Comment on "Decoupling of Time Scales of Motion in Polybutadiene Close to the Glass Transition"

In a Letter by Richter et al. [1] a study of the dynamic structure factor of polybutadiene (PB) is presented using the neutron spin-echo technique. The authors find that below 220 K the microscopic relaxation time does not slow down as much as the viscosity; relaxation rates are presented which follow an Arrhenius law and bifurcate from those corresponding to the viscosity at 10^8 Hz. The bifurcation temperature is above T_g (181 K) and close to the critical temperature T_c (216 K) discussed within the frame of mode-coupling theory (MCT). Above 220 K the time scales are proportional to each other, which is typical for the α process of glass-forming systems. Discussing the origin of this time scale, the authors exclude a slowing down of a fast relaxation process which has been identified by neutron scattering (NS) experiments on a time scale of 3×10^{-13} s. Furthermore, the amplitude of the process exhibits a temperature dependence which agrees with the one predicted by MCT and which is believed to be typical for structural relaxation. Hence, the authors conclude that below T_c the microscopic structural rearrangements decouple from the large-scale structural relaxation responsible for, e.g., the viscosity, and they stress the similarity to other decoupling phenomena discussed for supercooled liquids [2,3].

On the other hand, it has been shown in several papers [3-7] that the β process—which is a typical feature of supercooled liquids—bifurcates from the α process at relaxation rates of 10^6-10^8 Hz, corresponding to a temperature which is close to T_c. The β process shows an Arrhenius temperature dependence and persists also in the glassy state, and its relaxation strength changes with temperature [4,5,7]. Clearly, the β process is different from a structural relaxation. Although the fast relaxation process observed by NS (and discussed by the authors) often is also called the β process, the time scales and temperature dependences of both processes are completely different. This can be recognized if the various relaxation rates are compared as has been done for o-terphenyl (cf. Fig. 1). Three processes can be identified and similar rates are found as in the case of PB, in particular, a bifurcation happens at similar rates ($\sim 10^7$ Hz). Here, the fast β process is called the β_f process and the conventional (slow) β process, the β_s process. Whereas the α process and the β_f process exist for all temperatures the β_s process exists only below T_c.

Concluding, I think the authors have observed not a decoupling of structural relaxation time scales but the bifurcation of the α and β_s processes. This conclusion is further supported by the following: (i) The decoupling of time scales for transport coefficients discussed in the literature [2,3] is not as big at T_g as observed by the authors. (ii) The typical temperature dependence of a structural relaxation is not an Arrhenius one but a
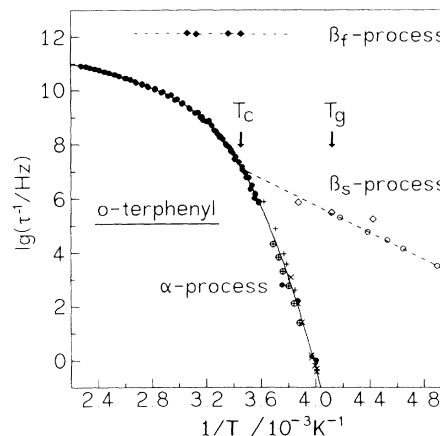

FIG. 1. Relaxation rates of o-terphenyl as given by different methods; solid and dashed lines are guides for the eye. α process: +, dielectric relaxation [8]; ×, dynamic Kerr effect [8]; ⊕, light scattering [9]; ●, NMR [10]. β_s process: O, dielectric relaxation [4]; ◇, time resolved optical spectroscopy [6]. β_f process: ◆, neutron scattering, applying an exponential decay law [11].

Vogel-Fulcher-Tammann behavior. (iii) The smallest rate reported (4×10^5 Hz) corresponds to a temperature of 10 K below T_g. This high rate is not expected for some kind of structural relaxation which should freeze near T_g.

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