Direct Comparison of Probe Reorientation and Linear Mechanical Measurements of Segmental Dynamics in Glassy Poly(methyl methacrylate)

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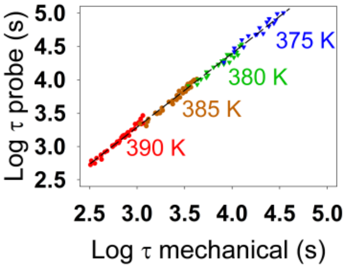

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Abstract

Optical probe reorientation experiments and mechanical stress relaxation measurements in the linear response regime were performed on a polymer glass. Segmental dynamics of lightly crosslinked poly(methyl methacrylate) (PMMA) were monitored via both methods at temperatures between 9 and 24 K below the glass transition temperature (T_g), and over the course of 8 hours of aging. Relaxation times from the two methods cover a range of ~1.7 decades. Similar results were obtained from the two experiments other than a slight difference in the aging rate. A difference of ~0.3 decades (a factor of approximately 2) is observed between the optically and mechanically obtained relaxation times, related primarily to the size of the probe. Both experiments give a value near 0.3 for the Kohlrausch-Williams-Watts (KWW) β parameter. These results provide an important baseline for the interpretation of optical probe reorientation experiments during nonlinear deformation.

Introduction

Polymer glasses form an important class of engineering materials and are increasingly employed in a variety of fields from biomedicine to aeronautics. In comparison with metals, polymers are typically substantially cheaper, lighter, and easier to process and shape. The diversity of applications underscores the necessity to gain a fundamental understanding of the structural and mechanical properties of these materials.

One key quantity characterizing a glassy polymer is the average segmental relaxation time τ. Many of the characteristic features of polymers arise from the long chain structure of the molecules, and their conformational changes. The rate at which segments of these chains can rearrange, quantitatively described by τ, sets the time scale for structural change in the material. A polymer material that can respond quickly to changes in its environment (small τ) behaves as a viscous liquid, while a sample with more restricted molecular motions (large τ) is more rigid and solid-like, and for very large τ is considered a glass. τ can also be used as a qualitative indicator of structural changes occurring in a glassy polymer, though the precise relationship between structure and dynamics in polymers is not fully understood. For example, as a polymer glass undergoes structural relaxation at a constant temperature, the density increases and τ can be observed to grow larger due to increasingly hindered chain motions.[1-4] On the other hand, nonlinear mechanical deformation of a sample can act in the opposite manner. For this case, τ can be observed to decrease as the polymer segments are forced to rearrange to keep pace with the dimensional changes imposed by the deformation.[5-10]

Segmental relaxation in polymer glasses is complex, particularly due to spatially heterogeneous dynamics (the presence of a spatial and temporal distribution of relaxation times), physical aging (the evolution of material properties over time), and a non-linear mechanical response to deformation. Translational diffusion of probe molecules in glasses, for example, has been observed to have a significantly weaker temperature dependence than rotational motion.[11] This effect has been attributed to the presence of heterogeneous dynamics,[12-13] with the average rotation time being limited by slower regions, while translational motion is primarily sensitive to faster regions. Physical aging (or structural recovery) can be observed in a wide range of material or structural properties, including τ, but measurements of different observables, such as the volume and the enthalpy, frequently show different rates of change and different times required to reach equilibrium.[14-18] The non-linear mechanical response of a polymer glass presents a particular challenge to the study of the dynamics of polymer glasses. In principle, the mechanical response provides information about the segmental relaxation time but nonlinear deformation changes the state of the glass and thus also changes the segmental relaxation time.[19-20]

Among these important features of polymer glasses, physical aging is the most directly relevant for the work reported here. There are a number of models[21-22] that can semi-quantitatively describe the slowing of molecular relaxation processes aging and recently more fundamental approaches have been suggested. [23-25] Computer simulations of aging can reproduce many experimental features of aging and are beginning to elucidate the connection between structural changes and changes in material properties.[26-30] Experimentally, measurements of thermodynamic properties such as volume[31-32] or enthalpy[17, 33] during aging are common, as are measurements of properties relevant to practical applications of polymer materials, such as gas permeation in membranes,[34-35] or mechanical properties.[20, 36] Optical methods involving fluorescent labeling or probe molecules form an important set of experiments that can provide a molecular perspective on aging. Effects related to changes in the local volume distribution during aging were studied by Sung and co-workers, who observed photo-induced cis-trans isomerization in both free probes and on probes incorporated into polymer chains at specific positions.[37] Torkelson and coworkers extended these studies with free probe experiments in many different polymers, and have shown that the observed changes correlate well with independent measurements of volumetric relaxation.[38-40] Similar methods have been more recently employed by van den Berg et. al. using a probe which responds to volume changes via a change in emission wavelength.[41] Single molecule fluorescence microscopy techniques have been employed to investigate spatially heterogeneous dynamics,[42-43] as well as orientation effects during deformation.[44] While these optical experiments with probe molecules reveal many interesting features of the aging process, they directly measure probe properties and only indirectly infer information about the relaxation time of the polymer segments.

Over the past decade, our lab has developed an innovative optical technique that employs fluorescent probe rotation to measure segmental dynamics in polymer glasses during physical aging and active deformation.[5, 7-8, 45-46] This technique has demonstrated that the average probe reorientation time can be reduced by 2-3 orders of magnitude, and that the spectrum of relaxation times narrows considerably as a sample is deformed through yield.[5] These results[5-6, 45] are in good qualitative agreement with theory[24, 47] and simulation.[29, 48-49] The validity of these comparisons relies on the assumption that the reorientation behavior of the probe molecules accurately reports on the dynamics of the polymer segments. In equilibrium above T_g, the temperature dependence of probe reorientation is quite similar to that of dielectric relaxation,[7, 50] indicating that probe reorientation is a reliable reporter of segmental dynamics in the melt. Ideally, a similar comparison could be performed in the glassy state between probe reorientation and a probe-free measurement of segmental dynamics.

In order to further understand the relationship between probe reorientation and probe-free measurements of segmental mobility in glasses, we report here a direct comparison with stress relaxation experiments performed in the linear response regime. Probe reorientation and stress relaxation experiments were performed on lightly crosslinked PMMA glasses in a temperature range between 9 and 24 K below T_g, and over the course of 8 hours of aging. Stress relaxation measurements in the linear response regime are a standard method to examine glassy polymer dynamics,[51-53] and can be used to provide a comparison with the probe rotation measurements. We find that the probe and mechanical measurements of τ are in close agreement. The probe reorientation times are systematically longer than the mechanical times by a factor of ~2, which is attributed to the size of the probe molecules. This factor increases slightly as the temperature is decreased, which implies that the two measurements of segmental dynamics have slightly different temperature dependences. The rate at which aging proceeds isothermally, quantified by the aging exponent μ, is approximately constant across the studied temperature range for both optical and mechanical measurements, with the value of μ for the optical experiments being slightly higher. Relaxation functions observed in both experiments exhibit a KWW stretching parameter $\beta \approx 0.3$. While these findings utilizing linear mechanical experiments cannot directly establish the relationship between probe reorientation and the dynamics of polymer segments during nonlinear deformation, they are an important step towards this goal.

Experimental Methods

Sample Preparation

PMMA samples were prepared via free radical polymerization. Methyl-methacrylate (MMA, Aldrich, 80-62-6) and the crosslinking agent, ethylene glycol dimethacrylate (EGDMA, Sigma Aldrich, 97-90-5) were purified using an alumina column to remove the inhibitors. EGDMA was added to the MMA at 1.5 wt % and the optical probe, N,N' dipentyl-3,4,9,10-perylenedicarboximide(DPPC, Aldrich, 76372-75-3) was added at a concentration of ~10^{-6} M. The probe molecule (shown in Figure 1a) does not react with the monomer or crosslinker during the polymerization process, and the concentration of the probe is sufficiently small that it does not act as a plasticizer in the polymer film. An initiating agent, benzoyl peroxide (Polysciences Inc., 94-36-0), was added at 0.1 wt %, and the resulting mixture was placed into a heated water bath held at 70°C for ~30 minutes. Polymerization that takes place during this step increases the viscosity of the solution considerably, allowing for easier manipulation of the material in later processing steps, and easier containment in the mold. The partially polymerized sample was then pressed between two double-wide microscope slides separated by aluminum foil spacers. The molds were clamped with large binder clips and placed in a vacuum oven at 70°C. The molds were held at this temperature, under nitrogen, for 24 hours, and then another 24 hours at 120°C to allow the polymerization process to proceed to completion. The resulting films were removed from the molds via sonication. A custom steel die was used to punch "dog-bone" samples from the films conforming to ASTM D1780-10 in shape, though scaled down in size. Film thicknesses ranged between 15-35 microns at the thinnest point. DSC measurements on these films indicate a T_g of 399 ± 1 K, as measured from the midpoint of the transition upon a second heating scan at 10 K/min.

Apparatus

During optical and mechanical experiments, the sample is held at each end by screw-plate clamps. The clamps are lined with 100 grit sandpaper to reduce slippage; in previous work we used 60 grit, but we find that the finer sandpaper better avoids damage to the sample from repeated loadings. The sandpaper is attached to the clamps with a high modulus epoxy suitable for high temperature work (J-B Weld steel-reinforced cold-weld formula). Previous experiments used a cyanoacrylate adhesive that exhibited a small compliance at high temperatures. While this small compliance had a negligible impact on previous experiments that utilized large deformation, it would play a larger role in these experiments where the applied strain is very small.

The sample and clamps are schematically illustrated in Figure 1b. With the exception of the alterations to the clamps described above, full details of the deformation apparatus have been published elsewhere.[5, 45] Briefly, the sample is housed in a temperature-controlled brass cell, in which one clamp is held stationary, while the other is attached to a 5 N load cell to monitor the force applied to the sample. The load cell is connected to an aluminum bar that is controlled by a linear actuator, allowing for uniaxial extension of the sample with control over both the rate and extent of the deformation. The entire deformation apparatus is stationed atop a confocal microscope. The brass cell includes a glass window to allow for optical measurements on the sample during deformation.

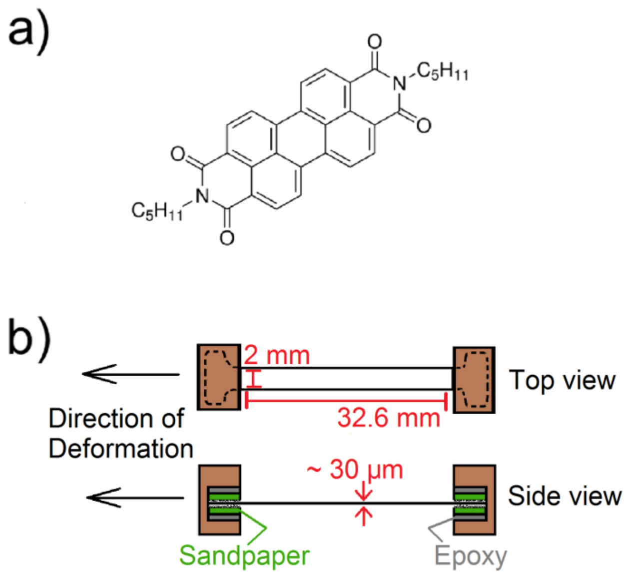

Figure 1. a) Chemical structure of DPPC, the probe molecule utilized in the optical experiments. b) Schematic diagram of PMMA samples and sample clips.

Thermal Protocol

For all stages of all experiments, the sample was housed in the temperature-controlled cell described above, allowing for complete control of the thermal history. Prior to experiments, the sample was brought to 410 K for 70 minutes to erase thermal and mechanical history. The sample was then cooled to the testing temperature at a rate of 1 K / min, and held isothermally for the duration of the experiment. Aging times (t_a) reported in this work reflect the elapsed time from the point during cooling at which the sample reached the calorimetrically determined T_g (399 K). The temperature accuracy of the heated cell is ±1 K, as observed from melting point tests performed within the cell. The temperature stability during the course of the experiment is ±0.2 K.

Mechanical Measurements

Stress relaxation experiments in the linear response regime were performed at four different temperatures. Preliminary stress relaxation measurements with imposed strains ranging between 0.0025 and 0.01 showed no differences in the relaxation time to within 0.1 decades, indicating a linear response. For the experiments reported here, the size of the strain step was selected to be 0.005 to be comfortably within the linear regime. The strain was imposed at a rate of 0.009 s^{-1}, i.e., over the course of about 0.5 s. Times recorded for the stress relaxation measurements reflect the elapsed time from the midpoint of the imposition of the strain.

The mechanical experiments followed a modified Struik protocol in which intervals between loadings increased by a factor of 2 for each loading (i.e. at t_a = 1800 s, 3600 s, 7200 s, etc.), and the duration of each loading was limited to 10% of the aging time at the time of the imposition of strain.[3-4, 54] This arrangement, illustrated in Figure 2, is intended to both hold the amount of aging occurring during each measurement to a negligible level, and to allow sufficient time between measurements such that the effects of one loading do not affect the results of the next.[3]

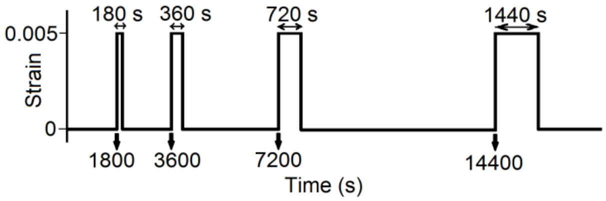

Figure 2. Schematic diagram of the Struik protocol employed for the stress relaxation experiments.

The measured stress relaxation curves were fit using the KWW expression (stretched exponential):

$$\sigma(t) = \sigma_0 e^{-(t/\tau)^{\beta}} \qquad (1)$$

Here σ_0 indicates the value of stress at time t =0 (assuming an instantaneous imposition of strain), τ is the stress relaxation time, and β is a measure of the non-exponentiality of the response. The τ value obtained from this expression is the time required for the stress to decay to $\frac{1}{e}\sigma_0$. While other definitions of the relaxation time can be found in the literature, in this work τ is exclusively used to indicate the time extracted from a KWW function as described above, with equation 1 used for mechanical data, and equation 2 (below) used for optical results. The β parameter is frequently linked to the concept of dynamic heterogeneity, and is typically interpreted to indicate the breadth of the distribution of relaxation times.

Master curves were prepared from the mechanical experiments at each temperature via time-aging time superposition. These master curves were fit to an unconstrained KWW function. The KWW β value resulting from this procedure was used to constrain fits to the individual experimental curves. The choice to constrain β when fitting the individual mechanical curves results in changes in τ of no more than 0.03 decades as compared to the unconstrained fits. This procedure was utilized to provide a common basis for comparison with the optical results discussed below.

Optical Measurements

Full details on the fluorescence recovery technique for measuring probe reorientation have been published elsewhere.[7] Briefly, the polymer sample contains a small concentration (~10^{-6} M) of fluorescent probe molecules (DPPC) which begin the experiment with an isotropic distribution of orientations. The measurement is initiated by the application of a linearly polarized beam that photobleaches a subset of the probes. The probes aligned such that their transition dipoles (located along the long molecular axis) are oriented parallel to the linearly polarized beam have the greatest likelihood to experience photobleaching. Thus, following the bleach, the orientational distribution of probes is anisotropic, with a greater fraction of the remaining probes aligned more closely perpendicular to the beam polarization. A circularly polarized reading beam is employed to induce fluorescence, which is collected and passed through a polarizing beam splitter, allowing for the independent measurements of fluorescence parallel and perpendicular to the orientation of the bleaching beam. The difference between these two measurements can be used to calculate the orientational anisotropy of the probes, R(t). As the measurement proceeds, the probes slowly reorient to recover an isotropic distribution, causing the anisotropy to decrease. The Struik protocol discussed above is not used for the optical experiments. Compared to the stress relaxation curves, the anisotropy decay curves display a larger degree of noise (as can be seen in Figure 3), which leads to larger uncertainties in the fitting parameters. These effects are largely mitigated by collecting more of the anisotropy decay. However, this means that some aging occurs during each optical run. The effects of this were judged to be small and are detailed more extensively in the results section. The cumulative effects of multiple optical measurements are not an issue of concern for these experiments, as each measurement is local (~10 microns), and the measurement locations are well separated from each other. For each set of optical measurements acquired during aging, the sample is held at a very small stress (~0.25 MPa, or ~3% of the stress employed for the linear mechanical measurements). This stress ensures that the sample is held immobile relative to the optical microscope and does not have a measureable effect on the dynamics.

The anisotropy decay function is fit using the same KWW functional form as that employed for the mechanical measurements:

$$R(t) = R_0 e^{-(t/\tau)^{\beta}} \qquad (2)$$

Here R_0 reflects the anisotropy immediately following the bleach. For the optical measurements, β is constrained to 0.31, a value previously obtained from equilibrium measurements on crosslinked PMMA.[46] This constraint leads to τ values with smaller error bars without introducing systematic shifts.

Optical measurements of probe reorientation and mechanical stress relaxation experiments were performed on the same sample, but not simultaneously. Collection of both types of data during the course of a single experiment was found to degrade data quality. The imposition and release of strain during a mechanical measurement frequently resulted in artifacts in optical data due to the sudden motion of the sample. In addition, the simultaneous operation of all data acquisition programs results in a loss of data density. Preliminary results from experiments in which both measurements were performed simultaneously gave results that were in close agreement with the independent experiments presented here. This is expected, as neither the optical measurements, nor the imposed step strains (within the limits of a linear response) have any measureable effect upon the segmental relaxation of the polymer.

Results

Stress Relaxation and Anisotropy Decay Measurements

Stress relaxation curves were collected from mechanical measurements during isothermal aging between T_g - 9 K and T_g - 24 K. Representative results are shown in Figure 3 (upper), with color indicating the aging time at the imposition of the strain step. Stress relaxation was measured following the imposition of a strain of 0.005 (imposed at a strain rate of 0.009 sec^{-1}). Mechanical experiments at a given temperature were designed according to a Struik protocol (Figure 2), such that the interval between impositions of strain increased by a factor of 2 for each measurement, and the strain was maintained for 10% of the aging time at the time of the strain step. Time-aging time superposition was employed for the mechanical curves, as illustrated in Figure 3 (upper). With horizontal and slight vertical shifts, mechanical data collected at a given temperature can be collapsed into a single curve, as shown. The observation that the curves collapse suggests that the distribution of relaxation times does not change significantly during aging. We note that this comparison is made over a relatively limited window of temperatures and aging times. While the superposition is successful for the data that we have collected, good superposition might not be observed over a broader range of experimental conditions.

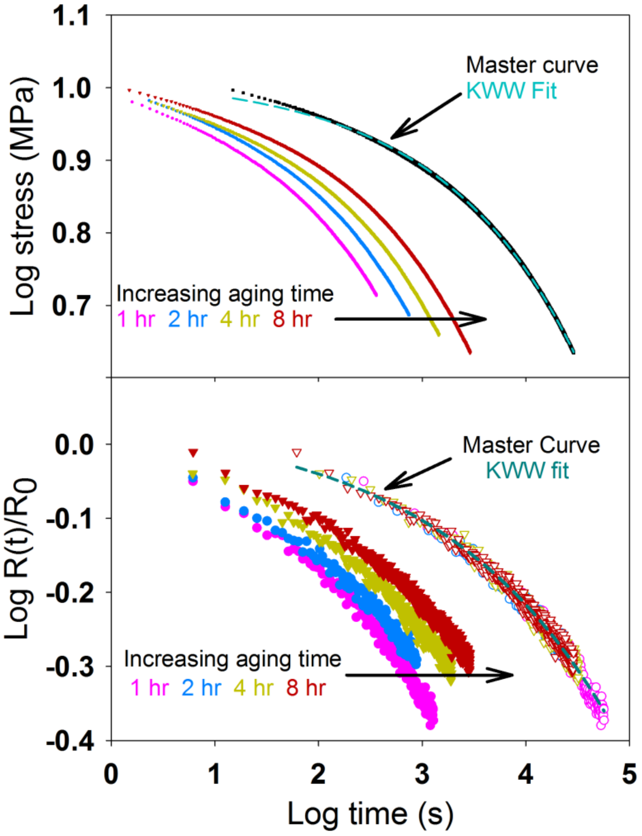

Figure 3. Mechanical stress relaxation experiments (upper panel) and optical anisotropy decay experiments (lower panel) collected during physical aging of PMMA glass at 385 K. Approximate aging

times are indicated by color. Also shown are a time-aging time master curve for each experiment (mechanical - black, optical – open points) and the corresponding KWW curve fit (cyan, dashed). The master curves and fits are offset to the right for clarity.

β values from KWW fits to the stress relaxation measurements can be seen in Figure 4, with aging temperature indicated by color. Arrows at the left of the figure indicate the β value obtained from a KWW fit to the time-aging time superposition master curve created from data at each temperature. An example of this fit is shown as the dashed cyan curve in Figure 3 (upper). In Figure 4, a slight temperature dependence in β is observed, but β remains approximately constant with respect to aging time. Similar results have been observed in previous mechanical experiments.[4, 55] These findings are interpreted as resulting from the limited observation window of the experiments, where relaxation at very short and very long times falls outside the range of the measurement. We have observed that the β parameter from a KWW fit depends sensitively on the data at very short times. There is a delay between the imposition of a perturbation (either mechanical or optical) and the beginning of data collection. This lag, which is typically about a second in the mechanical measurements, and about six seconds in the optical measurements, exerts a significant influence on the variability of β observed in individual runs. This is particularly true at higher temperatures and shorter aging times, where the amount of decay that occurs at early times is most substantial. Because the uncertainty in β leads to a larger uncertainty in the fitted τ values, and because the successful superposition supports the notion of a constant β, we constrain β at each aging temperature to the value obtained by fitting the master curve.

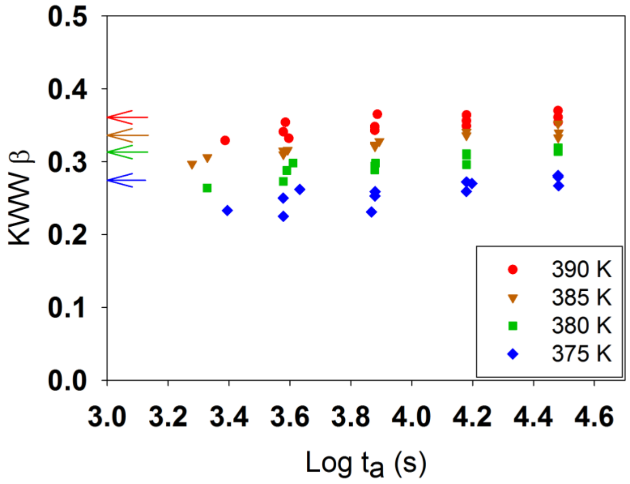

Figure 4. KWW β values obtained from unconstrained fits to individual stress relaxation measurements on PMMA glass, as a function of aging time, at four aging temperatures. Arrows at the left indicate the β value obtained from time-aging time master curves constructed from the data at each temperature.

Typical optical measurements of the anisotropy decay function are shown in Figure 3 (lower). In this plot, color indicates the aging time at the time of photobleaching. As shown, time-aging time superposition of the optical curves is possible and does not require vertical shifts. However, given the level of noise present in the anisotropy data, observations drawn from such a master curve include large uncertainties. Optical measurements were performed continuously throughout a given aging experiment, rather than at set intervals. Limiting the length of each anisotropy decay measurement according to the Struik protocol did not yield enough observed decay for a useful curve fit. The duration of the optical measurements was varied with temperature and aging time to allow for a consistent level of decay for all the optical measurements at a given temperature, reaching as high as 65% of the aging time at the imposition of the photobleach for some measurements.

For the optical experiments, average β values obtained from fits to the anisotropy decay curves at each aging temperature are as follows, where the stated uncertainties indicate one standard deviation: 390 K: 0.271 (± 0.030), 385 K: 0.252 (± 0.017), 380 K: 0.222 (± 0.024), 375 K: 0.237 (± 0.023).

We also determined β values from the master curves such as that shown in Figure 3B; values from 0.24 to 0.27 were obtained, in good agreement with the values described above. With respect to the KWW β values, we note that noise in the anisotropy decay curves leads to larger uncertainty in the determination of the KWW β in comparison to the mechanical data. Additionally, the shift factors determined from the superposition of the optical data are less robust than those from the mechanical curves; different, reasonable superpositions lead to changes of up to 0.03 in the β value from the fit to the master curve. Given the uncertainties in determining the KWW β parameter for the optical data, the agreement between the optical and mechanical values (within 0.1) is quite reasonable. In order to allow for the clearest comparison possible, we have opted to constrain β to a constant value, as we have with the mechanical data, to obtain the most reliable τ values from the anisotropy decay curves. For the optical data, we have selected a value of β=0.31 for all temperatures, which is drawn from previous experiments on the same polymer/probe system in equilibrium,[46] and is based on the assumption that the apparent temperature dependence in β is an artifact of the curve fitting; we return to this point in the Discussion section. The small temperature dependence observed in β is approximately the same for both mechanical and optical data, and a similar dependence has been observed in previous mechanical experiments, as described above.[4, 55]

Time-temperature superposition was performed on both the individual mechanical and optical decay curves presented here as well. The results are not shown, but the collapse of the data in both cases is at least as good as the time-aging time master curves shown in Figure 3. The success of time-temperature superposition for those experiments is interpreted as an indication that temperature has no significant effect on the shape of the distribution of relaxation times. McKenna and co-workers have obtained similar findings in mechanical experiments, and conclude that the assumption of a constant β is reasonable, and does not strongly influence the interpretation of the results.[55]

Comparison of optical and mechanical relaxation times

Figure 5 shows the characteristic relaxation times obtained from KWW fits to the stress relaxation curves (mechanical experiments) and the probe anisotropy decay curves (optical experiments). Solid (dashed) curves indicate linear fits to all mechanical (optical) data collected at a given aging temperature, indicated by color in the figure. Generally speaking, the two experiments show the expected behavior, with dynamics slowing logarithmically with aging time,[3] and with a temperature dependence of ~10 K/decade that is consistent with previous experiments on this polymer system in the linear response regime.[45-46]

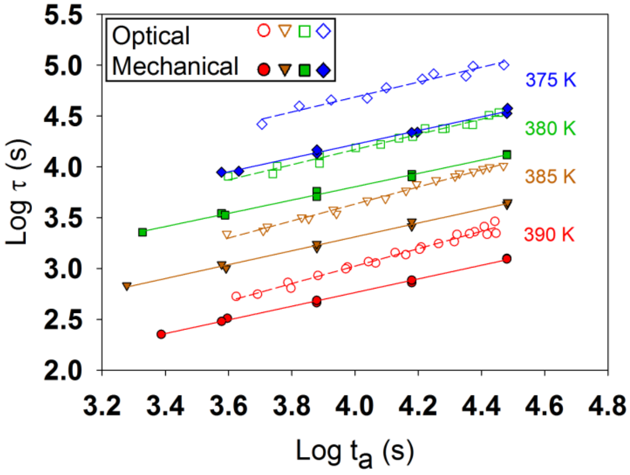

Figure 5. Characteristic relaxation times (τ) for PMMA glass obtained from KWW fits to the anisotropy decay curves characterizing probe reorientation (optical data, open points) and the stress relaxation curves (mechanical data, filled points). Lines indicate linear fits to the data at each aging temperature.

The optical measurements are vertically offset from the mechanical measurements. We ascribe this to the size of the probe molecule and we return to this point in the discussion section. Results shown in Figure 5 display two replicate trials of each experiment at each temperature obtained from a single PMMA sample. A third trial obtained from a different sample showed nearly identical behavior other than a uniform shift of about 0.12 decades towards smaller τ values. This shift is ascribed to differences in the production of the films, leading to a difference in T_g of about 1 K. Data from this third trial is included in Figures 4, 6 and 7, and in the average optical β values indicated in the previous section; it is omitted from Figure 5 for clarity.

Aging Behavior

Aging in polymer materials is typically expressed as the rate of change of an observable (log τ in this case) against the log of the aging time. On a log-log plot, linear curves similar to those shown in Figure 5 are commonly observed over a range of intermediate aging times such as those employed here, giving rise to the term "power law" aging. The aging exponent μ can be expressed as the slope of the line by a definition analogous to that proposed by Struik:[3]

$$\mu \equiv \frac{\Delta \log \tau}{\Delta \log t_a} \qquad (3)$$

The aging exponents observed in these experiments, obtained from the linear fits shown in Figure 5, are presented in Figure 6 with error bars that indicate a 90% confidence interval from 3 replicate measurements. We observe similar trends in μ for optical and mechanical experiments. For both experiments, μ remains approximately constant near 0.7-0.8 and is approximately independent of temperature in the range observed, with the optical values being slightly larger than the mechanical. In the case of the mechanical data, μ was also determined from the time-aging time shift factors used to create the master curves exemplified in Figure 3 (upper). The resulting μ values agree with those obtained from equation 3 to within 0.02.

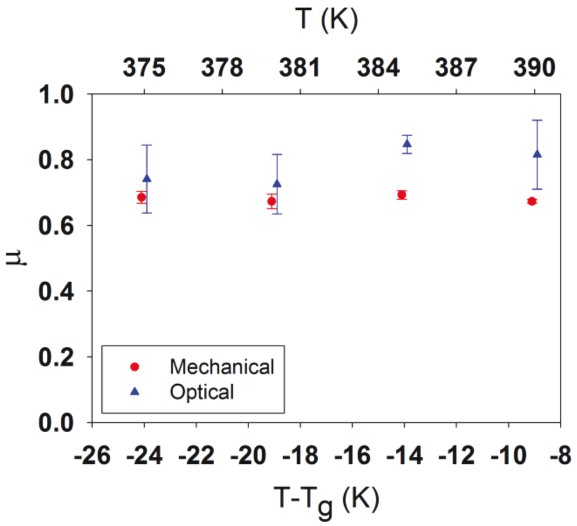

Figure 6. Aging exponents μ for PMMA glasses obtained from fits to dynamics data such as those shown in Figure 5. Error bars indicate a 90% confidence interval determined from 3 replicate measurements.

Aging During Data Acquisition

In contrast to the mechanical measurements, which were limited to an observation window of 10% of the aging time at the imposition of the strain, many of the optical measurements were collected for longer periods of time. The time required to collect an adequate fraction of the anisotropy decay varied, and was up to 65% of the aging time at the time of photobleaching (but only exceeded 50% in three experiments). This allows some aging to take place during the measurement, leading to a slight increase in the observed τ and a slight decrease in the observed β. For both τ and β, these effects are the result of a shift in the relaxation spectrum to longer times as the measurement proceeds. This effect likely accounts, at least partly, for the smaller KWW β values observed in the probe reorientation measurements in comparison to the stress relaxation experiments.

The shifting distribution of relaxation time during aging implies that the reported τ value will be averaged between the slightly faster dynamics at the start of the measurement and the slightly slower dynamics at the endpoint. To a first approximation, we address this issue by shifting the reported measurement time to the midpoint of the measurement range. This adjustment has shifted all the data points shown in Figure 5 to the right by a small amount. In the case of the mechanical data, this has a minimal impact because the Struik protocol makes these shifts uniform in logarithmic time and very small; in Figure 5, the mechanical data points have been uniformly shifted by 0.02 decades. For the optical measurements, the shift is larger and less uniform, with an average shift of 0.08 decades, and shifts at shorter times about 50% larger than the shifts at longer aging times. Because of this last factor, this correction increases the value of μ. If this correction had not been applied, the optical μ values reported in Figure 6 would be lower by ~0.05, and more closely in agreement with the mechanical values. The correction we have employed is approximate, and it is possible that a more detailed analysis may show closer agreement between the optical and mechanical aging exponents. A comparison of data with and without the time shift correction is shown in Figure S1.

Discussion

The results presented above show that probe reorientation times and stress relaxation times in glassy PMMA exhibit quite similar behavior, aside from a slight difference in the aging exponent, and a nearly constant offset in τ. These results provide support for the view that probe reorientation is a useful reporter of polymer segmental dynamics, as we discuss below. Despite the similarities in the reported τ values, the differences are systematic and meaningful. Figure 7 presents another comparison between the two sets of relaxation times. In this figure, the probe reorientation times are presented as a function of the stress relaxation times, with data from all aging times and all temperatures included. On this log-log plot, the strong correlation between the two types of relaxation times (independent of aging time and aging temperature) is evident, again supporting the view that probe reorientation is intimately connected with polymer segmental dynamics. If the mechanical and optical measures of τ agreed exactly, the data in Figure 7 would fall on the solid line of slope 1 provided as a reference. The deviations from this behavior will be discussed below.

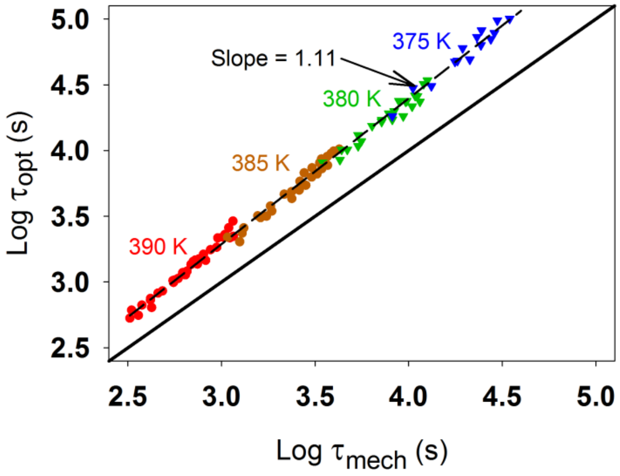

Figure 7. Probe reorientation times vs. stress relaxation times for PMMA glasses, including data for all temperatures and aging times studied. Color represents aging temperature as indicated. The solid line is a reference line representing $\tau_{opt} = \tau_{mech}$. The dashed line is a linear fit through all data. The stress relaxation times needed for the x-axis were obtained by interpolating the linear fits in Figure 5.

Why are the mechanical and optical relaxation times not identical?

Figures 5 and 7 clearly demonstrate that the optical relaxation times are somewhat longer than the mechanical times. This difference increases slightly at lower temperatures, and at longer aging times, ranging from about 0.2 decades in the regime where the dynamics are fastest to about 0.4 decades in the slowest regime. On average, this represents an offset of approximately a factor of 2 between the two measures of τ. This difference is attributed to the size of the probe molecule. Previous work from our lab has shown that larger probes reorient more slowly in a variety of polymer matrices, including the lightly crosslinked PMMA employed here.[13, 46, 50, 56] Kaufman et. al. have observed similar results in experiments performed near T_g in polystyrene.[42] We interpret the longer relaxation obtained with the optical experiment to indicate that the probe is slightly larger than the group of polymer segments that move cooperatively during the segmental relaxation process. To put this factor of 2 in perspective, we note that dielectric and mechanical relaxation times obtained in polymer melts above T_g can vary by up to an order of magnitude.[57]

The observation that DPPC reorientation in PMMA is roughly a factor of two slower than segmental relaxation measured mechanically is consistent with inferences from previous experiments on similar PMMA glasses performed during nonlinear deformation.[58] Bending et. al. performed constant strain rate deformations through yield followed by stress relaxation. The stress relaxation times were compared to optical measurements of DPPC reorientation acquired during deformation. Once the deformation of the sample had proceeded past yield and the acceleration of dynamics had reached steady-state, both optical and mechanical τ values became approximately constant and both measures of τ showed a similar scaling against the strain rate employed during the deformation (see Figure 10 A in ref. 58). In this regime, these optical and mechanical measurements of τ show good agreement other than an offset of a factor of approximately 2, with the probe reorientation being slower as in the results presented here. We are encouraged that our new work and results of reference 58 agree so closely in describing the relationship between optical and mechanical relaxation times, despite the large effect of the deformation on τ in the non-linear experiment.

Why do the mechanical and optical relaxation times have distinct temperature dependences?

Figure 7 indicates that the optical and mechanical relaxation times depend differently upon aging temperature. We observe a slightly stronger temperature dependence for the optical results as compared to the mechanical measurements. The difference persists across the entire window of aging time, but diminishes somewhat as aging proceeds. These effects can be most clearly seen in Figure 5. There are previous reports of different relaxation processes exhibiting different temperature dependences in the glassy state. Thurau et. al. observed this for the translational and rotational diffusion of probe molecules in polystyrene below T_g, and explained the results through spatially heterogeneous dynamics.[59] Simon et al. observed that the time required to reach equilibrium after a jump in temperature can exhibit different temperature dependences for different properties (most prominently volume and enthalpy); they concluded that the effect is likely due to differing degrees of non-linearity in the temperature response.[60] Plazek has reported different temperature dependences for the recoverable compliance and viscosity in the vicinity of the glass transition.[61] This has been explained by separating the viscoelastic relaxation spectrum into two components with distinct temperature dependences, as shown by Inoue et. al.[62] These two components can have apparent activation energies that differ by 25%, a larger effect than that shown in Figure 7. Collectively, these observations from the literature indicate that different probes of polymer motions often exhibit somewhat different temperature dependences near T_g.

Both optical and mechanical relaxation times represent some average of a very broad distribution of relaxation times. The measured β values in this work imply distributions of relaxation times that span three or four orders of magnitude. A relative shift of ~0.2 decades between the two measurements of τ (as seen in Figure 7) is quite small in comparison to the apparent distribution width or to the ~2 decades of relaxation times observed in these experiments. Given this context, Figure 7 supports the view that probe reorientation is an accurate reporter of segmental dynamics in the glassy state.

We have tested the extent to which the use of the KWW function in fitting our data might influence the comparison shown in Figure 7. For one test, we did not use the KWW function at all, instead using shift factors obtained by superposing the optical anisotropy curves and plotting these against shift factors obtained by superposing the stress relaxation curves. This analysis (shown in Figure S2) yields a version of Figure 7 that is noisier but has a very similar slope (1.06), strongly supporting the procedures used to produce Figure 7. We also tested whether the particular value of β (0.31) that we used to constrain the KWW fitting for the optical data had an important influence. In an alternate procedure, we constrained β to be equal to 0.245, the average value observed from unconstrained fits to the optical decays for this analysis. This test (Figure S3) shows a strong correlation between the mechanical and optical relaxation times with a power law slope of 1.32. The strong correlations between the optical and mechanical measurements of the segmental relaxation times seen in Figures 7, S2, and S3 support the view that probe reorientation is an accurate reporter of segmental dynamics in the glass.

Aging Exponents

In polymer materials, the aging exponent μ typically increases from 0 as the temperature is lowered below T_g, and will approach a value of ~1 (so-called "normal aging") within ~30 K below T_g. Typically, μ then levels off before eventually decreasing at low temperatures.[3-4] For uncrosslinked PMMA, available data suggests normal aging between T_g – 38 and T_g - 22.[3] In Figure 6, μ in the range of T_g – 24 K and T_g – 9 K is significantly smaller than that reported in reference 3. One important distinction between our polymer samples and those typically employed in aging experiments is that our samples are lightly crosslinked. Low degrees of crosslinking do not induce substantial changes in segmental dynamics, but can cause differences in deformation behavior, including increased breaking strain, and ductile deformation at temperatures for which the linear material experiences crazing or brittle fracture.[53, 63] The effects of crosslinking on aging behavior is incompletely understood. Previous experimental work has led to a range of results, with some researchers observing reductions in the rate of aging with the introduction of crosslinks,[2, 64] and others observing no obvious changes.[65] To our knowledge, the work most relevant to that presented here was recently published by Torkelson et. al., who compared aging behavior in polystyrene before and after a photoinduced crosslinking process.[66] They showed that crosslinking can reduce the maximum aging exponent, broaden the window of temperatures at which the maximum aging exponent is observed, and (at a high enough density of crosslinking) shift the peak aging temperature to lower values. Our findings are consistent with the idea that the maximum aging exponent is reduced by cross-linking. It is important to note that the level of crosslinking employed for our samples is considerably lower than those employed in the work of Torkleson et al.

Conclusion

In this work we have observed the dynamics of segmental relaxation in lightly crosslinked PMMA both optically, via probe reorientation measurements, and mechanically, through linear stress relaxation measurements. These experiments were performed over a temperature range between T_g - 9 K and T_g – 24 K, and over 8 hours of aging time. There were small systematic differences between the relaxation times obtained for probe reorientation and stress relaxation. An offset of roughly 0.3 decades is observed, which is attributed to the size of the probe. The probe reorientation time also shows a slightly larger temperature dependence than does the stress relaxation time. When considering all the data together (Figure 7), the correlation between the two relaxation times is very strong and supports the view that the reorientation of DPPC in PMMA is an accurate reporter of the segmental dynamics of the polymer.

These experiments will be extended in future work to uncrosslinked PMMA samples to assess the effects of crosslinking on the relationship between probe reorientation and stress relaxation. Another important issue is the potential influence of relaxation processes other than the primary α relaxation on the optical and mechanical measurements of segmental relaxation times. Similar experiments will be performed on polymers other than PMMA to test the generality of the conclusions established here for PMMA.

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Supporting Information

Methodology to account for aging during measurements; alternate analyses of data

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Supplemental material for:

Direct Comparison of Probe Reorientation and Linear Mechanical Measurements of Segmental Dynamics in Glassy Poly(methyl methacrylate)

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Influence of Aging During Optical Measurements on Reported Relaxation Times

During data collection, aging occurs during the acquisition of anisotropy decay curves (see main text). In Figure S1, we demonstrate our scheme to account for these effects. KWW τ values for optical (blue) and mechanical (red) data are shown plotted against the aging time at the time of the perturbation (raw data, open points), and against the aging time at the midpoint of the measurement (adjusted data, solid points). The data shown was collected at 380 K.

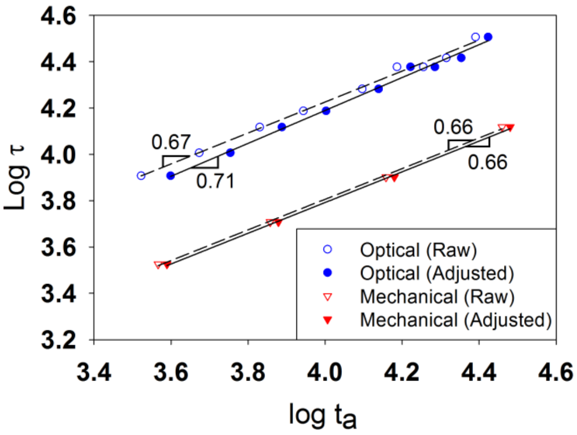

Figure S1. KWW τ values obtained from anisotropy decay measurements (blue) or stress relaxation measurements (red), plotted against the aging time at the onset of the measurement (open points), or the midpoint of the measurement (solid points). Lines represent linear fits through the raw data (dashed lines) or the adjusted data (solid lines). Slopes from the fits are indicated.

Alternate Comparisons of Optical and Mechanical Relaxation Times.

Figure 7, the main result of this work, plots relaxation times obtained from fitting optical and mechanical data to the KWW function, utilizing constrained values for the β parameter. In order to test the robustness of this result, here we present alternate versions of this comparison. Figure S2 is constructed entirely from shift factors obtained without utilizing the KWW function for either the optical or mechanical data. While there is considerable scatter as a result of the noise in the optical data, the data is qualitatively consistent to Figure 7 and has a very similar slope. Figure S3 is constructed in the same way as Figure 7 except that the optical data in Figure 7 was fit to the KWW function with a constrained value of β = 0.31, while the optical data in Figure S3 was fit to the KWW function with a constrained value of β = 0.245. Both Figure 7 and Figure S3 show a strong correlation between the optical and mechanical values of the segmental relaxation time, although the slope in Figure S3 is somewhat higher.

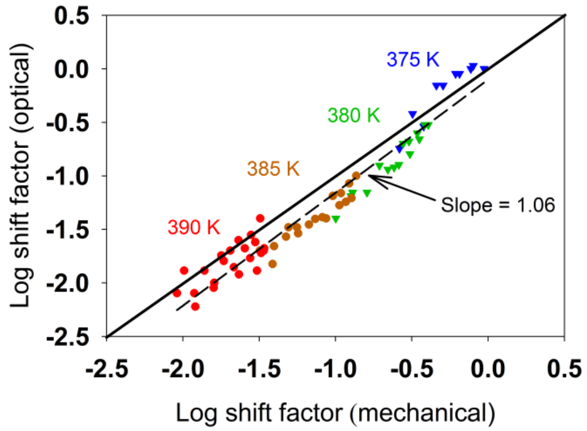

Figure S2. Horizontal shift factors obtained from superposition of anisotropy decay curves plotted against horizontal shift factors from the superposition of stress relaxation curves. The dashed line is a linear fit through all data, with the slope as indicated. The solid line is a reference curve showing the equality of the optical and mechanical shift factors. The mechanical shift factors shown on the x-axis were obtained by interpolating linear fits to the observed shift factors so that the mechanical shift factor was evaluated at the same aging time as the optical shift factor. For this comparison, the longest aging time data at 375 K was used as the reference curve.

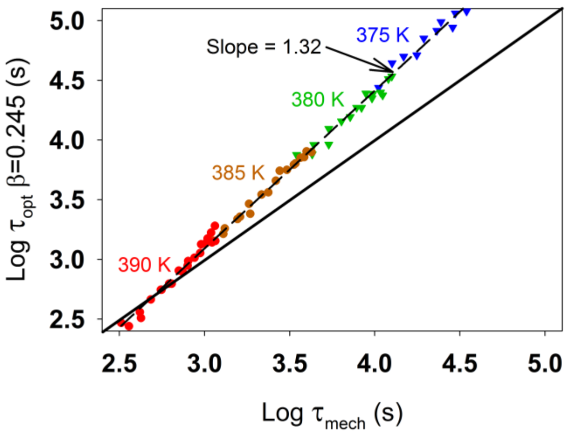

Figure S3. Probe reorientation times plotted against stress relaxation times. Probe reorientation times were obtained from KWW fits to anisotropy decay curves with the β parameter constrained to a value of 0.245, the average value observed across all data in unconstrained fits. The dashed line indicates a linear fit through all data, with the slope as indicated. The solid line is a reference curve indicating $\tau_{opt} = \tau_{mech}$. The times shown on the x-axis were obtained by interpolating linear fits to the stress relaxation data shown in Figure 5 (main text).