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# MOLECULAR MASS AND DYNAMICS IN PMA- $d_3$ IN THE GLASS TRANSITION REGION

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## Introduction

The segmental dynamics through the glass transition region, by which the glassy polymer becomes rubbery, are not well understood. Free volume, thermodynamic and kinetic theories<sup>1</sup> have been used to describe the phenomenon behind the glass transition and some of those theories were tested with computer simulations.<sup>2</sup> Different experimental techniques, such as NMR,<sup>3</sup> thermo-mechanical analysis (TMA),<sup>4</sup> differential scanning calorimetry (DSC),<sup>4</sup> dilatometry<sup>5</sup> and dynamic mechanical analysis (DMA)<sup>3</sup> have all been also used to probe this important phenomena.

Deuterium ( $^2\text{H}$ ) NMR has been a valuable tool for the investigation of the dynamics of macromolecules. Deuteration of macromolecules at specific locations on the chains does not significantly affect the properties of polymers. Spiess et al.<sup>6</sup> investigated motions in the glass transition region using 1D and 2D exchange NMR experiments on deuterated polystyrene. Rössler et al.<sup>7</sup> studied the molecular dynamics in deuterated binary liquids close to the glass transition temperature ( $T_g$ ) using 2D Exchange NMR.

Blum et al.<sup>9</sup> studied the effect of molecular mass on dynamics through glass transition for poly(methyl acrylate) (PMA). They found a "homogeneity" of the dynamics in the glass transition region for high molecular mass sample, but heterogeneity for the low molecular mass sample. In addition, the polydispersities of the samples were large. In this paper, we report studies of the dynamics of more monodisperse poly(methyl acrylate)- $d_3$  (PMA)- $d_3$  samples around the glass transition region using  $^2\text{H}$  quadrupole echo NMR and modulated DSC (MDSC).

## Experimental

**Monomer Synthesis.** Deuterated monomer, (methyl acrylate)- $d_3$ , was synthesized using methanol- $d_4$  (CIL), acryloyl chloride (Aldrich, 96%), triethylamine (Alfa Aesar, 99.9%) and toluene. Impurities were removed from acryloyl chloride by fractional distillation. The other chemicals were used without further purification. Methanol- $d_4$  (11.23 ml, 0.28 moles) was mixed with triethylamine (34.8 ml, 0.25 moles) in a round-bottomed flask containing 25 ml toluene. A mixture of acryloyl chloride (20.5 ml, 0.25 moles) and 15 ml toluene was added dropwise into the mixture prepared above at 0 °C in 30-45 min. The mixture was stirred at 0 °C for 3-4 hours and at room temperature for 20-24 hours. The reaction was stopped with addition of a concentrated  $\text{NaHCO}_3$  solution. The product was washed twice with concentrated  $\text{NaHCO}_3$  solution and three times with distilled water. The toluene and methyl acrylate- $d_3$  mixture was extracted and the product was dried over  $\text{CaH}_2$  for 18 hours. After vacuum distillation a 70-75% yield was determined.

**Polymer Synthesis.** Atom Transfer Radical Polymerization (ATRP) was used to synthesize poly(methyl acrylate)- $d_3$  with narrow polydispersities.<sup>10</sup> Methyl acrylate- $d_3$ , N,N,N',N'-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and ethyl 2-bromopropionate (2-EBP, Aldrich, 99%) were used without further purification. CuBr (Aldrich, 98%) was added to a 50 ml round-bottomed flask and the flask was sealed with a rubber septum. The flask was evacuated and purged with nitrogen twice to remove oxygen. Degassed toluene, monomer and amine ligand (PMDETA) were added with nitrogen-purged syringes and the mixture was purged with nitrogen for 10 min. Initiator (2-EBP) was added with nitrogen-purged syringes and flask was immersed in an oil bath at 90 °C. Depending on the molecular mass targeted, ratio of [monomer]/[initiator] was changed for each reaction.

Molecular mass measurements of the polymer samples were made using Wyatt Technology's (Santa Barbara, CA) OPTILAB DSP Interferometer Refractometer and a DAWN EOS Light Scattering Instrument with a LC-10AT Shimadzu HPLC pump.  $dn/dc$  (specific refractive index increment) value for PMA was determined to be 0.063 ml/gm at 690 nm in THF, using OPTILAB DSP Interferometer Refractometer. Similar measurements were made on deuterated polymers and  $dn/dc$  values for those polymers were found to be similar for protonated PMA. Molecular mass information and sample designation of the polymers are shown in Table 1.

NMR spectra of the samples were obtained using a VARIAN VXR-400/S spectrometer. The quadrupole echo pulse sequence (delay-90 $_y$ -tau-90 $_x$ -tau-acquisition) was used in the experiments with  $^2\text{H}$  frequency at 61.39 MHz. The 90° pulse width was 2.7  $\mu\text{s}$  with an echo time of 30  $\mu\text{s}$ .

A modulated differential scanning calorimeter (MDSC) (TA Instruments, New Castle, DE) was used for thermal characterization with a modulation rate of  $\pm 0.5$  °C per 40 s and a heating rate of 2.5 °C/min. Universal Analysis software (TA Instruments) was used to process the collected MDSC data.

Table 1. Molecular Mass Of The Poly(Methyl Acrylate)- $D_3$  Samples

Name	$M_w$ (g/mol)	$M_n$ (g/mol)	Polydispersity
PMA-5K	5,600	5,500	1.02
PMA-38K	38,000	33,000	1.15
PMA-77K	77,000	61,000	1.26
PMA-165K	165,000	116,000	1.42

## Results and Discussion

Solid-state deuterium NMR line shapes are mainly dominated by the quadrupolar interaction<sup>5</sup> and are sensitive to the orientation of labeled methyl groups on the polymer chain. Due to the coupling of the C-D bond directions with the cooperative motion of the polymer chains,<sup>6</sup> deuterium NMR line shapes provide information about dynamics through the glass transition.

The powder pattern for a solid sample collapses to a single line with increasing temperature due to the change in mobility of methyl groups on the polymer chains.<sup>8</sup>  $^2\text{H}$  NMR spectra for bulk PMA-5K are given in Figure 1 for different temperatures. Line shapes for PMA-5K indicate the presence of different motional components in the glass transition region from 26 °C to 45 °C. At 26 °C, a middle peak due to segments with fast motions appears and the intensity increases through the glass transition region until the powder pattern completely collapses to a single resonance. The appearance of this mobile (motionally narrowed) component was attributed to chain ends,<sup>9</sup> since they are the most mobile portions of the polymer chains. The broader powder pattern is due to the rigid component in the spectra which are mostly from the less mobile parts of the polymer chains. The superposition of these components in the glass transition region of the PMA-5K sample indicates the heterogeneity of the dynamics through the glass transition region.

$^2\text{H}$  NMR spectra for PMA-38K were also taken at different temperatures and are shown in Figure 2. Due to a molecular mass effect, the glass transition region for this sample moved to higher temperatures than those of the PMA-5K sample. At 25 °C, the line shape is that of a solid powder pattern. At higher temperatures, the powder pattern collapses (starting at 35 °C), with different components present in the spectra through the glass transition region. Again, the heterogeneity of segmental motions through the glass transition region is obvious for PMA-38K from 35 °C to 55 °C.

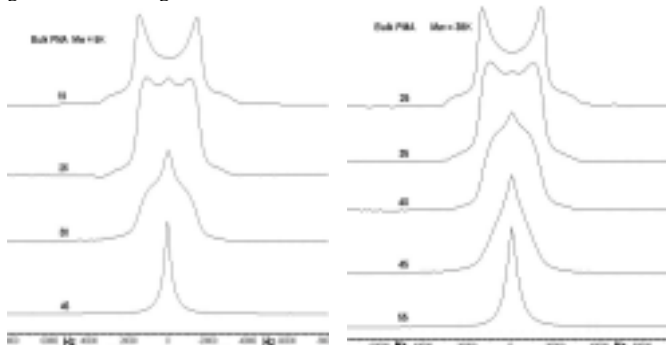


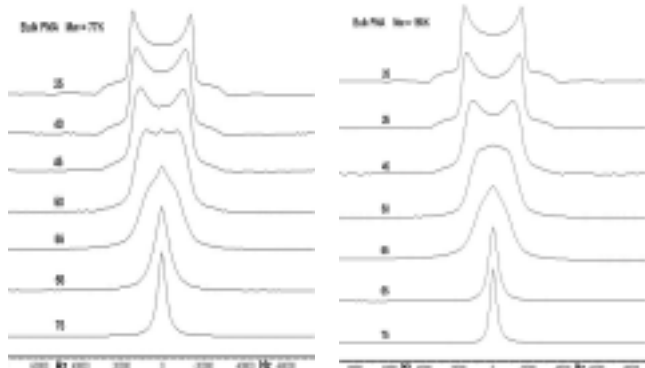
Figure 1.  $^2\text{H}$  NMR spectra for bulk PMA-5K at different temperatures (°C).

Figure 2.  $^2\text{H}$  NMR spectra for bulk PMA-38K at different temperatures (°C).

The lower molecular mass (LMM) samples, PMA-5K and PMA-38K, clearly showed the heterogeneity of segmental motions through the glass transition region. Another sample, PMA-77K, with a higher molecular mass than the previous two samples, was also analyzed. The  $^2\text{H}$  NMR line shapes are given in Figure 3. From 25 °C to 40 °C, there is little change in the powder pattern indicating that the mobility of the polymer chains has not changed considerably on the  $^2\text{H}$  NMR timescale. After a temperature of 40 °C is reached, different components appear on the spectra that are similar to those in Figures 1 and 2. While the intensity of the middle component, due to

the chain ends, was more prominent in the LMM samples, there was a similar but less intense component in the PMA-77K sample. The dynamics through glass transition was still heterogeneous, but not as much as it was for the LMM PMA-5K and PMA-38K samples.  $^2\text{H}$  NMR spectra of each sample with increasing molecular mass indicated a trend toward homogenous dynamics through the glass transition region.

A high molecular mass sample, PMA-165K was studied. The  $^2\text{H}$  NMR spectra for this sample are given in **Figure 4**. It has been shown<sup>4</sup> that, after certain molecular mass is attained, the glass transition temperature does not change significantly. This is observed in the spectra for PMA-77K (Figure 3) and PMA-165 K (Figure 4), where the glass transition region does not change much with molecular mass.

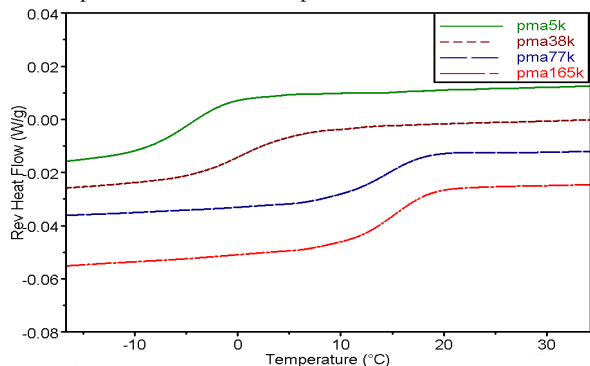


**Figure 3.**  $^2\text{H}$  NMR spectra for bulk PMA-77K at different temperatures ( $^{\circ}\text{C}$ ).

**Figure 4.**  $^2\text{H}$  NMR spectra for bulk PMA-165K at different temperatures ( $^{\circ}\text{C}$ ).

In the glass transition region of PMA-165K, collapse of the powder pattern does not occur with the presence of significantly different motional components. The number of chain ends in a high molecular mass (HMM) polymer sample would be considerably fewer than the number of chain ends in a LMM sample. Thus, the intensity from the central component, due to chain ends, would be expected to decrease with increasing molecular mass in the glass transition region. **Figure 4** also shows that, through glass transition, this middle component does not occur for the PMA-165K sample. This more clearly indicates the trend to more homogeneous dynamics (segmental motions) during glass transition with increasing molecular mass.<sup>9</sup>

Thermal experiments, using modulated differential scanning calorimetry (MDSC), were performed on the deuterated PMA samples in order to compare the phenomenon behind glass transition. Glass transition curves for the deuterated samples are shown in **Figure 5**. Qualitatively, it can be seen that LMM samples have broader glass transition widths and lower glass transition temperatures than HMM samples.



**Figure 5.** Glass transition curves for deuterated PMA samples from MDSC experiments.

MDSC experiments were also performed using protonated PMA samples; the results of these experiments are shown in **Table 2** along with the results for the deuterated samples. Transition widths were calculated using the derivative of reversible heat versus temperature curve and estimated as the width at half height of the glass transition peak. Transition widths showed that HMM samples are narrower than those of the LMM samples.

**Table 2.** Glass Transition Temperatures ( $T_g$ ) And Widths Of Protonated And Deuterated (\*) PMA Samples Measured With MDSC

$M_w$ (g/mol)	$T_g$ ( $^{\circ}\text{C}$ )	$T_g$ width ( $^{\circ}\text{C}$ )
5,600*	-4.5	7.4
12,000	-0.82	7.5
29,000	0.17	8.2
38,000*	0.65	8.6
41,000	5.2	7.6
68,000	12	6.7
77,000*	14	5.8
100,000	15	5.7
165,000*	15	5.7

**Table 3** compares the results of the glass transition values for both NMR and MDSC experiments for deuterated PMA samples. NMR  $T_g$  values were estimated using the temperature value at which the powder pattern collapsed to a single (broad) line. This collapse occurred at 30  $^{\circ}\text{C}$  for PMA-5K, 40  $^{\circ}\text{C}$  for PMA-38K, and 55  $^{\circ}\text{C}$  for PMA-77K and PMA-165K. **Table 3** shows that NMR  $T_g$  is higher than MDSC  $T_g$  by about 35-40  $^{\circ}\text{C}$ , due to the frequency difference in the experiments.

**Table 3.** NMR And MDSC Glass Transition Temperatures Of The Deuterated PMA Samples.

Name	MDSC $T_g$ ( $^{\circ}\text{C}$ )	NMR $T_g$ ( $^{\circ}\text{C}$ )
PMA-5K	-4.5	30
PMA-38K	0.65	40
PMA-77K	14	55
PMA-165K	15	55

The results of MDSC experiments are in agreement with  $^2\text{H}$  NMR experiments where the width of the glass transition indicates the homogeneity of segmental motions for higher molecular mass samples through the glass transition region.

### Conclusions

While lower molecular mass samples showed heterogeneity of the dynamics, higher molecular mass samples indicated a trend towards a more homogenous dynamics through the glass transition region. The middle peak in the  $^2\text{H}$  NMR spectra indicated the faster dynamics of chain ends in the glass transition region. The intensity of this resonance decreased with increasing molecular mass. Homogeneity of the dynamics manifested itself in the narrower glass transition widths for HMM samples via the MDSC experiments. These results compared nicely with the  $^2\text{H}$  quadrupole echo NMR experiments.

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