

Use of Lateral Force Microscopy to Elucidate Cooperativity and Molecular Mobility in Amorphous Polymers and Self-Assembling Molecular Glasses

D. B. Knorr, Jr., J. P. Killgore, T.O. Gray and R.M. Overney

University of Washington, Seattle, WA, USA, roverney@u.washington.edu

ABSTRACT

Intrinsic friction analysis (IFA), a novel methodology based on lateral force microscopy is presented wherein isothermal kinetic friction measurements, obtained as a function of velocity, are used to deduce apparent Arrhenius-type activation energies (E_{ac}) of molecular mobilities. If cooperativity exists between molecular mobilities involved, the dissipation energy can carry a significant entropic energy contribution, accounting for the majority of E_{ac} depending on the coupling strength between molecular actuators involved. IFA also provides a means of directly separating enthalpic contributions to E_{ac} from entropic contributions by employing a combination of a relaxation model based on absolute rate theory with thermal activation of plastic deformation. As such, the degree of cooperativity in the system can be discerned. This methodology is illustrated with nanoscale tribological experiments on two systems, (1) monodisperse, atactic polystyrene and (2) self assembling molecular glassy chromophores.

Keywords: tribology, mobility, cooperativity, lateral force microscopy.

1 INTRODUCTION

In many nanoscale technologies the ability to obtain information regarding molecular mobility and cooperativity is critical to understanding processes as well as directing molecular engineering to obtain desired results. Many experimental techniques have been developed to provide insight into molecular relaxations such as dielectric spectroscopy[1], dynamic light scattering[2] and multidimensional NMR[3] to name just a few. In a more recent development, Sills et al. showed that, due to nanoscale contact between the tip and the sample in lateral force microscopy[4], insight into molecular dissipation mechanisms can be obtained for molecular systems providing relaxation information analogous to dielectric spectroscopy[5]. However, the ability to distinguish between entropic (cooperative) and enthalpic (non-cooperative) contributions to the resulting apparent Arrhenius activation energy of a molecular process was not achieved. In this work, we develop a methodology that allows access to such information via nanoscale friction experiments and we apply this methodology to a well understood model system (atactic polystyrene) and a system of practical interest (self-assembling glassy chromophores).

2 METHODOLOGY

2.1 Experimental

The experimental setup for IFA is provided below in Fig. 1. As shown, an atomic force microscope (AFM) is used to scan the surface of a sample isothermally at various velocities ($0.1\mu\text{m/s}$ to $10\mu\text{m/s}$). Scan areas were chosen to be $1\mu\text{m}^2$, and the line spacing was set to be 20 nm, which exceeds the contact diameter. The left to right (torsional) photodiode signal is sent to an oscilloscope so that friction loops[6] can be obtained. Experiments were conducted using a Topometrix Explorer AFM using Nanosensor PPP-CONT uncoated cantilevers ($C_N \sim 0.2\text{N/m}$). Cantilevers were calibrated on a silicon surface with the native oxide layer present as described in the literature[7]. Subsequently, the tips were scanned on the sample material at temperatures above the glass transition temperature of the material for approximately 1 hour. According to our experience, this process passivates the tip and produces better friction signals.

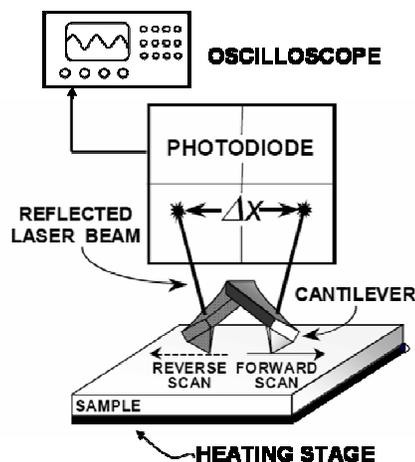


Figure 1: Experimental set-up for IFA.

Samples themselves were prepared as follows. Polystyrene samples were prepared by spin casting a 0.28wt% solution of 56k MW polystyrene in toluene onto a silicon surface, where the native oxide had been removed by HF treatment. Self assembling glassy chromophores were spin-cast onto indium tin oxide (ITO) coated glass substrates from a filtered 5% chromophore solution dissolved in 1,1,2-trichloroethane. Film thicknesses were

on the order of 300nm, which is sufficiently thick to avoid confinement effects.

2.2 Data Analysis

Data obtained are friction force as a function of scanning velocity at various isothermal temperatures ($F_F(v)|_T$). As such, these data can be analyzed in a manner similar to that used for dielectric spectroscopy measurements. Friction isotherms are first plotted as a function of $\ln(v)$ and then, employing the time-temperature superposition principle[8, 9], are shifted horizontally to form a master response curve, with each temperature having a unique shift factor a_T . An apparent Arrhenius activation energy, E_{ac} , is available by plotting $\ln(a_T)$ vs. $1/T$ according to the following equation:

$$\ln(a_T) = \frac{E_{ac}}{R} \left(\frac{1}{T} - \frac{1}{T_R} \right) \quad (1)$$

As will be discussed below, in some cases vertical shifting is actually necessary in some cases for certain temperatures, thereby introducing a vertical shifting term, $\Delta F_F(T)$. Justification for this, as well as substantial insight into the processes involved in the system can be obtained by comparing Starkweather's understanding of relaxation phenomena in organic systems[10, 11] with Briscoe and Evan's model for activated shear processes[12].

Starkweather employs absolute reaction rate theory to develop the following expression for an apparent Arrhenius activation energy in terms of the relaxation temperature T_R , the peak frequency (f_R), and the activation entropy of the relaxation ΔS^* as[10, 11]:

$$E_{ac} = kT \left[1 + \ln \left(\frac{kT}{2\pi\hbar f} \right) \right] + T\Delta S^* \quad (2)$$

Starkweather also noted that for polymer systems where relaxations were isolated phenomena (e.g., side chain rotation) $\Delta S^*=0$. These relaxations he dubbed "non-cooperative."

Briscoe and Evans[12] developed an activation model for shear processes with apparent activation energy E'_{ac} that involves a slider exerting pressure P over a pressure activation volume, Ω , resulting in shear stress τ acting over stress activation volume, ϕ , being resisted by potential barrier of height Q' .

$$E'_{ac} = Q' + P\Omega - \tau\phi \quad (3)$$

By equating E'_{ac} and E_{ac} , setting $\tau = (F_F + \Delta F_F)/A$, where A is the true contact area, introducing a term $\phi' = \phi/A$, called the apparent stress activation length[13], and employing thermodynamic identities[12] one may show that:

$$\Delta F_F = -\frac{kT}{\phi'} \left[1 + \ln \left(\frac{kTv}{2\pi\hbar v_o} \right) \right] - \frac{T\Delta S^*}{\phi'} \quad (4)$$

where v_o is a characteristic velocity of the system. The key point in this discussion is that equation (4) establishes a clear connection between vertical shifting of $F_F(v)$ data and the cooperativity of the system. As such, cooperativity in the system is indicated by the need for vertical shifting to form the master response curve. We now turn our attention to the first system of interest, a well understood amorphous polymer, atactic polystyrene.

3 POLYSTYRENE

Friction measurements on polystyrene following the IFA method are provided in Fig. 2. As shown, initial raw data over the temperature range 37°C to 123°C (Fig. 2 inset) can be shifted using the procedure described in Section 2 to provide a master curve containing the peak of the α -relaxation (low values of $\ln(a_T^*v)$) and the shoulder of the β -relaxation (high values of $\ln(a_T^*v)$).

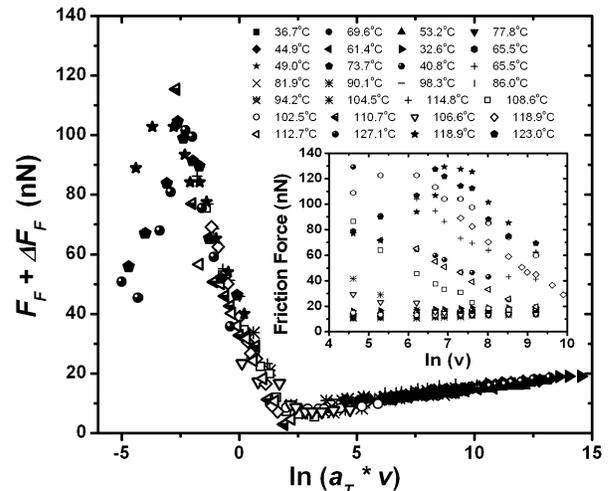


Figure 2: Master curve established for polystyrene from IFA data. (Inset) Raw friction data before horizontal and vertical shifting.

Figure 3 provides plots of $\ln(a_T)$ as a function of $1/T$ (inset) as well as a plot of vertical shifting (ΔF_F) as a function of temperature. Apparent Arrhenius activation energies obtained are 22 kcal/mol and 90 kcal/mol for regions below and above the glass transition temperature, respectively. These values are in reasonable agreement with literature values for the β -relaxation (17.4 kcal/mol [14], 21.5kcal/mol [15] and 24 kcal/mol [16]) and the α -relaxation (80-90kcal/mol[17]), respectively. To determine the degree of cooperativity ($T\Delta S^*$) with Eq. (2), a peak frequency, f , is required, which can be obtained for the α -

relaxation from measured peak velocities (Fig. 2) and dissipation lengths, ξ , available from the literature for polystyrene as $f = v/\xi$ [5]. Using this process for data above T_g (α -relaxation) reveals an entropic contribution of ~ 70 kcal/mol to E_{ac} . The entropic contribution was determined from $V_R = 0.8 \mu\text{m/s}$ at $T_R = T_\alpha = 396.2$ K with the previously determined [5] dissipation length of 0.4 nm. Such a large ($\sim 80\%$) energy contribution is expected for the highly cooperative process of the α -relaxation in polymeric glass formers.[18].

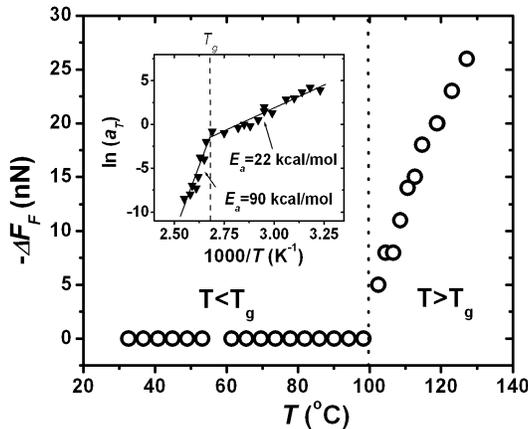


Figure 3: Vertical shifting ($-\Delta F_F$) necessary to produce master curve. (Inset) Plot of $\ln(a_T)$ as a function of $1/T$ resulting in apparent Arrhenius activation energies of 22kcal/mol below T_g and 90 kcal/mol above T_g .

4 SELF ASSEMBLING GLASSY CHROMOPHORES

Having established that the methodology is successful for determining extent of cooperativity in a well understood model system we now turn to a more interesting system of practical interest. For self assembling glassy chromophores which show optical non-linearity [19], the challenge is to acentrically align the chromophores while preventing undesirable aggregation due to dipole-dipole interactions. One such strategy is to add dendrons to the chromophores that are capable of self assembly by face to face phenyl-perfluorophenyl interactions due to complementary quadrupolar moments. Such interactions provide 4-7kcal/mol[20-22] of additional stability to the system per interaction and allow the molecules to create physically linked chains, with each molecule acting as a link in that chain. One such system, dubbed HDFD (Fig. 4 inset), has been shown to have two transition temperatures, at $T_1=59^\circ\text{C}$ and $T_2=70^\circ\text{C}$ [19].

Understanding the dynamics of such systems is critical to designing molecules with improved electro-optical activity (EO activity). As such, the degree of

intermolecular cooperativity ($T\Delta S^*$) was deduced using the above methodology (Fig. 4). For temperatures below T_1 , no cooperative motion was expected due to the fact that $\Delta F_F=0$; however, between T_1 and T_2 , vertical shifting was required as well as for $T>T_2$ (Fig. 4 inset). In this case no dissipation length data was available, so a reasonable range was assumed (0.1-20 nm, Fig. 4) and it was found that the entropic contribution to the apparent Arrhenius activation energy was ~ 0 for $T<T_1$, but increased to be the majority contribution for $T_1<T<T_2$ and $T_2<T$ (Table 1).

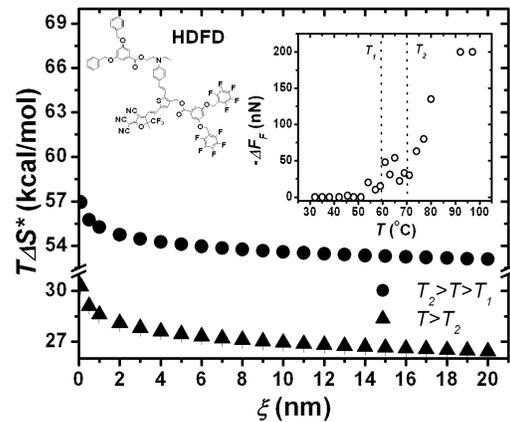


Figure 4: Plot of $T\Delta S^*$ as a function of dissipation length. (Right Inset) Vertical shifting required to generate master curve. (Left Inset) Depiction of HDFD.

The molecular dynamics of the system can be understood as follows. Below T_1 there is only isolated motion of HDFD molecules, as they associate and dissociate with each other locally. Above T_1 there is enough mobility in the system that groups of linked molecules can act cooperatively in rotation or translation. Above T_2 , the system exhibits a high degree of cooperativity, although the linkages between molecules have broken down. This is similar to a polymer melt close to the glass transition temperature.[18]

	$T < T_1$	$T_1 < T < T_2$	$T_2 < T$
E_{ac} (kcal/mol)	23	44	71
$T\Delta S^*$ (kcal/mol)	-	26-30	52-56
% entropic	$\sim 0\%$	59-68%	73-79%

Table 1. E_{ac} and $T\Delta S^*$ contributions for HDFD.

5 CONCLUSIONS

As shown in the examples of polystyrene and self-assembling glassy chromophore HDFD, the intrinsic friction analysis technique provides substantial insight into molecular relaxations in a system. Apart from determination of an apparent Arrhenius activation energy,

this technique is capable of providing information relating to the cooperativity, with the presence and extent of vertical shifting necessary to develop a master response curve. This technique promises to provide substantial insight for other organic systems in the future.

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