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DYNAMICS OF PIPA-*d₇* ON SILICA

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Introduction

Molecular motion of polymer chains is an important determinant in understanding the physical properties of polymeric materials. Glass transition temperature (T_g) is a physical property of polymers, which is of primary interest. The study of the dynamics of polymer segments assists in understanding the dependence of T_g on polymer structure.[1] For decades, studies have addressed the molecular motion in various polymers. Some of them have probed the dynamics of polymer backbones.[2,3] The properties of a polymer at an interface may change because of the type of polymer, the substrate, or other variables. The side chain of a polymer can also play an important role in terms of the interaction between a polymer and a substrate at an interface.[4] The strength of the surface-segment interaction affects the mobility of polymer-chain segments. Several techniques have been used to investigate the effects, including modulated differential scanning calorimetry (MDSC)[5,6] and nuclear magnetic resonance (NMR).[2,3,7,8]

In this work, relatively narrow polydispersity poly(isopropyl acrylate)-*d₇* (PIPA-*d₇*) has been selected for study. The large and bulky group on the PIPA side-chain, would provide a different probe for segmental mobility than that of previously studied poly(methyl acrylate)-*d₃* (PMA-*d₃*).[9-11] The PIPA side-chain contains two methyl groups, branched at a methane carbon atom. Additionally, when different amounts of polymers are deposited on a surface, individual unique behaviors become evident that are different from the behavior of bulk polymers.

Deuterium solid-state NMR was used to characterize the polymer segmental motions in both bulk deuterium-labeled PIPA and polymer thin films on silica. The ²H quadrupole-echo NMR spectra were collected as a function of temperature. The interpretation of those spectra can provide valuable information on the molecular motion and the physical properties of the polymer including glass transition temperatures. Calorimetry, the most widely accepted technique for measuring the glass transition temperature (T_g), was also performed for comparison. This work is an update of that previously presented.[12]

Experimental

Isopropyl acrylate-*d₇*, was prepared via an interchange reaction between 2-propanol-*d₈* (CIL) and acryloyl chloride (Aldrich, 96%). Triethylamine (Alfa Aesar, 99.9%) was added to neutralize the hydrochloric acid produced by the reaction. Acryloyl chloride was purified before use, and then added dropwise to the mixture of 2-propanol-*d₈*, triethylamine and toluene at 0 °C. The product was washed twice with a 5% NaHCO₃ solution and then with distilled water in a separatory funnel. The aqueous phase was discarded and the organic layer was dried over calcium hydride. The isopropyl acrylate-*d₇* monomer was distilled under vacuum; the final product yield was 60%. The reaction is

$$CH_2\!=\!\overset{\overset{O}{\|}}{C}\!-\!Cl \;+\; CD_3\!-\!\overset{\overset{CD_3}{|}}{CD}\!-\!OD \;\longrightarrow\; CH_2\!=\!\overset{\overset{O}{\|}}{C}\!-\!O\!-\!\overset{\overset{CD_3}{|}}{CD}\!-\!CD_3 \;+\; DCl$$

PIPA-*d₇* was polymerized by atom transfer radical polymerization (ATRP)[13] at 70 °C. The molecular mass of PIPA-*d₇* was measured to be 89 kg/mol (M_w) with a polydispersity of 1.31, using an OPTILAB DSP Interferometer Refractometer and a DAWN EOS light scattering instrument (Wyatt Technology, Santa Barbara) connected to a gel permeation chromatography instrument.

The absorbed PIPA-*d₇* samples on silica were prepared by dissolving the polymer in toluene, and mixing it with a known amount of silica in capped test tubes. Cab-O-Sil MP-5 fumed silica (Cabot Corp., Tuscola, IL), with a surface area of 200 m²/g, was used and was dried in a furnace at 450 °C for 24 h before use. All samples were shaken in a mechanical shaker for 72 h, and then centrifuged for an hour at 2500 rpm. The supernatant was decanted and the polymer-adsorbed silica samples were dried by passing air through the wet samples. The samples were kept in a vacuum oven for 36 h. The adsorbed amounts were measured using thermogravimetric analysis (Hi-Res Thermogravimetric Analyzer 2950, TA Instruments, New Castle, DE).

NMR spectra of both bulk and adsorbed samples were obtained using a VARIAN VXR-400/S spectrometer. The quadrupole-echo pulse sequence (delay-90ᵧ-τ-90ₓ-τ-acquisition) was used at a ²H frequency at 61.39 MHz. The 90° pulse width was 2.7 μs with an echo time of 30 μs. The number of scans used for the bulk and for the adsorbed samples were 256 and 1024, respectively. The spectra were processed using the Mestre-C software package (Santiago de Compostela University, Spain).

TA Instruments model 2920 modulated differential scanning calorimeter (New Castle, DE) was used for the thermal analysis of the bulk and adsorbed PIPA-*d₇*. Two heating scans and one cooling scan were taken from –40 to 70 °C, with a modulation amplitude of ± 0.5 °C and a period of 60 s. A heating rate of 10 °C /min and 3 °C/min were used for bulk and adsorbed samples, respectively. The second heating scan was used to determine the glass transition temperature (T_g). The maximum of the derivative reversible heat flow peak obtained for each sample was reported as the T_g of the sample.

Results and Discussion

²H Solid-state NMR. The spectra of PIPA-*d₇* at -36 °C and PMA-*d₃* at 20 °C, are shown in **Figure 1**. Both spectra were collected at the temperatures below their bulk NMR T_g. The Pake powder patterns for both spectra have a similar residual quadrupole splitting of 37 kHz, which is dominated by the fast rotation of methyl groups. In the PIPA-*d₇* spectrum, another powder pattern superimposed in the spectrum can be observed, as marked by the circle. The outer portion of the powder pattern with a much larger quadrupole splitting of 120 kHz is due to the static C-D from the methine. Unlike PIPA-*d₇*, the PMA-*d₃* spectrum was obtained with a sharp powder pattern, dominated by the methyl group.
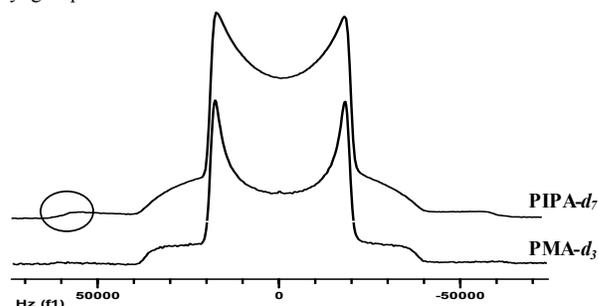

Figure 1. ²H NMR spectrum of bulk PIPA-*d₇* at -36 °C and bulk PMA-*d₃* at 20 °C. The circle indicates the part of the powder pattern from a single methine in PIPA-*d₇*.

Sets of deuterium NMR spectra for bulk PIPA-*d₇* and surface samples with different adsorbed amounts were collected as a function of temperature. A Pake powder pattern was obtained in the low temperature region. The splitting between the two horns was approximately 37 kHz, as expected for the fast methyl-group rotation and also same as for PMA-*d₃*.[6] **Figure 2** shows the spectra of the bulk, low, medium, and high adsorbed amounts of polymer at -5 °C. The Pake pattern for the bulk sample was broadened. The intensity of the middle component increased, and the intensities of the shoulders decreased with the increasing temperature. The Pake pattern with a flattened top was obtained for all surface samples at low temperature. The spectra provided evidence for the heterogeneity in the adsorbed PIPA-*d₇* sample. At least two components from at least two different dynamic groups were found in the spectra. The filled middle between the two horns, giving the flat Pake pattern, is due to partially motionally-narrowed polymer segments. The tightly bound segments, however, are observable from the spectra. The sharp edge of the powder pattern was indicative of chain segments tightly bound onto the silica with lower mobility.

At higher temperatures, the spectrum sharpened further compared to the one at -5 °C, with no apparent residual powder pattern present in the spectrum of bulk PIPA-*d₇*. The collapse of the powder pattern to a single resonance indicated the increase in segmental mobility of PIPA-*d₇*. The superposition of

the motionally-narrowed component with the broad powder pattern in the spectra of the bulk sample was due to the heterogeneity of the segmental mobility through the glass transition region, although this heterogeneity was not as large as that for the adsorbed polymer, as shown in **Figure 3**.

A small narrow resonance appeared in the center in the spectra of adsorbed PIPA-d_7 samples, showing that one component was moving fast as compared to the quadrupole splitting, and the stronger signal intensity was attained as the temperature increased.
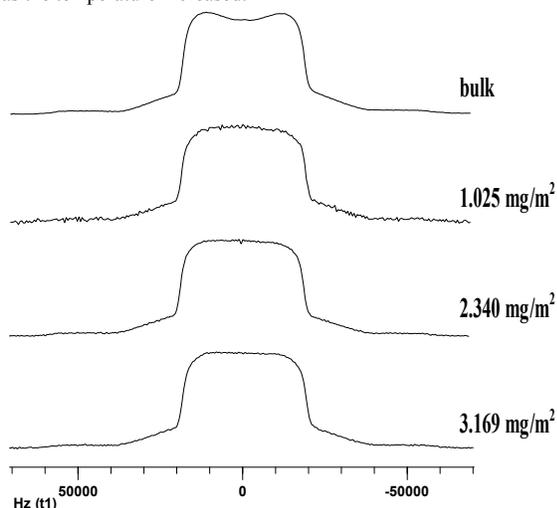

Figure 2. ^{2}H NMR spectra at -5 °C for bulk, low (1.02 mg/m^2), medium (2.34 mg/m^2), and high (3.17 mg/m^2) adsorbed amounts of PIPA-d_7 on silica.
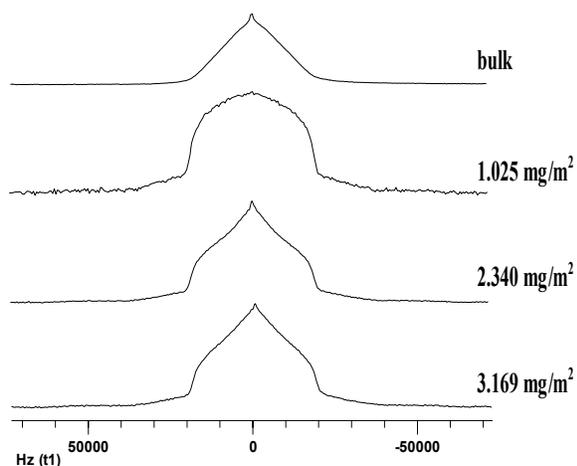

Figure 3. ^{2}H NMR spectra at 24 °C for bulk, low (1.02 mg/m^2), medium (2.34mg/m^2), and high (3.17 mg/m^2) adsorbed amounts of PIPA-d_7 on silica.

The intensity of the two horns of the powder pattern of the adsorbed sample gradually decreased with increasing temperature; nevertheless they still had significant intensity, even at the highest temperature. The presence of the residual of the powder pattern in the adsorbed sample spectra indicated that some of the segments associated with the silica surface through hydrogen bonding.

The mobility of the polymer chain in adsorbed samples rose when the adsorbed amount increased. The polymer thin films with medium and high adsorbed amounts behaved more like bulk polymer, due to the more mobile components contained in the samples. The adsorbed polymers, however, have more motional heterogeneity than the bulk polymer, even with high adsorbed amount samples. A rigid component of the spectra near the silica surface is observed even at the high temperatures.

MDSC. The glass transition temperatures (T_g) for bulk and adsorbed PIPA-d_7 samples were determined using DSC. The derivatives of the reversing heat flow thermograms, with 5 °C smoothing for all samples, are shown in **Figure 4**. The T_g for the bulk sample was found to be -11°C. For a relatively low adsorbed amount of 1.025 mg/m^2, the transition region was indistinguishable in the DSC thermogram. A big broadened peak at about 0 °C was apparent in the thermogram of the adsorbed samples, and a small hump was seen at -10 °C as well. The intensity for the transition evidently increased as the adsorbed amount increased. Therefore, two components are found in the thermograms for the adsorbed samples, one at 0 °C representing the polymer segments tightly bound to the surface, and the other at close to -10 °C, represents the loosely bound polymer segments.
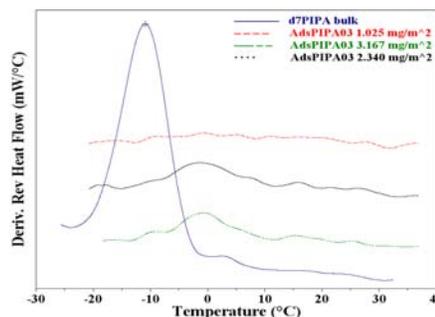

Figure 4. Thermograms for bulk and adsorbed PIPA-d_7 on silica at different adsorbed amounts.

Conclusions

PIPA-d_7 displayed different characteristics at low temperature, compared to PMA-d_3. This difference is due to the presence of two rapidly-moving methyl groups and one static methine in the PIPA-d_7 side chain. The surface PIPA-d_7 exhibited different thermal behavior from that of the bulk PIPA, depending on the amount of adsorption on the surface. The spectra of the adsorbed sample showed the presence of at least two motionally different components and, consequently, indicated the heterogeneity of segmental dynamics at the interface. A residual powder pattern for the absorbed sample at higher temperatures indicated the presence of segments strongly attached on the surface via hydrogen bonding. Moreover, MDSC thermograms indicated two transitions were found in the adsorbed samples. A transition that was apparent at a temperature close to T_g of the bulk PIPA-d_7, is believed due to the freely moving chain segments. A similar transition for the adsorbed samples, slightly shifted from the bulk T_g, shows effects of attachment at the polymer-silica interface.

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