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SEGMENTAL DYNAMICS OF POLY(ISOPROPYL ACRYLATE)-d_7 ON SILICA

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Introduction

For a polymer film deposited on a surface, the strength of the surface-segment interaction affects the mobility of polymer-chain segments. The self-consistent field lattice model of Scheutjens and Fleer,[1] based on mean-field lattice models of polymer at interfaces,[2] has been used to describe the distribution of conformations of polymers on surfaces. Adsorbed-polymer segments may be classified as belonging to loops, trains or tails. There are different techniques used to study the molecular motion of the polymer including modulated differential scanning calorimetry (MDSC)[3] and nuclear magnetic resonance (NMR).[4,5]

In this work, solid-state deuterium (^{2}H) NMR was used to characterize the polymer segmental motions. Solid-state ^{2}H NMR is an excellent tool for studying segmental dynamics. The interpretation of solid-state ^{2}H NMR spectra of a deuterium-labeled polymer can provide valuable information on the molecular motion and the physical properties of the polymer.[6,7]

Relatively narrow polydispersity poly(isopropyl acrylate)-d_7 (PIPA-d_7) has been studied using deuterium NMR. PIPA has two methyl groups, branched at a methine carbon atom. Substitution of deuterons onto these methyl groups provides a different probe for the segment mobility than that used in previous studies.[7-9] The structure of the side chains of PIPA-d_7 is different than that of poly(methyl acrylate) previously studied. Bulk and surface-adsorbed PIPA-d_7 polymers were investigated using the ^{2}H quadrupole-echo NMR technique as a function of temperature.

Experimental

Isopropyl acrylate-d_7, was synthesized from 2-propanol-d_8 (CIL), acryloyl chloride (Aldrich, 96%), triethylamine (Alfa Aesar, 99.9%) and toluene. Distilled acryloyl chloride was added dropwise to the mixture of 2-propanol-d_8, triethylamine and toluene. This mixture was stirred at 0 ^{o}C for 3-4 h and again at room temperature for another 20-24 h. The product was washed twice with a concentrated $NaHCO_3$ solution and then with distilled water in a separatory funnel. The aqueous phase was discarded and the organic layer was dried over calcium hydride for 18 h. The isopropyl acrylate-d_7 monomer was distilled under vacuum; the final product yield was 70%. PIPA-d_7 was synthesized by atom transfer radical polymerization (ATRP)[10] at 80 ^{o}C. The molecular masses of the polymers were determined by 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 PIPA-d_7 had MW of 89 kDaltons with polydispersity of 1.31.

Cab-O-Sil MP-5 fumed silica (Cabot Corp., Tuscola, IL), with a surface area of 200 m^2/g, was dried in a furnace for 24 h before use. The absorbed PIPA-d_7 sample on silica was prepared by dissolving the polymer in toluene, and mixing it in centrifuge tubes with a know amount of treated silica. After the tubes were shaken in a mechanical shaker for 72 h, they were centrifuged for an hour. The supernatant was decanted and the polymer-adsorbed silica was dried in a vacuum oven for 36 h before the adsorbed amount was determined 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-90_y-τ-90_x-τ-acquisition) was used at a ^{2}H frequency at 61.39 MHz. The 90^o pulse width was 2.7 μs with an echo time of 30 μs. For the bulk sample, we used 256 scans, and 1024 scans for the adsorbed samples. A line broadening of 1 kHz was applied for the adsorbed sample data set. The spectra were processed using the Mestre-C software package (Santiago de Compostela University, Spain).

Results and Discussion

Bulk PIPA-d_7. The spectrum of PIPA-d_7 at 36 ^{o}C is shown in **Figure 1**. The top spectrum shows a Pake powder pattern which is dominated by the methyl groups with a residual quadrupole splitting of 37 kHz. In addition to the intense methyl groups (6 deuterons), the spectrum also shows the powder pattern for the C-D (methine, 1 deuteron) with a much larger quadrupole splitting of 120 kHz. The inset shows the outer portion of the powder pattern for the single C-D.

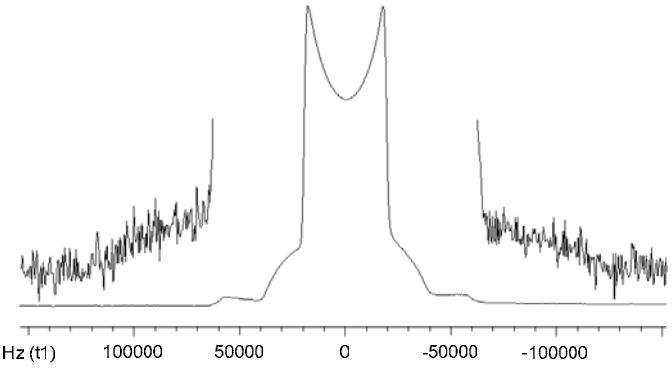

Figure 1. ^{2}H NMR spectrum of bulk PIPA-d_7 at -36 ^{o}C**.** The magnified portion shows the presence of the shoulders due to the outer portion of the resonance for the methine deuteron.

A set of ^{2}H NMR spectra for bulk PIPA-d_7 is shown in **Figure 2**. In the low temperature region, a Pake powder pattern was obtained. The splitting between the two horns was approximately 37 kHz, as expected for the fast methyl-group rotation in PMA-d_3.[7,8] The splitting between the two horns, decreased as the temperature increased. The Pake pattern collapsed at 16 ^{o}C into a very broad resonance. As the temperature increased, the intensity of the center component increased, while the intensities of the shoulders decreased. At 33 ^{o}C, the broader components further narrowed. The signal at higher temperatures sharpened further, with no apparent residual powder pattern present in the spectrum. The collapse of the powder pattern to a single resonance was due to the increase in segmental mobility of PIPA-d_7. The superposition of the motionally-narrowed component with the broad powder pattern in the spectra of the bulk sample indicated the heterogeneity of the segmental mobility through the glass transition region, although this heterogeneity was not as large as that for the adsorbed polymer (*vide infra*).

Surface PIPA-d_7 Dynamics. ^{2}H NMR spectra of a sample with an adsorbed amount of 1.025 mg/m^2 PIPA-d_7 on silica are shown in **Figure 3**. This is a relatively small adsorbed amount. A Pake pattern with flattened top was obtained in the low temperature range. There seems to be at least two different components from at least two different dynamical groups in the spectra. The sharp edge of the powder pattern was indicative of tightly bound chain segments with lower mobility. The filled in the middle between the two horns, giving the flat pattern, was due to motionally-narrowed polymer segments. Thus, the heterogeneity of the spectra for the adsorbed PIPA-d_7 sample was obvious. A small narrow, middle resonance appeared at 33 ^{o}C, showing that one component was moving fast compared to the quadrupole splitting. Its intensity increased as the temperature increased. The presence of the middle component in the adsorbed sample indicated that some segments of the polymer chain, like those in the tails and loops were more mobile than those more intimately associated with the surface.

The intensity of the "horns" of the powder pattern of the adsorbed sample gradually decreased with increasing temperature, but they still had significant intensity, even at the highest temperature studied. The train conformations, through which the polymers directly bind to the silica surface through hydrogen bonding, were likely responsible for the broader (more rigid) components in the spectra.

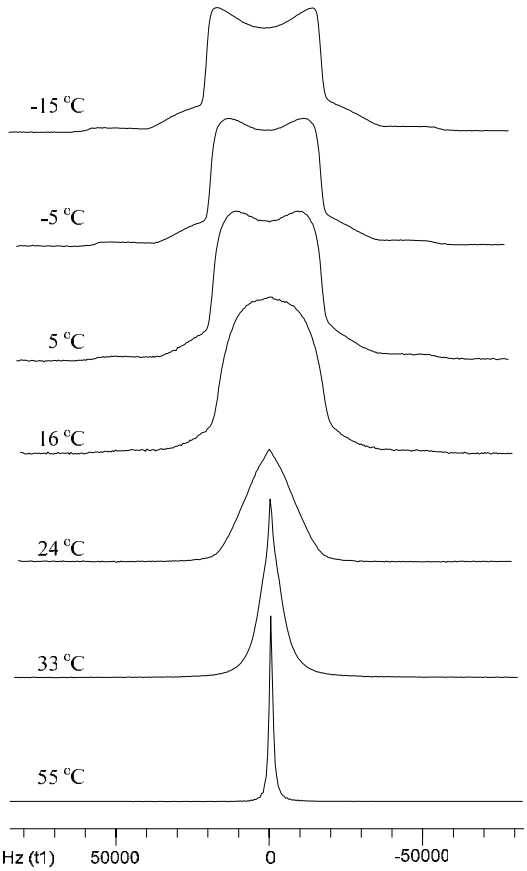

Figure 2. ^{2}H NMR spectra for bulk PIPA-d_7 as a function of temperature.

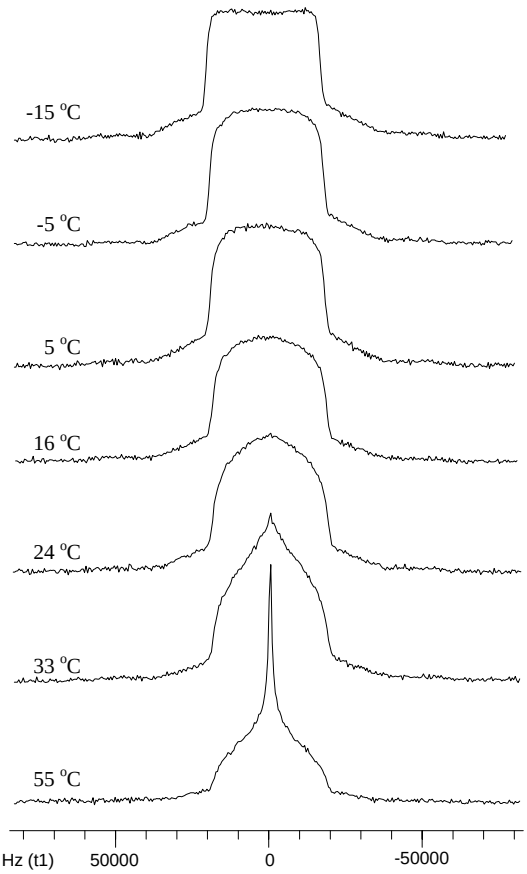

Figure 3. ^{2}H NMR spectra for 1.025 mg/m^2 adsorbed PIPA-d_7 on silica as a function of temperature.

Comparison of the spectra in **Figure 3** with those in **Figure 2** illustrates that the spectra of the adsorbed sample were more heterogeneous than those for the bulk polymer. At higher temperatures, the broad components in the adsorbed samples are due to segments which are still highly restricted. The H-bonding at the polymer-silica interface undoubtedly restricts the movement of the chain segments. The rigid component near the silica surface is observed spectra even at the high temperatures.

Conclusions

Two types of deuterons each show their own characteristic spectrum for bulk PIPA-d_7 at low temperatures. One shows a rapid rotational motion of the methyl group and the other shows a static C-D bond. These collapsed to a single narrow resonance at high temperature.

The surface sample exhibited different behavior from that of the bulk PIPA. A residual powder pattern for the absorbed sample at higher temperatures indicated the presence of segments with highly restricted mobility 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 on the surface.

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