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## SEGMENTAL MOBILITY OF CHAIN ENDS IN POLY(METHYL ACRYLATE)- $d_3$

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### Introduction

Better control of polymeric materials can be achieved with a thorough understanding of the dynamics of their constituents. In the present study, we consider polymer chains as composed of chain *middles* and chain *ends*. Even though chain ends do not comprise much of the sample by mass, they may play a crucial role in the ultimate properties of the polymers.

Although chain ends have been assigned a higher mobility, as compared to chain middles, there have not been a large number of experimental studies that directly probe their mobility. Among those, the studies of Kitahara et al.<sup>1</sup> and Miwa et al.<sup>2</sup> demonstrated the higher mobility of chain ends using ESR for polyethylene and polystyrene (PS), respectively. They observed that the transition temperatures for the onset of rapid molecular motion at the chain ends were 5 K lower than those inside the chains. A molecular mass dependence was also observed for the transition for the chain ends. A specular neutron reflectivity (SNR) study<sup>3</sup> indicated that segments in the center sections of PS have a lag in mobility across a welded interface, as compared to chain ends.

Previous deuterium NMR studies,<sup>4,5</sup> by our group, have shown the a molecular-mass dependence on segmental dynamics through the glass-transition region. More heterogeneous segmental dynamics were observed in the NMR spectra of lower molecular mass poly(methyl acrylate) (PMA) compared to those of higher molecular mass. This heterogeneity was attributed to the presence of a higher concentration of *more-mobile* chain ends. In this study, the segmental dynamics of the PMA samples, with methyl-group-deuterated chain ends, was studied using the  $^2\text{H}$  quadrupole-echo NMR technique. These results provided significant insight into the role of chain ends in the glass transition region of polymers.

### Experimental

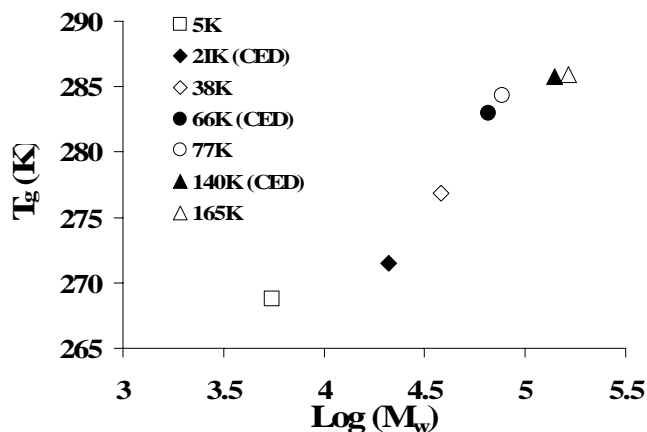
A detailed description of the synthesis of the methyl acrylate- $d_3$  and PMA- $d_3$  samples is given elsewhere.<sup>5</sup> For simplicity, the term "chain ends" refers to a limited number of segments at one end of the macromolecule rather than being limited only to the last (or first) segment at the end. Chain-end deuterated (CED) PMA samples were synthesized using atom transfer radical polymerization (ATRP).<sup>6</sup> The polymerization was carried out initially using protonated-methyl acrylate (Aldrich, 99%) monomer. The propagation of the reaction was monitored using the proton ( $^1\text{H}$ ) NMR signals of the monomer. After 10 h of reaction, a methyl acrylate- $d_3$  and toluene mixture was injected with a  $\text{N}_2$  purged syringe into the reaction vessel to insert deuterated-methyl groups at one of the chain ends. The reaction was stopped 2 h after the injection of the deuterated monomer. CED samples of PMA-21K, PMA-66K, and PMA-140K were synthesized. The numbers, next to each PMA, represent the molecular mass of the sample. The details of the polymer characterization techniques are given elsewhere.<sup>5</sup>

The number of mers deuterated, at the chain ends of each polymer, were estimated by comparing the  $^1\text{H}$  NMR peak intensities of the methyl groups to those of the methylene protons on the PMA (CED) samples. A PMA-100K (no deuteration) sample was used as a standard to check whether any correction factor was needed for the ratio of these two intensities. The percentages of the deuteration were calculated to be 0.13% (~1 unit) for the PMA-21K sample, 0.7% (~5 units) for the PMA-66K sample, and 1.2% (~19 units) for the PMA-140K (CED) sample.

The NMR spectra were obtained using a VARIAN VXR-400/S spectrometer. The quadrupole echo pulse sequence (delay- $90_y$ - $\tau$ - $90_x$ - $\tau$ -acquisition) was used with a  $^2\text{H}$  frequency of 61.39 MHz. The  $90^\circ$  pulse width was 2.8  $\mu\text{s}$  with an echo time of 30  $\mu\text{s}$ . 256 scans were used for the polymers (PMA-5K, 38K, 77K, and 165K). 32K scans were used for the CED PMA-21K, 66K, and 140K samples due to the very small number of deuterated-methyl groups on these polymers.

### Results and Discussion

The changes in the  $T_g$  with molecular mass for various PMA samples are shown in **Figure 1**. Deuteration at the methyl group was shown to have no significant effect on the  $T_g$ s of the PMA samples.<sup>5</sup> This concept may also be extended to CED samples. For similar polymers with similar molecular mass distributions, the segmental dynamics of the chain ends or chain middles should be similar to each other if their  $T_g$ s are alike. The differences in the  $T_g$ s of the PMA-66K (CED) ( $T_g$  at 10  $^\circ\text{C}$ ) and PMA-77K ( $T_g$  at 11.3  $^\circ\text{C}$ ) samples; and the PMA-140K (CED) ( $T_g$  at 12.8  $^\circ\text{C}$ ) and PMA-165K ( $T_g$  at 12.9  $^\circ\text{C}$ ) samples were very small. A larger difference was found between the PMA-5K ( $T_g$  at -4.2  $^\circ\text{C}$ ), PMA-21K (CED) ( $T_g$  at -1.5  $^\circ\text{C}$ ), and PMA-38K ( $T_g$  at 3.8  $^\circ\text{C}$ ) samples. However, the  $T_g$  of this CED sample was in between the other two fully-labeled samples.



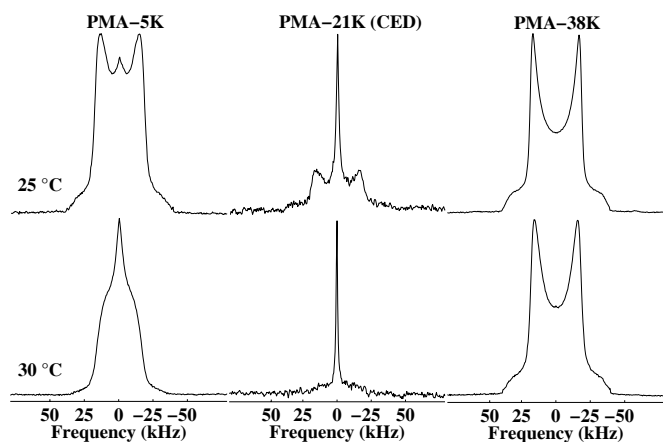
**Figure 1.** The change in  $T_g$  with molecular mass for the polymers of PMA with different molecular mass and deuteration. The 5K, 38K, 77K, and 165K samples were methyl deuterated on the whole chain, while the CED 21K, 66K, and 140K samples were methyl-deuterated at one end of the chains.

The  $^2\text{H}$  NMR spectrum for a glassy deuterated polymer consists of a Pake-powder pattern. When the motional rates on the order of the reciprocal of the quadrupole splitting occurs, the splitting between the horns of the powder pattern will get narrower. The spectrum eventually collapses to a single resonance at faster motional rates. However, the spectrum may contain the superposition of powder patterns for less-mobile species and narrower resonances for more-mobile species due to motional differences in the chains.

The NMR spectra of the bulk PMA-5K, PMA-21K (CED), and PMA-38K samples are shown in **Figure 2**. At 25  $^\circ\text{C}$ , the PMA-5K spectrum was comprised of a superposition of less-mobile and more-mobile components. The motionally-narrowed component in the middle of the spectrum was believed to be due to the more-mobile chain ends in the polymer. A sharper powder pattern without a middle component, indicative of less mobility, was present at 25  $^\circ\text{C}$  for the PMA-38K sample. The spectrum of the PMA-21K (CED), at 25  $^\circ\text{C}$ , was composed of an intense sharp resonance (fast component) in the middle with a weaker, broader, and distorted powder pattern (from the less-mobile segments).

At 30  $^\circ\text{C}$ , the spectrum for the PMA-5K sample collapsed to a broad multi-component resonance. For the PMA-38K sample at 30  $^\circ\text{C}$  the horns broadened a little, indicating the slower segmental dynamics as compared to PMA-5K. For the PMA-21K (CED) sample, a sharp single resonance was present in the spectrum, with very little residual powder pattern, at 30  $^\circ\text{C}$ .

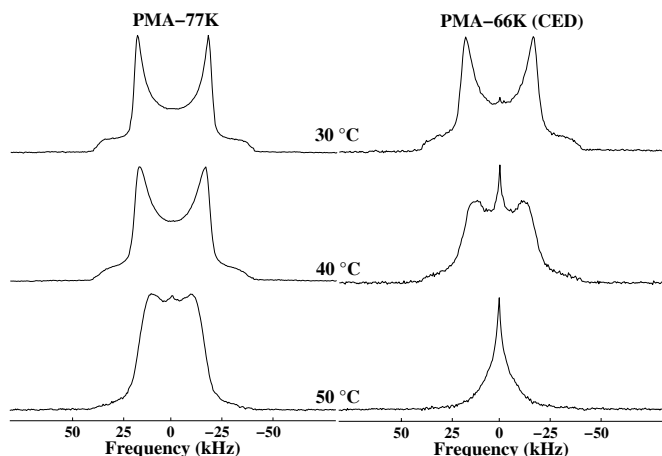
The NMR spectra from the PMA-21K (CED) clearly indicated the higher mobility of the chain ends as compared with those of the fully methyl-labeled samples with higher and lower molecular mass. At each temperature, the spectra from the chain ends contained significantly more-mobile features. The PMA-21K (CED) sample would be expected to have dynamics in between that of the 5K and 38K samples. The NMR spectra, from the chain ends of the 21K sample, showed faster dynamics than either of the samples.



**Figure 2.**  $^2\text{H}$  NMR spectra for the bulk PMA-5K, PMA-21K (CED), and PMA-38K samples.

$^2\text{H}$  NMR spectra of the PMA-77K and PMA-66K (CED) samples are shown in **Figure 3**. The spectra did not change much with temperature until 50 °C for the PMA-77K sample. The quadrupole splitting narrowed a little at 40 °C. At 50 °C, the horns became broader and partially collapsed. A motionally-narrowed component, with less intensity, as compared to PMA-5K and PMA-38K samples,<sup>5</sup> appeared in the middle, together with a distorted powder pattern, at 50 °C. The presence of this middle component was again attributed to more-mobile chain ends in the polymer.<sup>4,5</sup> A PMA-66K (CED) sample was studied to understand the mobility of chain ends in this higher molecular mass region. A more-mobile component in the middle appeared at 30 °C, and its intensity clearly increased with temperature. The spectra collapsed to a broad central resonance at around 50 °C.

When compared with the spectra of the PMA-77K sample, the chain ends on the PMA-66K (CED) sample clearly indicated faster dynamics of the chain ends. However, the contrast in dynamics of the chain ends and chain middles, in these samples, was not as great as it was in the previous lower molecular mass samples, as shown in **Figure 2**.



**Figure 3.**  $^2\text{H}$  NMR spectra for the bulk PMA-77K and PMA-66K (CED) samples.

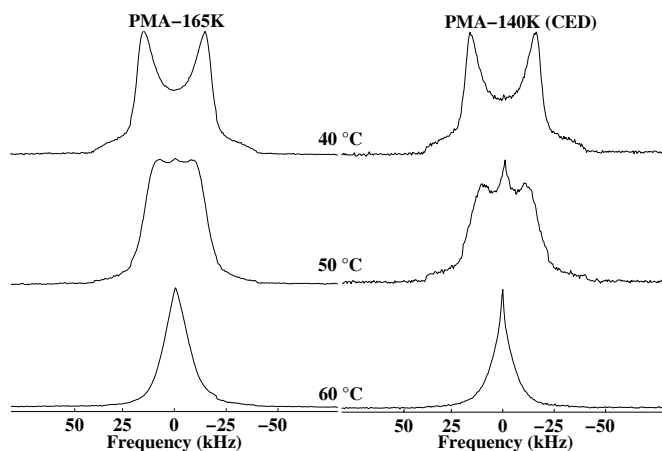
$^2\text{H}$  NMR line shapes of the PMA-165K and PMA-140K (CED) samples are shown in **Figure 4**. A powder pattern with broader horns appeared at 40 °C for the PMA-165K sample. The collapse to a single broad resonance occurred around 60 °C due to an increase in mobility of the segments with temperature. The spectra of the PMA-165K sample resembled those of the PMA-77K sample since the difference in their  $T_g$ s were relatively small. However, a more direct comparison of similar molecular mass samples (140K and 165K) seems more appropriate. A motionally-narrowed component appeared at 40 °C

for the PMA-140K (CED), and its intensity increased with temperature. The spectrum also collapsed to a single broad resonance at around 60 °C.

A more-mobile component was also present in the middle at 50 °C for the PMA-165K. The intensities of the middle components of the PMA-77K and 165K samples were not as large as they were in the lower molecular mass (PMA-5K and PMA-38K) samples. Again, this more heterogeneous behavior, superposition of more-mobile and less-mobile components in the lower molecular mass samples, was attributed to the presence of a high number of more-mobile chain ends.

The fast chain end dynamics were also apparent in **Figure 4** for the CED sample. The intensity of the more-mobile middle was stronger for the PMA-140K (CED) sample at 50 °C. The single resonance, at 60 °C, was narrower for the PMA-140K (CED) than the one for the PMA-165K sample. However, the magnitude of the difference in mobility was again not as great as it was in the other PMA samples of lower molecular mass.

The contrast in dynamics of chain ends and chain middles decreased with molecular mass, as seen in the NMR spectra. A molecular mass-dependent segmental mobility, on the chain ends, was concluded to be present. These results were consistent with the observation of the molecular mass dependent  $T_g$ s of the chain ends.<sup>2</sup> The increasing free volume associated with an increasing number of chain ends is concluded to be the reason for the molecular-mass dependence of the mobility of the chain ends.



**Figure 4.**  $^2\text{H}$  NMR spectra for the bulk PMA-165K and PMA-140K (CED) samples.

## Conclusions

The segmental dynamics on the chain ends appeared to be more mobile than the rest of the chain. The mobility difference, between the chain ends and the chain middles, was more prominent for the lower molecular mass PMA samples. The chain ends, in the higher molecular mass PMA samples, were also more-mobile. However, the spectral features indicated the similarity of the dynamics at the chain ends and the chain middles for the higher molecular mass samples.

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