

Arbe *et al.* Reply: The preceding Comment by Heuer and Spiess [1] questions the analysis of neutron scattering experiments on the α relaxation of the four glass-forming polymers (PI, PB, PIB, and PVE) given in [2]. Especially the conclusion that the α relaxation has been found to be homogeneous provoked the criticism. First some of the more technical points addressed shall be clarified.

(i) “The observed approximate $\tau_w \propto Q^{-4}$ behavior is simple Rouse dynamics.”—Neutron spin-echo (NSE) experiments show that the Rouse theory is valid only in the low Q small angle neutron scattering (SANS) regime (see Fig. 1). It is clear that in the Q range used for the analysis of the α relaxation the Rouse theory is not applicable. Moreover, Q dependencies of τ_w close to $Q^{-2/\beta}$ ($\beta \cong 0.5$ being the stretching parameter) for Q values up to $2 \text{ \AA}^{-1}$ have been reported for other polymers [3] and also for low molecular weight glass-forming systems as orthoterphenyl and glycerol [4] where the Rouse dynamics cannot be invoked.

(ii) “The heterogeneous contributions of the α relaxation are mainly visible close to the first maximum of $S(Q)$.”—Since our experiments detect the *incoherent* neutron scattering we observe single particle (proton) dynamics which is not expected to relate directly to structures in $S_{\text{coherent}}(Q)$.

(iii) “The validity of the Gaussian approximation.”—As the Guinier approximation in SANS the Gaussian approximation holds necessarily for shorter times since any distribution of finite extension [probability cloud $w(r, t)$ that evolved from a pointlike distribution at $t = 0$ by some diffusive process] has a finite “radius of gyration,” R_g . As long as $QR_g \leq 1$ the corresponding $S(Q, t)$ may be approximated by a Gaussian irrespective of details of $w(r, t)$.

The main objection issued in the Comment seems to be motivated by the application of a peculiar definition of what is called *homogeneous* or *heterogeneous* which

is coined in Ref. [5]. There, any process is called heterogeneous which has some kind of rate fluctuation with temporal memory. Observed over a time interval longer than the typical rate fluctuation times this leads to non-exponential behavior like the observed stretched exponential decays. Whereas in earlier publications Spiess *et al.* find a separation of 2 orders of magnitude of the slow (α -relaxation) rate, κ_s , and the fluctuation rate, Γ , in PVAc using a 4-dimensional NMR technique [6], more recent publications from this group report a separation of much less than 1 order of magnitude, i.e., $\kappa_s/\Gamma = 1, \dots, 2$ [7]. Whereas the former separation of time scales would lead to a heterogeneous finding—according to our definition and analysis—also in terms of the incoherent neutron scattering spectra, the later found rate ratio is perfectly consistent with the image of a sublinear diffusion process composed of many rapidly changing small steps. Following [5], we might call it heterogeneous. However, the result we obtained is the following: within the time scale of the experiment (a few ns) each individual scattering center (a proton located in a polymer segment) undergoes the same (= homogeneous) sublinear diffusion process. We exclude the presence of scattering centers that behave differently for longer than a few tenths of a nanosecond. This has been called homogeneous by us. The main objection issued in the Comment obviously stems from differences in the semantics of the notions heterogeneous/homogeneous in this context.

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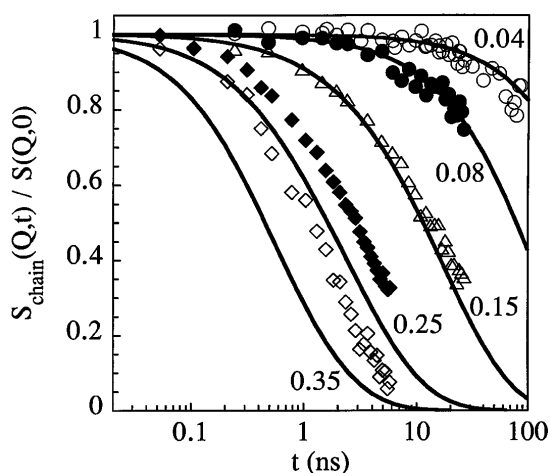


FIG. 1. Comparison between the dynamic structure factor for single chain dynamics of PIB as measured by NSE (symbols) and the Rouse dynamics prediction (solid lines). The numbers at the curves indicate the Q values in $\text{\AA}^{-1}$.

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