

Confined dynamics in nanophase-separated side chain polymers

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The relaxation behavior of different series of nanophase-separated side chain polymers with long alkyl groups is studied and compared with corresponding results from the literature. Characteristic for these homopolymers is that alkyl groups - belonging to different monomeric units and chains - aggregate to alkyl nanodomains with a typical dimension of about 0.5-2 nm. Relaxation spectroscopy data and calorimetric results show that a polyethylene-like glass transition (α_{PE}) occurs within these alkyl nanodomains. The α_{PE} process appears at temperatures below the conventional glass transition (α) where the main chains soften. The features of the α_{PE} process in higher poly(n-alkyl methacrylates), poly(n-alkyl acrylates), poly(di-alkyl itaconates), poly(α -n-alkyl β -L-asparates) or hairy rod polyimides are similar [1]. The influence of the alkyl nanodomain size on the α_{PE} process is studied in detail.

Common trends have been observed in all homologous series [1]. With increasing length of the alkyl groups and increasing size of the alkyl nanodomains (i) the glass temperature $T_g(\alpha_{PE})$ increases (cf. full symbols in Fig. 1a) and (ii) the α_{PE} process shows a strong-to-fragile transition (Fig. 1b). It starts as an Arrhenius-like process in the butyl members with $C=4$ alkyl carbons per side chain and alkyl nanodomains having a typical dimension of about $d \approx 0.5$ nm and approaches a steepness index of $m \approx 50$ for dodecyl members with $C=12$ and $d \approx 2$ nm (Fig. 1c) [2].

These findings are interpreted in the picture of a hindered glass transition and are related to the discussion about dynamic heterogeneities in glass forming liquids. The process observed for the butyl members can be understood as a Johari-Goldstein process in alkyl nanodomains (β_{PE}). The question whether or not this process survives in larger alkyl nanodomains with a truly cooperative α_{PE} process is discussed [3]. First experiments on quenched side chain polymers seem to indicate that similar localized motions exist also in higher members. The general importance of nanophase separation effects for an understanding of the dynamics of complex materials in nanotechnology and nature will be discussed.

References

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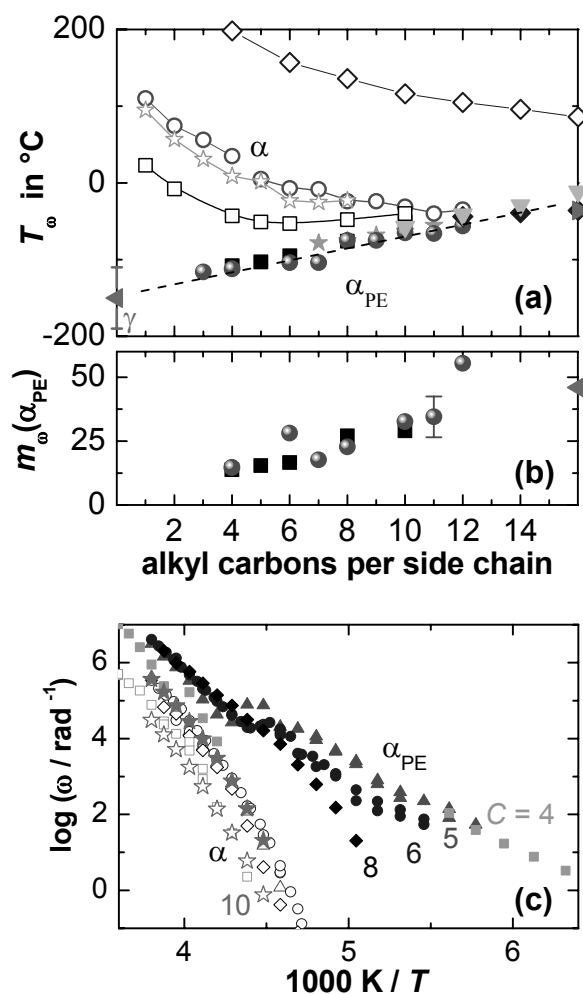


Fig. 1. (a) Relaxation temperatures T_ω for the α (open symbols) and α_{PE} (full symbols) processes as function of the number of alkyl carbons per side chain for different homologous series (■□-poly(n-alkyl acrylates) [1], ●○-poly(n-alkyl methacrylates) [4], ★*-poly(di-alkyl itaconates) [5], ◆◇-hairy rod polyimides [6], ▼- poly(α -n-alkyl β -L-asparates) [7]) and amorphous polyethylene (◄►) [8]. The data are taken at a frequency of $\omega = 10 \text{ rad/s}$. (b) Steepness index $m_\omega = -d \log \omega / d(T_\omega / T)|_{T=T_\omega}$ as obtained for the α_{PE} process in higher poly(n-alkyl methacrylates) (●) and poly(n-alkyl acrylates) (■). (c) Arrhenius plot for α and α_{PE} processes in higher poly(n-alkyl acrylates). The relaxation frequencies are taken from dielectric data. The labels indicate the number of alkyl carbons per side chain.