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DEUTERIUM NMR STUDIES OF BULK AND SILICA-ADSORBED POLYSTYRENE

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Introduction

Thin polymer films are used in applications such as electronics, biomedical devices and coatings. As the trend to make the devices smaller continues, a film's influence on a material's overall properties becomes more prominent. Previous studies have shown that thin polymer films have characteristics slightly different from those of bulk polymers.¹ Film behavior has been characterized by examining thermal expansion, diffusion, conformation, density and glass transitions.

The dynamics of glassy polystyrene has been investigated using a wide variety of theoretical and experimental methods. Schaefer et al., using ¹³C NMR, reported that ~7% of phenyl rings in polystyrene undergo \square -flips.² Using deuterium NMR on ring-deuterated polystyrene, E. Rossler, et al. determined that a powder pattern of a rigid solid is obtained at room temperature.³ At 383 K, two low intensity peaks are present in the middle of the powder pattern and, at 433 K, a Lorentzian line was found. While the broad powder pattern was characteristic of deuterated polystyrene with no chain motion, the two low intensity middle peaks were attributed to the phenyl rings undergoing \square -flips.

Kulik and Prins also showed that the deuterium powder pattern for polystyrene contained two weak middle peaks.⁴ Upon altering the relaxation delay, Kulik et al. determined that, for a partially relaxed sample (short relaxation delay), the two middle peaks were dominant over the 'outer horns' but, when given enough time for complete relaxation, the converse is true. They concluded that the line shapes are superpositions of roughly two contributions from phenyl rings performing relatively slow and fast flipping motions. Zhao et al., using deuterium NMR on ring-deuterated polystyrene, found a strong dependence of the line shape on temperature and echo delay, indicating motion at the microsecond time scale at the temperatures studied.⁵

In this study, we investigate the dynamics of polystyrene in bulk and silica-adsorbed samples as temperatures approach the glass transition temperature (T_g).

Experimental

The starting sample was a ring-deuterated polystyrene-*d*₅ (PS-*d*₅), prepared by bulk polymerization of styrene-*d*₅, using AIBN as the initiator. The molecular mass of the polymer was $M_n = 45000$ and $M_w = 56000$ Da. About 0.5 grams of this polymer was used in the bulk sample studies. To a solution of 0.4g of PS-*d*₅ in 10 ml of toluene, was added 1 g of silica (CAB-O-SIL M-P5, surface area 200 m²/g, Cabot Corp, Tuscola, IL). The mixture was shaken for 48 h at 23 °C. The test tubes were then centrifuged and the supernatant liquid discarded. The residue was then thoroughly mixed using a shaker, and allowed to dry in the air for 48 h. This was followed by drying in a vacuum oven at 50 °C for another 48 h. The adsorbed amount was determined to be 0.8 mg/m² using thermogravimetric analysis (TGA).

The ²H NMR experiments were performed at 61.3 MHz on a Varian VXR-S spectrometer with an Oxford 400 89 mm magnet. A fixed frequency 8 mm probe (Doty Scientific), with a 90° pulse width of 2.7 \square sec, was used. The quadrupolar echo pulse sequence of 90_x- \square -90_y- \square -Acquisition, was used. Fourier transformation started at the top of the echo. The spectra for the bulk samples were obtained with 2048 transients, while those for the adsorbed samples were with 8192 transients.

Results and Discussion

A typical ²H NMR spectrum of ring-deuterated polystyrene that was obtained at 23 °C on the bulk sample is shown in **Figure 1**. A powder pattern is evident, with two small peaks in the middle. The broad powder pattern and middle resonance are characteristic of rigid segments and phenyl rings undergoing rapid \square -flips around the symmetry axis, respectively.

The spectra obtained from running ²H NMR on the bulk sample at different temperatures are given in **Figure 2a**. The intensity of the signal decreases as the temperature increases, which probably indicates that the rate of relaxation increases as temperature increases.

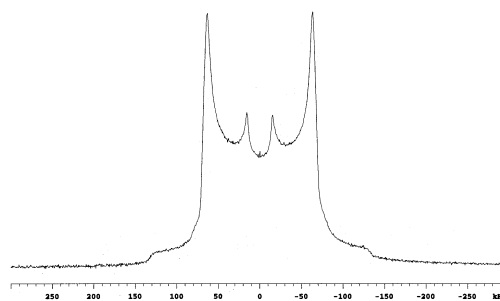


Figure 1. A typical ²H NMR spectrum of PS-*d*₅ taken at 54 °C.

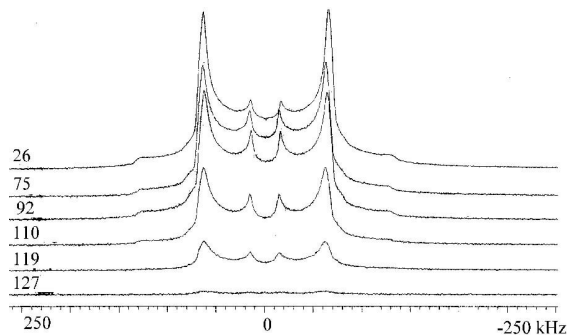


Figure 2a. Variable temperature ²H NMR spectra for bulk PS-*d*₅. The temperatures (°C) are shown in the figure on the left side.

Figure 2b shows the ²H NMR spectra of the silica-adsorbed sample at different temperatures. Like the bulk sample, the intensity of the signal decreases as the temperature increases. The spectra, though noisy, had to be obtained from 8192 transients. The powder pattern persisted even at higher temperatures indicating that at least some portion of the silica-adsorbed sample remains rigid at these temperatures.

We performed experiments on both the bulk and the adsorbed samples at 131 °C; and the spectra are shown in **Figure 3**. The powder pattern for the bulk sample had disappeared at this temperature and was replaced by a Lorentzian peak characteristic of mobile samples. The adsorbed sample still had a broad powder pattern, though a small peak can be seen beginning to emerge at the center, indicating that a fraction of the sample is becoming mobile.

Our results indicate that the T_g of the adsorbed sample is higher than that of the bulk sample. This is consistent with the results reported by Porter and Blum from their studies using a modulated differential scanning calorimeter (MDSC).⁶

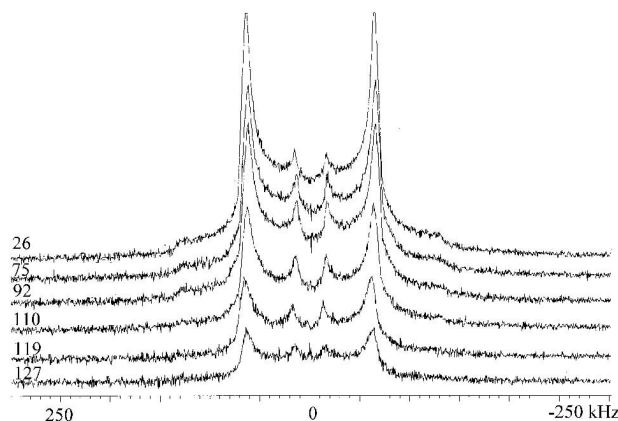


Figure 2b. Variable temperature ²H NMR spectra for silica adsorbed PS-*d*₅. The temperatures (°C) are shown in the figure on the left side.

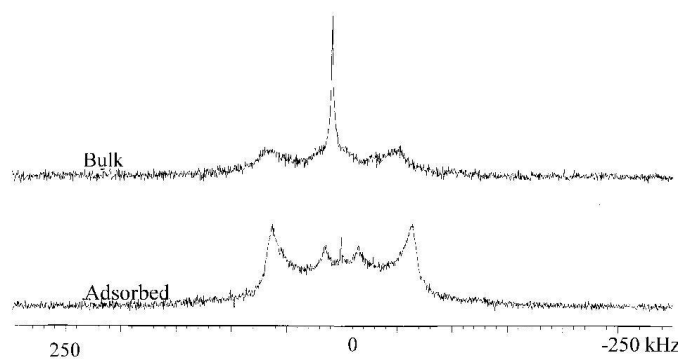


Figure 3. ^2H NMR Spectra for bulk and adsorbed samples obtained at 131 °C.

Conclusion

The silica adsorbed PS- d_5 shows a higher T_g than the bulk polymer. To provide a better explanation for these transitions, we are in the process of determining relaxation times for both bulk and adsorbed samples at the different temperatures.

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