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Ultrathin Polymer Films near the Glass Transition: Effect on the Distribution of α-Relaxation Times As Measured by Second Harmonic Generation

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Introduction. The nature of the glass transition in amorphous materials is incompletely understood although it has been studied for decades.[1] A phenomenon gaining attention recently is the modification of properties associated with the glass transition temperature, T_g, in ultrathin polymer films,[2−11] i.e., films with thicknesses ca. 200 nm or less. Spectroscopic ellipsometry,[2−5] X-ray reflectivity,[6−9] and Brillouin scattering[10] have indicated that T_g itself may be a function of film thickness and whether the film is free-standing or in contact with a substrate, with the extent of polymer−substrate interaction of importance. Depending on the polymer−substrate system, increases[8] or decreases[10] as much as 50−70 °C in T_g as compared to bulk values have been inferred, with the largest deviations occurring for the thinnest films. It is not yet clear how substrate and free surface effects modify polymer dynamics. Understanding this is important for high-performance application of ultrathin polymer films.

None of the techniques used examines how polymer film thickness affects the distribution of cooperative segmental mobility (α-relaxation) near T_g.[12] We present the first such measurement employing second harmonic generation (SHG) of a copolymer with a covalently attached nonlinear optical dye, Disperse Red 1 (DR1). We have previously shown that DR1 reorientation dynamics measured by SHG are coupled to cooperative segmental dynamics and may be used as a probe of the α-relaxation.[13−17] Here, we show that film thickness can alter the breadth of the distribution of α-relaxation times in films as thin as 7 nm with little change in average relaxation time, $\langle\tau\rangle$.

Experimental Details. DR1-functionalized monomer, 4-(2-methacryloyloxyethyl)ethylamino-4′-nitroazobenzene, was synthesized and copolymerized[16] with isobutyl methacrylate, yielding a copolymer with 36 mol % functionalization (UV−vis) and M_w = 59 000 and M_n = 37 000 (GPC, relative to poly(methyl methacylate) in tetrahydrofuran). For bulk copolymer, T_g = 93 °C (DSC, 10 K/min, onset mode). SHG samples were spin coated from 2-butanone onto quartz patterned with planar chrome electrodes (800 μm gap). Films were dried 12 h above T_g under vacuum; thicknesses were measured by a Tencor P10 profilometer. SHG decay was measured using a Q-switched Nd-YAG laser (10 Hz frequency) with a 1.064 μm fundamental beam. A 15 kV/cm dc-poling field was used with poling times and temperatures chosen to minimize extraneous charge effects. Dynamics from 20 s onward were measured by monitoring SHG intensity after switching off the dc-poling field permanently. Dynamics from 5 μs to 2 s were monitored using a variable time delay for switching off the poling field with respect to the laser pulse. See ref 14.

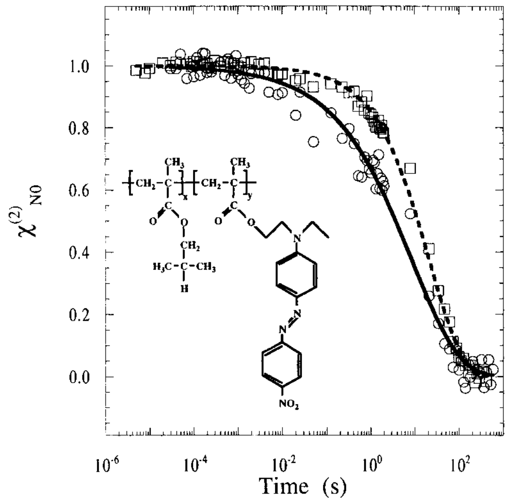

Figure 1. $\chi^{(2)}_{NO}$ as a function of decay time at 98 °C for (○) 23 nm thick film and (□) 520 nm thick film. Curves are best fits to eq 1 with $\beta_w = 0.42$ for the 23 nm film (solid curve) and $\beta_w = 0.59$ for the 520 nm thick film (dashed curve). Inlay: Random copolymer of isobutyl methacrylate (64 mol %) and Disperse Red 1 functionalized monomer (36 mol %) used in this study.

Results and Discussion. The SHG intensity is proportional to the square of the second-order macroscopic susceptibility, $\chi^{(2)}$. Reorientation dynamics of DR1 chromophores after removing the dc field may be followed by monitoring the decay in $\chi^{(2)}_{NO}$, where $\chi^{(2)}_{NO}$ is the ratio of $\chi^{(2)}$ normalized to that measured just before switching off the dc field and corrected for dc-field-induced third-order effects.[13−17] $\chi^{(2)}_{NO}$ was measured above and below the bulk T_g for 7 nm to 1 μm thick films. Figure 1 shows the decay of $\chi^{(2)}_{NO}$ for 23 and 520 nm thick films at 98 °C. The decays are modeled by the Kohlrausch−Williams−Watts (KWW) equation:[18]

$$\chi^{(2)}_{NO}(t) = \exp(-(t/\tau)^{\beta_w}) \tag{1}$$

where τ is the characteristic relaxation time and β_w takes values between 0 and 1; $\beta_w = 1$ corresponds to a single-exponential relaxation process while $\beta_w < 1$ indicates a distribution of relaxation times. For the 520 nm film, $\beta_w = 0.59$ while for the 23 nm film, $\beta_w = 0.42$, indicating a broader relaxation distribution for the ultrathin film.

The average reorientation relaxation time constant, $\langle\tau\rangle$, is given by

$$\langle\tau\rangle = \int_0^\infty \exp(-(t/\tau)^{\beta_w})\,dt = \tau\Gamma(1/\beta_w)/\beta_w \tag{2}$$

where Γ is the gamma function. We have previously shown with this copolymer[16,17] that $\langle\tau\rangle$ follows a Williams−Landel−Ferry[19] temperature dependence above T_g and an apparent Arrhenius dependence below T_g, with $\langle\tau\rangle$ at T_g being ca. 100−200 s, a time scale associated with the α-relaxation.[20] Thus, for this copolymer the DR1 reorientation dynamics are coupled to the α-relaxation and can be used to probe α-relaxation dynamics. (A complete discussion of SHG characterization of α-relaxation dynamics is found in refs 14 and

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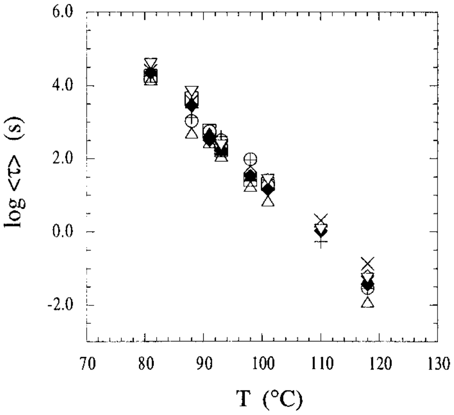

Figure 2. Average relaxation time, $\langle\tau\rangle$, as a function of temperature for (○) 7 nm, (□) 23, (◇) 25, (△) 70, (×) 90, (+) 135, (▽) 190, (◆) 520, and (▲) 1000 nm thick films.

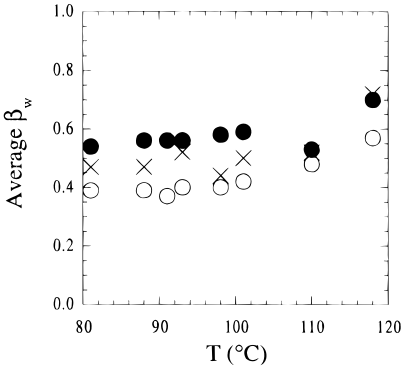

Figure 3. Average KWW β_w parameter as a function of temperature for (○) 7−90, (×) 135 and 190, and (●) 520 and 1000 nm thick films. Standard deviations are approximately the symbol size except at the highest temperature, where they are slightly larger.[21]

15.) Although the 23 and 520 nm films differ in their relaxation distribution at 98 °C, $\langle\tau\rangle$ values are nearly identical. Figure 2 shows $\langle\tau\rangle$ as a function temperature for 7 nm to 1 μm thick films. Within experimental error, there is no trend of $\langle\tau\rangle$ with thickness. As $\langle\tau\rangle$ is a strong function of $T - T_g$, changing as much as an order of magnitude with a 5 °C temperature change near T_g, there must be little or no change in T_g from the bulk value of 93 °C as thickness decreases from 1 μm to 7 nm. Consistent with this, studies[4] on a related system, poly(methyl methacrylate) on SiO_2, have indicated at most a slight (<6 °C) change in T_g from the bulk value for ultrathin films.

Inspection reveals that the β_w values fall in several bands.[21] Figure 3 shows the average β_w values for the film thicknesses that lie within these bands. At all temperatures except one,[22] the average β_w value for the thickest films (>190 nm) is at least 0.13 higher than that for the thinnest films (≤90 nm). The β_w values for the 135 and 190 nm thick films typically lie between these two bands with $\beta_w(190\ \text{nm}) \geq \beta_w(135\ \text{nm})$, indicating a transition from ultrathin film behavior with a very broad distribution of relaxation times to thin film behavior taking on bulk polymer characteristics. Using τ and β_w, this difference in the distribution may be quantified using an algorithm proposed by Emri and Tschoegl[23] and developed by Dhinojwala[17] for interpreting SHG decays. Employing the conditions in Figure 1, Figure 4 illustrates the dramatic broadening of the relaxation distribution in ultrathin films as compared to thin films, with limited additional relaxation at 1−2 orders of magnitude shorter times.

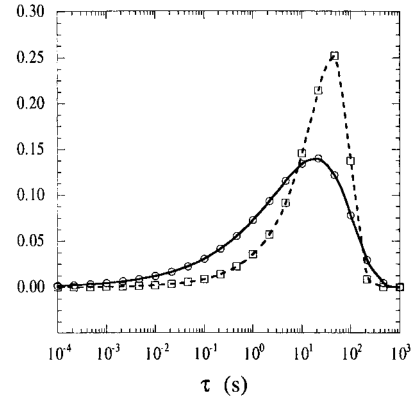

Figure 4. Discrete distributions of reorientation relaxation times for (○) 23 and (□) 520 nm thick films calculated using fits to eq 1 and the algorithm by Emri and Tschoegl[23] as developed by Dhinojwala.[17] (Curves drawn to guide the eye only.)

Changes in the breadth of the relaxation distribution and thus β_w with thickness may be caused by changes in local-scale heterogeneity. For example, the broadening of the α-relaxation distribution in bulk polymers as temperature is decreased toward T_g has been linked to increased heterogeneity caused by local density fluctuations.[24,25] Concentration fluctuations in miscible polymer blends have also been attributed to yield broadening of the α-relaxation distribution relative to that of homopolymers.[24] The broadening of the relaxation distribution in ultrathin polymer films shown here may also be linked to increased local-scale heterogeneity. It is known that polymer behavior may be modified by surfaces and interfaces. Specific interactions near an impenetrable interface may cause adsorption, density changes,[26] or decreased entanglements.[27] Surface rubbing,[28] atomic force microscopy,[29] and scaling analyses[30] have also indicated that free surfaces have enhanced mobility. The magnitude and size scale of these interactions depend on temperature and the polymer and interface. Usually, macroscopic polymer dynamics are modified insignificantly by interfacial/surface effects as the vast majority of chains is not located in these regions. However, for an ultrathin film, these regions may dominate behavior as chain segments may experience distinct mobilities in the free surface, substrate, and interior regions. Thus, the cooperative segmental mobility of an ultrathin film may be expected to have an anomalously broad relaxation distribution; this study is the first to demonstrate such effects for polymers near T_g.

The film thickness at which significant deviations from bulk polymer behavior appear may provide an alternative way to define an "ultrathin" polymer film. For the system examined here, films with thicknesses ≤90 nm exhibit a distinct broadening of the relaxation distribution and may be defined as ultrathin; however, other polymer−substrate combinations and free-standing films may elevate or depress the thickness which defines an "ultrathin" polymer film. SHG studies on different polymer−substrate systems are underway in order to elucidate more fully the effect of substrate interactions on α-relaxation dynamics of ultrathin polymer films. The added breadth in the relaxation distribution may cause significant changes in the translational diffusion of small molecules in ultrathin relative to thin polymer films, as diffusion has been hypothesized to be dominated by the short-time side of the relaxation distribution.[25,31,32] Studies are also being done to quantify the effects of film thickness on translational diffusion of small molecules whose motions are partially or wholly coupled to the polymer α-relaxation.[33]

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References and Notes

(1) (a) Kauzmann, W. *Chem. Rev.* **1948**, *43*, 219. (b) Gibbs, J. H.; Di Marzio, E. A. *J. Chem. Phys.* **1955**, *28*, 373. (c) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1961**, *34*, 120. (d) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394. (e) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139. (f) Grest, G. S.; Cohen, M. H. *Adv. Chem. Phys.* **1981**, *48*, 455. (g) McKenna, G. B. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon: Oxford, 1989; Vol. 2, p 311. (h) Angell, C. A. *Science* **1995**, *267*, 1924. (i) Frick, B.; Richter, D. *Science* **1995**, *267*, 1939.

(2) Beaucage, G.; Composto, R.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 319.

(3) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.

(4) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219.

(5) Keddie, J. L.; Jones, R. A. L. *Isr. J. Chem.* **1995**, *35*, 21.

(6) Orts, W. J.; van Zanten, J. H.; Wu, W. L.; Satija, S. K. *Phys. Rev. Lett.* **1993**, *71*, 867.

(7) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, R3329.

(8) van Zanten, J. H.; Wallace, W. E.; Wu, W. L. *Phys. Rev. E* **1996**, *53*, R2053.

(9) Wu, W.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771.

(10) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002.

(11) Studies of low molecular weight, organic glass formers in small-length-scale environments (pores) have also shown deviations from bulk T_g values. See, for example: Jackson, C. L.; McKenna, G. B. *J. Non-Cryst. Solids* **1991**, *131*−*133*, 221. Zhang, J.; Liu, G.; Jonas, J. *J. Phys. Chem.* **1992**, *96*, 3478. Schüller, J.; Mel'nichenko, Y. B.; Richert, R.; Fischer, E. W. *Phys. Rev. Lett.* **1994**, *73*, 2224.

(12) Although no study has yet reported on modification of the distribution of α-relaxation times in polymer films near T_g with decreasing film thickness, a broadening of the relaxation distribution has been noted (Blum, G.; Kremer, F.; Jaworek, T.; Wegner, G. *Adv. Mater.* **1995**, *7*, 1017) in a dielectric relaxation study of poly(γ-octadecyl L-glutamate-*co*-methyl L-glutamate) Langmuir−Blodgett films ca. 11 nm thick and in dielectric studies of propylene glycol and its oligomers confined in 10 nm pores (Schüller, J.; Mel'nichenko, Y. B.; Richert, R.; Fischer, E. W. *Phys. Rev. Lett.* **1994**, *73*, 2224).

(13) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 7395.

(14) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5943.

(15) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *J. Chem. Phys.* **1994**, *100*, 6046.

(16) Dhinojwala, A.; Hooker, J. C.; Torkelson, J. M. *J. Non-Cryst. Solids* **1994**, *172*−*174*, 286.

(17) Dhinojwala, A.; Hooker, J. C.; Torkelson, J. M. *ACS Symp. Series* **1995**, *61*, 318.

(18) (a) Kohlrausch, R. *Ann. Phys. (Leipzig)* **1847**, *12*, 393. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(19) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(20) Angell, C. A. *J. Non-Cryst. Solids* **1988**, *102*, 205.

(21) Average β_w values were calculated from the individual β_w values found for each film thickness in the specified range. The standard deviation of the average values are ca. the symbol size in Figure 3 except at the highest temperature where they are slightly larger. By performing constrained fits on the $\chi^{(2)}{}_{NO}$ decay curves, the uncertainties in the individual β_w were found to be approximately ±5 to ±7% of the β_w value except for the 7 nm film curves, which were ±15% (higher uncertainty due to lower signal to noise ratio afforded by the thinnest film), and certainly could not explain the differences between thin and ultrathin films.

(22) Extraneous effects associated with charge injection were a problem in certain samples near 110 °C. Only measurements in which these effects were absent or for which they could be accounted are presented.

(23) Emri, I.; Tschoegl, N. W. *Rheol. Acta* **1993**, *32*, 311.

(24) Ngai, K. L.; Plazek, D. J. *Rubber Chem. Technol.* **1995**, *68*, 376 and references therein.

(25) Cicerone, M. T.; Ediger, M. D. *J. Chem. Phys.* **1996**, *104*, 7210.

(26) Fernandez, M. L.; Higgins, J. S.; Penfold, J.; Shackleton, C. *Polym. Commun.* **1990**, *31*, 124.

(27) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798.

(28) Toney, M. F.; Russell, T. P.; Logan, J. A.; Kikuchi, H.; Sands, J. M.; Kumar, S. K. *Nature* **1995**, *374*, 709.

(29) Meyers, G. F.; DeKoven, B. M.; Seitz, J. T. *Langmuir* **1992**, *8*, 2330.

(30) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.

(31) Deppe, D. D.; Dhinojwala, A.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 3898.

(32) Deppe, D. D.; Miller, R. D.; Torkelson, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 2987.

(33) Hall, D. B.; Torkelson, J. M., manuscript in preparation.

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