Electronic Supplementary Material (ESI) for Soft Matter.

Polarizability Responses of a Glass-forming Liquid Reveal Inherent Structure Motion and Interbasin Transitions

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Deconvolution Procedure

We deconvolute the OHD-OKE signal with the usual procedure developed by McMorrow and Lotshaw.[1,2] The OHD-OKE signal, $S(t')$, is proportional to the convolution of the instrument response function (IRF), $G(t)$, and the third-order nonlinear optical response, $R^{(3)}(t)$, of the interrogated system:

$$S(t') \propto \int_{-\infty}^{\infty} \mathrm{d}t G(t) R^{(3)}(t - t'), \tag{S1}$$

where t' is the delay between the probe and pump pulses. According to Eq S1, the Fourier transform of the OHD-OKE signal is the product of the transforms of the IRF and the third order response. Thus,

$$\int_{-\infty}^{\infty} \mathrm{d}t R^{(3)}(t - t') e^{i\omega t} = \frac{\int_{-\infty}^{\infty} \mathrm{d}t S(t') e^{i\omega t}}{\int_{-\infty}^{\infty} \mathrm{d}t G(t) e^{i\omega t}} = D(\omega), \tag{S2}$$

where ω is the angular frequency of the transform. By backtransforming $D(\omega)$, $R^{(3)}(t)$ is retrieved with the effects of the IRF removed. From Eq S2, it is clear that the IRF must be known accurately to retrieve the correct nonlinear response.

Within the Born-Oppenheimer approximation, $R^{(3)}(t)$ comprises the instantaneous electronic response, $\gamma(t)$, and the noninstantaneous nuclear response, $R_{nuc}(t)$,

$$R^{(3)}(t) = \gamma(t) + R_{nuc}(t). \tag{S3}$$

For optically transparent materials, $R_{nuc}(t)$ is an odd function and $\gamma(t)$ is an even function in time. Thus,

$$ImD(\omega) = \int_0^\infty \mathrm{d}t R_{nuc}(t)\sin(\omega t), \tag{S4}$$

and

$$ReD(\omega) = \int_0^\infty \mathrm{d}t \gamma(t)\cos(\omega t). \tag{S5}$$

Therefore, $R_{nuc}(t)$ may be isolated from the OHD-OKE signal by backtransforming the imaginary component of the deconvoluted signal and considering causality:

$$R_{nuc}(t) = \frac{1}{\pi}\left[\int_{-\infty}^{\infty} \mathrm{d}\omega ImD(\omega)e^{-i\omega t}\right]\theta(t), \tag{S6}$$

where $\theta(t)$ is the Heavyside step function.

In practice, $S(t')$ must be shifted in time to find the correct overlap between it and the measured IRF to arrive at the correct nonlinear response. To find this overlap, we adjust the time of the OHD-OKE signal in the frequency domain by adjusting the phase of the transformed and deconvoluted spectrum until the high frequency components of the resultant spectral density that lie within the bandwidth of the excitation pulse smoothly decay to zero intensity. This adjustment usually amounts to no more than a 10 fs shift in time. Figure S1 gives an example of the effects of the time adjustment. The red line shows the deconvoluted spectrum after the correct overlap between $S(t')$ and $G(t)$ has been found.

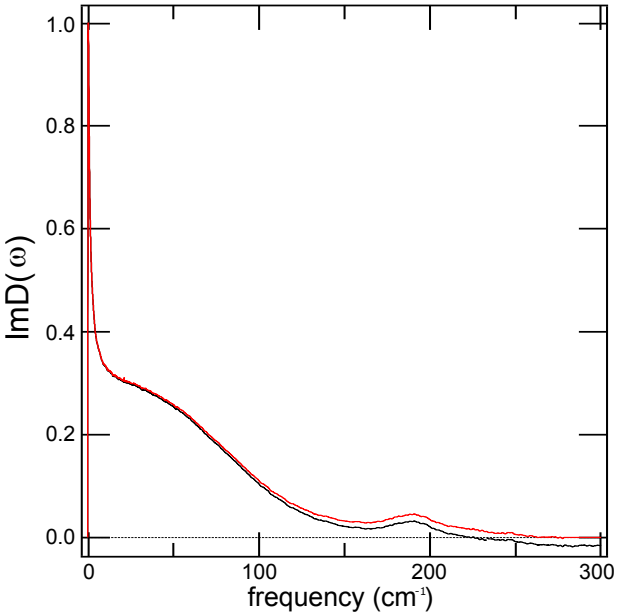

Figure S1: Example of the $ImD(\omega)$ before (black line) and after (red line) the time was adjusted to find the correct overlap with $G(t)$.

Diffusive Response Fits

The fit parameters for the diffusive relaxation in PC. The diffusive relaxation response was below the noise floor for data taken at 130 K and 150 K.

Table S1: Amplitudes (A_d), Time Constants (τ_d), and Stretching Constants (β_{KWW}) from Fits to the Diffusive Response Function[1]

$T(K)$	A_d	τ_d (ps)	β_{KWW}
170	0.03(±0.3)	$8.7(\pm 121.1) \times 10^3$	0.58(±0.02)
185	0.1(±0.3)	$2.5(\pm 10.8) \times 10^3$	0.61(±0.03)
210	0.35(±0.07)	$1.2(\pm 0.4) \times 10^3$	0.65(±0.007)
230	0.537(±0.003)	151(±1)	0.737(±0.002)
240	0.702(±0.005)	87.3(±0.9)	0.751(±0.003)
265	0.907(±0.008)	34.1(±0.3)	0.823(±0.007)
295	0.926(±0.002)	14.60(±0.04)	0.911(±0.001)
310	0.893(±0.006)	10.07(±0.05)	0.931(±0.004)
320	0.86(±0.01)	8.4(±0.1)	0.92(±0.01)
335	0.75(±0.02)	6.7(±0.1)	0.97(±0.01)

[1] Numbers in parentheses are errors at one standard deviation estimated from the fits.

Intramolecular Vibrational Response Fits

The fit parameters for the intramolecular mode at $\sim$190cm^{-1}, which corresponds to an out-of-plane ring deformation for PC.

Table S2: Amplitudes (A_v), Damping Coefficients (g), Vibrational Frequency (ω_v), and Phase (ϕ) from Fits to the Intramolecular Vibrational Response[1]

$T(K)$	$A_v \times 10^3$	$g\ (ps^{-1})$	$\omega_v\ (ps^{-1})$	ϕ
130	3.7($\pm$0.2)	2.7($\pm$0.2)	5.99($\pm$0.03)	20.37($\pm$0.04)
150	2.36($\pm$0.05)	2.03($\pm$0.05)	5.971($\pm$0.007)	20.47($\pm$0.02)
170	2.97($\pm$0.04)	2.62($\pm$0.04)	5.939($\pm$0.006)	20.52($\pm$0.01)
185	4.0($\pm$0.05)	3.31($\pm$0.05)	5.910($\pm$0.007)	20.432($\pm$0.009)
210	2.7($\pm$0.08)	2.4($\pm$0.1)	5.90($\pm$0.03)	20.42($\pm$0.04)
230	2.9($\pm$0.07)	2.74($\pm$0.08)	5.87($\pm$0.01)	20.61($\pm$0.02)
240	3.2($\pm$0.09)	3.3($\pm$0.1)	5.89($\pm$0.01)	20.61($\pm$0.02)
265	2.7($\pm$0.07)	2.93($\pm$0.09)	5.80($\pm$0.01)	20.66($\pm$0.02)
295	3.9($\pm$0.05)	3.98($\pm$0.05)	5.744($\pm$0.006)	20.532($\pm$0.006)
310	2.6($\pm$0.03)	3.25($\pm$0.04)	5.701($\pm$0.005)	20.554($\pm$0.007)
320	3.1($\pm$0.04)	3.58($\pm$0.04)	5.666($\pm$0.005)	20.556($\pm$0.007)
335	2.46($\pm$0.03)	2.94($\pm$0.05)	5.627($\pm$0.006)	20.508($\pm$0.009)

[1] Numbers in parentheses are errors at one standard deviation estimated from the fits.

Librational Response Fits

The fit parameters for the librational response in PC.

Table S3: Amplitudes (A_l), Dephasing Constants (τ_l), Spectral Frequency (ω_l), Spectral Width (σ), and First Moment ($\langle\tau\rangle$) from Fits to the Librational Response Function[1]

$T(K)$	A_l	τ_l (ps)	ω_l (ps^{-1})	σ (ps^{-1})	$\langle\tau\rangle$ (ps)
130	0.16(±0.01)	0.258(±0.006)	2.18(±0.02)	0.91(±0.02)	0.13(±0.02)
150	0.184(±0.005)	0.373(±0.03)	2.20(±0.03)	0.99(±0.02)	0.17(±0.03)
170	0.193(±0.005)	0.418(±0.002)	2.19(±0.02)	1.04(±0.01)	0.19(±0.03)
185	0.1974(±0.0009)	0.465(±0.003)	2.18(±0.02)	1.04(±0.02)	0.20(±0.03)
210	0.209(±0.003)	0.56(±0.02)	2.17(±0.03)	1.08(±0.04)	0.23(±0.04)
230	0.203(±0.002)	0.465(±0.007)	2.11(±0.03)	1.12(±0.02)	0.22(±0.03)
240	0.198(±0.002)	0.430(±0.006)	2.08(±0.03)	1.09(±0.02)	0.21(±0.03)
265	0.212(±0.002)	0.503(±0.007)	2.01(±0.03)	1.12(±0.02)	0.23(±0.07)
295	0.212(±0.002)	0.634(±0.006)	1.98(±0.02)	1.20(±0.01)	0.28(±0.05)
310	0.213(±0.001)	0.455(±0.003)	1.87(±0.04)	1.22(±0.02)	0.24(±0.06)
320	0.215(±0.002)	0.481(±0.007)	1.89(±0.02)	1.21(±0.03)	0.24(±0.06)
335	0.241(±0.002)	0.600(±0.004)	1.77(±0.02)	1.28(±0.02)	0.28(±0.06)

[1] Numbers in parentheses are errors at one standard deviation estimated from the fits.

Intermediate Response Fits

The fit parameters for the intermediate response in PC.

Table S4: Amplitudes (A_c), and Time Constants (τ_c) from Fits to the Intermediate Response Function[1]

$T(K)$	A_c	τ_c (ps)
150	0.014(±0.006)	4.8(±0.3)
170	0.038(±0.006)	3.02(±0.04)
185	0.052(±0.005)	2.17(±0.04)
210	0.056(±0.006)	1.8(±0.6)
230	0.076(±0.005)	1.68(±0.07)
240	0.085(±0.007)	1.53(±0.07)
265	0.095(±0.007)	1.59(±0.05)
295	0.119(±0.006)	1.91(±0.05)
310	0.136(±0.004)	1.4(±0.1)
320	0.14(±0.01)	1.50(±0.05)
335	0.169(±0.008)	1.79(±0.03)

[1] Numbers in parentheses are errors at one standard deviation estimated from the fits.

Full Fit to Model

An example of the data fit to the full model described in the text and the previous section of this supplement.

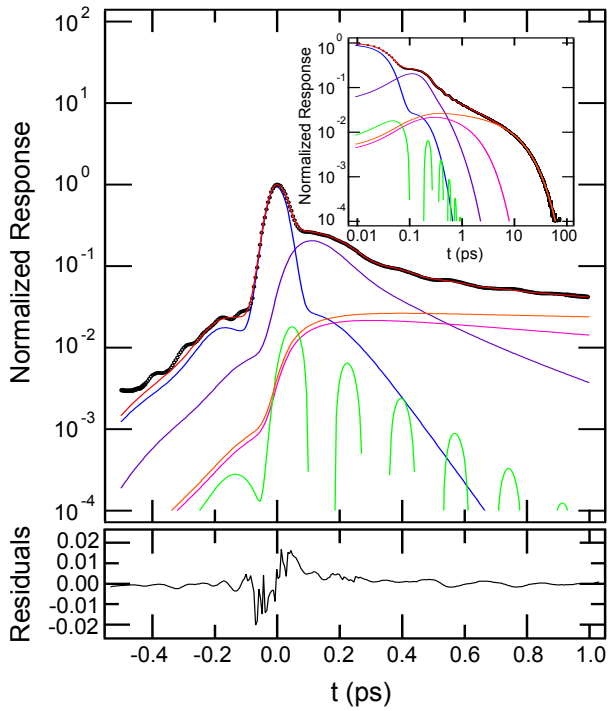

Figure S2: (Top panel) Example of raw data (open black circles) with the full fit (red line) and the constituent electronic (blue line), librational (purple line), intermediate (magenta line), vibrational (green line), and diffusive responses for PC at 310 K. The inset is the same plot on a full scale logarithmic plot. (Bottom panel) Residuals of the fit.

Comparison of Several Stretching Parameters

Several stretching parameters taken from dielectric relaxation and light scattering experiments for PC.

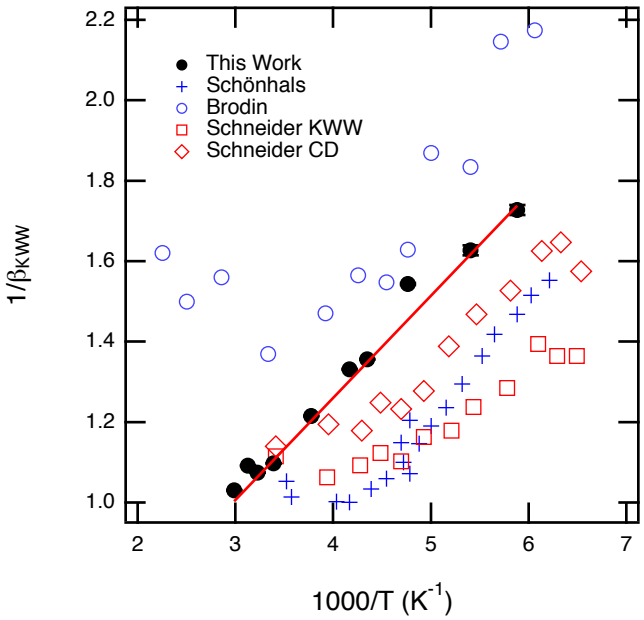

Figure S3: Temperature-dependent evolution of the stretching parameter taken from several studies of PC.[3–5]

References

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(5) Brodin, A.; Rössler, E. A. Universal and Non-universal Features of the Dynamic Susceptibility of Supercooled Liquids. *J. Phys.: Condens. Matter* **2006**, *18*, 8481–8492.