 1A. After the acetone solvent was completely evaporated, the films were used for IR measurement again. As presented in Figure 3, the RAIR spectrum shows clearly the dichroism character at bands 1450, 1273, and 1257 cm^{-1}. This structure also has a good thermal stability similar to that shown in Figure 2. Moreover, pure i- and s-PMMAs have no such property. On the basis of these data, it is reasonable to suppose that in a suitable solvent environment the ester groups of i- and s-PMMA segment at a surface easily interact with each other, which leads to the formation of PMMA stereocomplexes. The interaction may induce the oriented structures in order to obtain a lowest surface energy on the substrate.

Conclusion

In conclusion, some oriented structures in thin films of the stereoregular PMMA (i:s = 1:1) mixture can be produced by casting its solution with strong-complexing acetone solvent onto a golded substrate, while no such kind of structure was observed in solution cast film with chloroform as solvent. These structures are thermal stable up to 195 °C, reflecting the formation of PMMA stereocomplexes. A droplet of acetone solvent could lead to the rearrangement of the thin films of mixed stereoregular PMMA without stereocomplex and result in the formation of PMMA stereocomplexes. Considering that acetone is in favor of the interaction between i- and s-PMMA segments, the oriented structures are most likely related to the strong interactions between the ester groups.

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Supporting Information Available: Effect of free i- and s-PMMA on the oriented structure of i- and s-PMMA mixture film cast from acetone on a gold substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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