Single Chain Dynamic Structure Factor of Linear Polymers in an All-Polymer Nano-Composite

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Estimation of Characteristic Times for Hydrogen Self-Motions and Collective Dynamics of the Nano-Composite Components at 435K

We estimate the incoherent and collective characteristic times for the two components in the nano-composite at the temperature investigated by NSE (435 K) as function of momentum transfer. We start with the slow (PMMA-based) component. From Dielectric measurements, the segmental relaxation of bulk PMMA is described in terms of the Vogel-Fulcher (VF) function

$$\tau_{seg}(T) = \tau_{\infty} e^{\frac{B}{T - T_0}} \tag{1}$$

with $\tau_{\infty}^{bulkPMMA} = 1.48 \times 10^{-11}$ s, $B^{bulkPMMA} = 843$ K and $T_0^{bulkPMMA} = 371$ K.¹ The effective glass transition temperature of SCNPs in the nano-composite is deduced as 293 K resulting ~107 K lower than that of bulk PMMA. Assuming this shift in the Vogel temperature and the same values for the pre-factor τ_{∞} and B in the VF expression, the $\tau_{seg}(T)$ values for SCNPs in the nano-composite can be estimated. For T = 435 K, $\tau_{seg}^{SCNP/NC} \approx 2$ ns. It is usually found that the relaxation time determined from dielectric spectroscopy coincides with the characteristic time obtained from neutron scattering for the incoherent scattering function of hydrogen motions $\tau_{self}^{H}(Q,T)$ at the value $Q \approx 1$ Å⁻¹.^{2,3} The Q-dependence of τ_{self}^{H} for PMMA has been reported to follow well the prediction of the anomalous jump diffusion model,^{4,5}

$$\tau_{self}(Q,T) = \tau_0 \left[1 + \frac{1}{Q^2 \ell^2} \right]^{1/\beta}$$
(2)

which extends the case of an underlying distribution of jumps in the diffusion process to systems where anomalous diffusion leads to a sublinear increase of the mean squared displacement at long times as $\langle r^2 \rangle \propto t^\beta$. For PMMA, it has been reported $^6\beta \approx 0.5$ and a value of $\ell \approx 0.6$ Å for the most probable jump distance. Thus, considering these values for β and ℓ also for the SCNPs in the nano-composite and imposing that $\tau^H_{self}(Q = 1\text{\AA}^{-1}) = 2 ns$ in Eq. 2, we have obtained the estimated function τ^H_{self} for SCNPs in the nano-composite plotted in Fig. 1 as solid blue line.



Figure 1: Momentum transfer dependence of the characteristic times estimated for the two components in the nano-composite at the temperature investigated by NSE, T = 435 K. Solid lines: self-correlation times for hydrogen atoms; dashed-dotted lines: collective times. PEO-component data are represented in red; PMMA-component data are shown in blue. The structure factors obtained from MD-simulations^{7,8} are also shown (dotted lines). Their $Q \rightarrow 0$ limit has been assumed to be 0.25 in both cases. Shadowed area marks the Q-range explored in the NSE experiments.

Now we estimate the characteristic time for collective motion, $\tau_c(Q)$. An ansatz has recently been proposed to predict this time in polymeric systems in the neighborhood of the structure factor peak and in the intermediate length scales regime.⁹ It consists of an interpolation formula that embeds the mesoscopic (non-diffusive) and the high-Q (diffusive) limits of the collective times in an analytical expression as proposed by Novikov et al.:¹⁰

$$\frac{1}{\tau_c(Q)} = \frac{1}{\tau_c(Q \to 0)} e^{-Q^2 \xi_c^2} + \frac{1}{\tau_c^D(Q)}.$$
(3)

The first term of this expression contains the inverse of a non-diffusive (Q-independent) relaxation time $\tau_c(Q \to 0)$. For the case of polyisobutylene, where this ansatz has proved to be satisfactory, it has been found that $\tau_c(Q \to 0) \approx \tau_{self}^H(Q = 1\text{\AA}^{-1})$.¹¹ The contribution of this first term to the total collective time is affected by a Gaussian cutoff factor $e^{-Q^2\xi_c^2}$ to ensure that it is present only on length scales beyond a characteristic length ξ_c , which is assumed to be $\xi_c \sim 2\pi/Q_{max}$. Here, Q_{max} is the location of the peak corresponding to the inter-molecular correlations in the static structure factor S(Q). For sublinear diffusion, the diffusive time $\tau_c^D(Q)$ was proposed to be given by $\tau_c^D(Q) = \tau_{self}(Q)S(Q)^{1/\beta}$. Assuming that $\tau_{self}(Q) \approx \tau_{self}^H(Q)$ (above obtained) and using the S(Q) obtained from MD-simulations for PMMA⁸ we have deduced the collective times shown as the dashed-dotted line in Fig. 1, which we expect to be an approximation for the collective times of SCNPs in the nano-composite.

Moving now to the PEO component in the nano-composite, its hydrogen dynamics was studied by some of us in a previous work.¹² A sample where protonated PEO chains were mixed with deuterated SCNPs was investigated by backscattering and time-of-flight techniques, addressing the incoherent scattering function of PEO hydrogens in the temperature range 350 K $\leq T \leq 400$ K and Q-range $0.5 \leq Q \leq 1.8$ Å⁻¹. For T = 400 K, τ_{self}^{H} in this system could be described by Eq. 2 with $\tau_0 = 0.127$ ps, $\ell = 0.41$ Å and $\beta = 0.5$. Assuming the T-dependence deduced for PEO dynamics in the nano-composite (see manuscript), the expectation for the characteristic times for hydrogen self-motions shown as a blue continuous line in Fig. 1 is obtained. Now, applying the same ansatz with similar approximations as above described to obtain the collective times and taking for the structure factor the results reported from MD-simulations for bulk PEO,⁷ we arrive to the red dashed-dotted line in Fig. 1 for the PEO component in the nano-composite.

We note that along these calculations we have treated the nano-composite as a bulk sample. To our knowledge, there is no up to date any theoretical or even phenomenological approach to predict or describe the situation in all-polymer nano-composites. Within these hypotheses, we can thus state that we expect that the dynamics of both nano-composite components –regardless of the particular correlation function followed– maintain a high asymmetry even in the high temperature range explored by NSE. This is estimated to be about two orders of magnitude for self motions and could be even larger for collective dynamics.

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