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## DYNAMICS OF POLYACRYLATES IN CONCENTRATED CHLOROFORM SOLUTIONS

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### Introduction

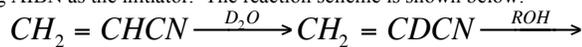
The dynamics of polymers in polymer solutions have not been probed in great enough detail to provide a coherent picture of the behavior of these polymers, especially in more concentrated solutions. To help understand this behavior further, we have prepared a series of backbone-labeled polymers including poly(n-butyl acrylate)-d<sub>1</sub> (PNBA). These provide a basis for comparison of the behavior among a group of related polymers.

The dynamics have been probed by using deuterium relaxation times. Since the relaxation times are relatively fast and the quadrupolar relaxation mechanism is well understood, data from this technique provide a convenient means for comparison of dynamics for different acrylates. We have chosen to use the relaxation times T<sub>1</sub> and T<sub>2</sub> as the basis set because they probe the spectral densities of the polymers at rather different frequencies (vide infra).

We have previously reported the dynamics of poly(iso-propyl acrylate) (PIPA) in chloroform solution.<sup>1</sup> At that time we found that the relaxation times measured could not be adequately evaluated by the motional models tested at that time. Our original results showed that the models yielded results which were not physically realistic and resulted in, for example, correlation times getting slower with increasing temperatures. This problem has now been solved for the logχ<sup>2</sup> model by the proper normalization of the mean, and other models for polymer segmental motion.<sup>2</sup>

### Experimental

The acrylates used were synthesized with deuterium labels in the methine position. Monomeric acrylates were prepared from acrylonitrile, exchanged with D<sub>2</sub>O with hydroquinone and CaO as previously reported for poly(iso-propyl acrylate).<sup>1</sup> The nitrile group was then converted to the appropriate acrylate ester with the proper alcohol and sulfuric acid. Subsequently other more effective techniques have been developed for the methine exchange reaction.<sup>3</sup> The polymerization was carried out in toluene using AIBN as the initiator. The reaction scheme is shown below:



where the type of acrylate was determined by the R-group on the alcohol.

Deuterium NMR experiments were performed at 13.7 MHz on a JEOL FX 90Q NMR spectrometer. The T<sub>1</sub> measurements were made by inversion recovery technique and the T<sub>2</sub>\*'s estimated from the line-widths.

### Results and Discussion

Relaxation measurements have been made for poly(n-butyl acrylate)-d<sub>1</sub> (PNBA), poly(iso-propyl acrylate)-d<sub>1</sub> (PIPA), and poly(ethyl acrylate)-d<sub>1</sub> (PEA), but only the results for PNBA are reported here. The T<sub>1</sub> and T<sub>2</sub>\* data were interpreted using a log-normal distribution of correlation times. The relaxation times are determined by:

$$\frac{1}{T_1} = \frac{3\pi^2}{20} (e^2 qQ/h)^2 [J(\omega_0) + 4J(2\omega_0)] \quad (1)$$

and

$$\frac{1}{T_2} = \frac{3\pi^2}{40} (e^2 qQ/h)^2 [3J(0) + 5J(2\omega_0) + 2J(2\omega_0)] \quad (2)$$

where the first term is the quadrupole coupling constant, and the J's are the spectral densities. We note that the spectral densities probe frequencies which are on the order ω (13.7 MHz) for T<sub>1</sub>, and ω and 0 (indicative of slower motions) for T<sub>2</sub>. The spectral densities are the relative amount of motion at a given frequency and are the Fourier transforms of the autocorrelation function, G(τ,σ) or:

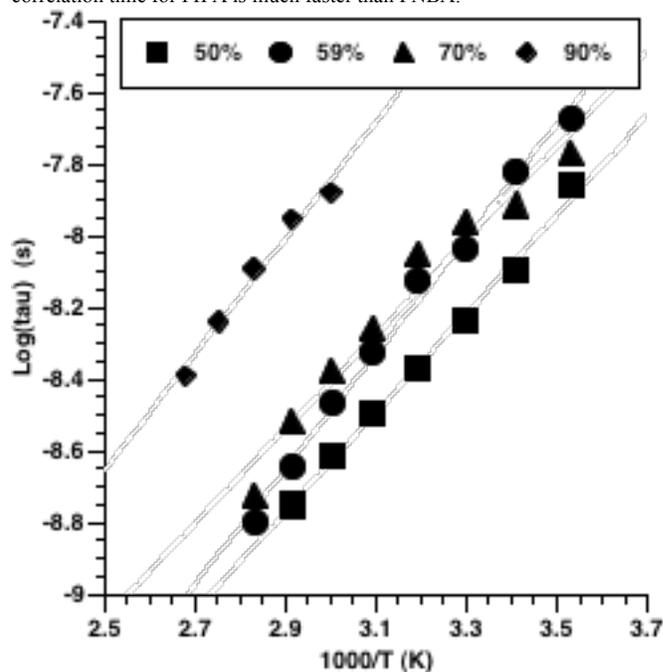
$$J(\omega) = \int_{-\infty}^{\infty} G(\tau, \sigma) e^{i\omega\tau} dt \quad (3)$$

The autocorrelation function embodies the complexity of the decay of motion in the system. We have chosen to represent this with the log-normal distribution of correlation times or

$$G(\tau, \sigma) = \frac{1}{\pi^{1/2} \sigma \tau_r} e^{-(\ln\tau_r / \sigma + \sigma / 4)^2} \quad (4)$$

where τ<sub>r</sub> = τ/τ<sub>0</sub>.

The results of fitting the relaxation data to the log-normal function for PNBA are shown in Figure 1. As can be seen in the figure, the correlation times vary systematically with both concentration and temperature. The variation of each concentration is markedly non-exponential with downward curvature, consistent with the finding for PIPA. The width parameter, σ, varied between 2.3 and 3.1, and increased with decreasing temperature and increasing concentration. The variation in σ was not as systematic as that for the correlation time. Roughly, the width of the distribution did not change a great deal over the range of composition and temperatures studied. A comparison to the previously published data on PIPA<sup>3</sup> reveals that the correlation time for PIPA is much faster than PNBA.



**Figure 1.** Correlation times for PNBA in chloroform in concentrated solutions as a function of temperature and concentration (given in wt. % polymer)

### Conclusions

The use of the log-normal distribution of correlation times can be used to fit the relaxation data from concentrated polymer solutions. The data provide reasonable variations of the mean correlation times as width (not shown) with concentration.

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