Effects of quenching and physical aging on the relaxation behavior of nanophase-separated side chain polymers

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Abstract. The influence of quenching and physical aging on the relaxation behavior of poly(n-alkyl methacrylates) with long alkyl groups in the side chain is studied by dielectric spectroscopy. Typical for these side chain polymers is a nanophase separation of incompatible main and side chain parts and the existence of alkyl nanodomains with a typical dimension of 0.5-1.5nm. In larger alkyl nanodomains a polyethylene-like glass transition \( \alpha_{PE} \) occurs at temperatures below the conventional \( \alpha \) relaxation. For quenched samples additional peaks on the high frequency wing of this \( \alpha_{PE} \) process have been detected in a similar frequency-temperature range where the Arrhenius-like \( \beta_{PE} \) process is observed for slowly cooled side chain polymers with short alkyl groups and small alkyl nanodomains. This is interpreted as an amplification of the localized dynamics in the alkyl nanodomains and related to the production of additional free volume in quenched samples which disappears during physical aging slightly below \( T_g(\alpha) \). Similarities to the aging behavior of conventional glasses and the importance of non-equilibrium effects for the properties of nano-structured materials in the glassy state are discussed.

1. Introduction
In the recent years relaxation behavior and structure of polymers containing long alkyl groups in the side chain have been investigated in detail [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Common aspects of such side chain polymers have been reported which are independent on the microstructure of the main chain [4]. It has been observed that alkyl groups belonging to different monomeric units and chains aggregate in small alkyl nanodomains (Figure 1). The typical dimensions of these alkyl nanodomains depend on the number of alkyl carbons per side chain. For short side chains with \( C = 4 \) alkyl carbons a typical dimension is \( d = 0.5nm \) while for longer alkyl groups the size increases. A typical size for \( C = 10 \) alkyl carbons is \( d = 1.5nm \). This nanophase separation of incompatible main and side chain parts is indicated by a pre-peak in x-ray scattering data which shifts systematically to lower \( q \)-values with increasing side chain length. This effect is basically main chain independent and has been reported for higher members of several polymer series like methacrylates [2], acrylates [4], itaconates [7] or hairy rod polyimides [8]. In all these cases the typical dimension of the alkyl nanodomains is similar and depends basically on the number of alkyl carbon per side chain. As long the alkyl groups in the side chain are not too long the frustration by the immobile main chains is sufficient to prevent the polymers from crystallization. Only for very long alkyl groups side chain crystallization occurs within the alkyl...
nanodomains [12]. For the amorphous members with shorter side chains nanophase separation is indicated by the occurrence of an additional relaxation process ($\alpha_{PE}$) at temperatures below the conventional glass transition ($\alpha$ or $\alpha'$) where the main chains become mobile (Figure 2a). The intensity of the $\alpha_{PE}$ process increases systematically with side chain length or volume fraction of the alkyl groups. For long alkyl groups ($C > 6$) and large alkyl nanodomains this process shows typical features of a dynamic glass transition: (i) the trace in the Arrhenius plot is significantly curved, (ii) the peak in the relaxation spectrum is much broader than a simple Debye process and (iii) dynamic heat capacity measurements show a second transition below the conventional glass transition [5]. Obviously, there are two coexisting glass transitions in nanophase-separated side chain polymers with long alkyl groups: During cooling the main chain mobility freezes in first at the conventional glass transition temperature ($T_g(\alpha)$). In a certain temperature range below the alkyl groups are still mobile before the alkyl nanodomains freeze in at the glass temperature of the $\alpha_{PE}$ process ($T_g(\alpha_{PE})$).

Due to the demixing of main chains and alkyl groups both glass transitions coexist in nanophase-separated side chain polymers with large alkyl nanodomains. For the shortest alkyl groups where nanophase separation has been found ($C = 4, d \approx 0.5\text{nm}$) the $\alpha_{PE}$ process degenerates to an Arrhenius-like relaxation process (Figure 2b). The temperature dependence in the Arrhenius plot is linear and the prefactor obtained from an extrapolation of the relaxation times to $T \to \infty$ is about $10^{-14}\text{s}$. Based on these findings it was speculated [13] that the process in very small alkyl nanodomains might be the local process belonging to the cooperative motions ($\alpha_{PE}$) in the higher members. Thus, the process in PnBMA might be called $\beta_{PE}$ and can be interpreted as a Johari-Goldstein process [14] within the alkyl nanodomains. Following this idea the question arises whether or not this $\beta_{PE}$ process survives in the higher members showing an $\alpha_{PE}$ process shifted to higher temperatures and lower frequencies (Figure 2b). This question is hard to answer based on data for slowly cooled samples since $\alpha_{PE}$ process and conventional glass transition $\alpha$ are not well separated in many cases and since the relaxation strength of the $\alpha$ process is often much larger than that of the $\alpha_{PE}$ process. An even weaker $\beta_{PE}$ process on the high frequency wing of the $\alpha_{PE}$ process is hard to resolve under these conditions. A possible way to amplify the local dynamics might be an increase free volume by quenching [14, 15, 16]. Due to the structure of nanophase-separated systems the high temperature glass transition will fix the environment in which the side chain dynamics has to occur. A study of the relaxation behavior of quenched samples will also enable us to study the effects of physical aging in nano-structured systems containing small alkyl domains of size of about one nanometer. Although known for a long time [17] the slow equilibration process in glasses at temperatures below the equilibration-to-non-equilibrium transition at $T_g$ - called physical aging - is not really understood so far. The nature of physical aging in nanophase-separated side chain polymers is surely different from equilibration effects in chemically homogeneous glasses below $T_g$ but experiments on such materials may help to understand special aspects which are of interest for an understanding of the properties of nano-structured materials used in several fields of application.
2. Experimental

Dielectric measurements in the frequency range 0.1Hz-1MHz on quenched samples have been performed using Novocontrol Alpha analyzer. Thin polymer films with a thickness of about 200μm have been placed between electrodes with a diameter of 20mm. In order to increase the quenching rates very thin gold-plated brass electrodes with a thickness of about 250μm have been used.

Three atactic poly(n-alkyl methacrylates) have been studied: poly(n-decyl methacrylate) [PnDMA], poly(n-heptyl methacrylate) [PnHepMA], and poly(n-butyl methacrylate) [PnBMA]. All samples are synthesized by free radical polymerization, have a relatively high molecular weight and a broad molecular weight distribution (PnDMA: $M_w>$100kg/mol, $M_w/M_n>$2; PnHepMA: $M_w=31$kg/mol, $M_w/M_n=2.2$; PnBMA: $M_w=330$kg/mol, $M_w/M_n=2.3$).

Quenched samples have been prepared in the following way: The capacitor is prepared and re-heated to a temperature 50K above the glass temperature $T_g(\alpha)$ of the sample. After 5min annealing at this temperature the samples were quenched by immersing the complete capacitor in liquid nitrogen. Estimated quenching rates at $T_g(\alpha)$ are -1000K/min. Then, the capacitor was transferred as fast as possible to the chamber of the dielectric instrument which was already at -120°C. Isothermal sweeps have been performed at eight temperatures between -110 and -67°C. Afterwards the sample was reheated to a temperature close to $T_g(\alpha)$ (PnDMA: -40°C, PnHepMA: 25°C), annealed there for 20min, rapidly cooled to -120°C and a second set of isothermal sweeps has been performed. Then, this program is applied again and again in order to measure 3rd and 4th set of isothermal sweeps at low temperatures (-110...-67°C).
3. Results and Discussion

The results of dielectric measurements on a quenched poly(n-decyl methacrylate) sample after different periods of physical aging close to the conventional glass temperature \( T_g(\alpha) \) are shown in Figure 3a. Obviously, a pronounced and narrow peak appears at frequencies which are higher than the relaxation frequency of the \( \alpha_{PE} \) process. Note, that the underlying wing includes probably contributions of the relatively weak \( \alpha_{PE} \) process occurring in the alkyl nanodomains without significant dipole moment and contributions from the strong \( \alpha \) peak occurring at even lower frequencies but having a much larger intensity due to the strong dipole moment of the carboxyl groups close to the backbone (cf. Figure 2a). Maxima of both the processes can not be detected in our frequency window. Expectedly, the additional peaks observed for quenched samples disappear if we anneal the system close to the conventional glass transition temperature incorporating the main chains. If the main chains soften the complete system is able to equilibrate and relaxes to a state with higher density as in case of classical aging experiments \[17, 18, 19\]. In the course of this densification process the additional peaks observed for the quenched sample will disappear. Note, that the equilibration process is seemingly relatively fast if we anneal close to \( T_g(\alpha) \) while annealing at or even slightly above \( T_g(\alpha_{PE}) \) is much less efficient. Isothermal annealing for 30min at temperatures below -75°C is not affecting the shape of the additional peaks in dielectric isotherms of quenched samples. This shows clearly that it is the main chain mobility which determines the situation here. The structure freezes in if the main chains become immobile. The dynamics in the alkyl nanodomains is affected by the frozen structure. Only if the main chains become mobile again the system can equilibrate.

Figure 3b shows that a similar effect occurs in case of quenched poly(n-heptyl methacrylate) samples. The findings are quite similar. Additional peaks appear when quenched which disappear after annealing close to \( T_g(\alpha) \). Extra peaks have been observed for both samples, PnHepMA and PnDMA, in the temperature range from -67 to -110°C. The peak position shifts
Figure 4. Arrhenius plots for (a) poly(n-decyl methacrylate) and (b) poly(n-heptyl methacrylate). The peak maxima from dielectric measurements on quenched samples (1st sweeps as shown in Figure 3) are indicated by full triangles. The relaxation frequencies for the conventional glass transition $\alpha$ or $\alpha'$ (open symbols) and for the polyethylene-like glass transition $\alpha_{PE}$ (symbols with dot at center) in these samples are shown for comparison. Data from dielectric spectroscopy (triangles), shear (diamonds) and heat capacity spectroscopy (squares) are included. The thick dashed line corresponds to the $\beta_{PE}$ process in PnBMA as shown in Figure 2b.

with increasing temperature slightly to larger frequencies. Interestingly, two coexisting peaks are observed for both the samples measured at temperatures around -85°C. At temperatures below the high frequency peak seems to dominate but contributions of the other peak can be still seen as a weak shoulder on the low frequency side of the pronounced peak in the isotherms (Figure 3b). Note, that the peak width of all additional peaks in quenched samples is relatively small but larger than that of a Debye process. This indicates that the relevant motions occur in a relatively homogeneous environment. Why two separated peaks coexist is not really clear so far.

The frequency position of the peaks in the $\varepsilon''$ isotherms of quenched PnDMA is compared in an Arrhenius plot with the position of the $\alpha_{PE}$ process as obtained for slowly cooled samples by different methods (Figure 4a). Obviously all peaks occur at frequencies which are higher than that of the $\alpha_{PE}$ process. The frequency position of both additional peaks in the quenched samples shows an Arrhenius-like temperature dependence. The trace of the peak occurring at lower frequencies is in good agreement with the $\beta_{PE}$ process in PnBMA ($C = 4$). The other peak occurs at higher frequencies but the temperature dependence remains Arrhenius-like. Similar behavior is found for PnHepMA (Figure 4b). Also in this case two new peaks occur in quenched samples. The low frequency peak fits fairly well to the $\beta_{PE}$ process in PnBMA while the second peak is shifted to slightly higher frequencies. Both peaks follow an Arrhenius-like temperature dependence. This seems to indicate that the local dynamics is amplified in quenched samples being non-equilibrium systems containing a larger fraction of free volume compared to slowly cooled samples.

The occurrence of extra free volume is a general observation for quenched glasses since a liquid state belonging to a higher temperature is frozen-in, i.e. $T_g$(quenched glass) > $T_g$(slowly
Figure 5. Schematic picture of the situation in nanophase-separated side chain polymers at the conventional glass temperature $T_g(\alpha)$ and after further cooling to the glass temperature of the alkyl nanodomains $T_g(\alpha_{PE})$. The production of free volume in the inner or outer parts of alkyl nanodomains is indicated. Note, that $T_g(\alpha)$ depends on the quenching rate, as larger the rate as larger main chain cage and final free volume in this picture.

cooled glass) [17, 18, 19]. That this free volume is concentrated in the alkyl nanodomains of nanophase-separated side chain polymers seems to be understandable considering the differences in the mobility of both the components. There are two different $T_g$'s in this system. At the conventional $T_g(\alpha)$ the main chain mobility freezes in. The main chains behave below this temperature like a solid. The alkyl groups, however, are still mobile and behave like a liquid above $T_g(\alpha_{PE})$. This should cause significant differences in the thermal contraction. The main chains form something like a immobile cage surrounding the alkyl nanodomains. The volume of the mobile alkyl groups inside the alkyl nanodomains will shrink significantly during cooling as long they behave liquid-like. Free volume will be produced since the volume of the main chain cage is not significantly changing at the same time.

The question arises how this free volume is distributed in the alkyl nanodomains. An intuitive assumption might be that the additional free volume is concentrated in the middle of each alkyl nanodomain since the alkyl groups are connected by chemical bonds to the main chains. However, one can also argue that the parts of the alkyl groups close to the main chain are highly frustrated and that only the parts far away from the main chains can approach the more densely packed equilibrium state (Figure 5). In both the cases the additional free volume is heterogeneously distributed in each alkyl nanodomain. Note, that the volume fraction of the alkyl groups may influence the morphology of the nanophase-separated systems and could modify the situation. In samples with long side chains the volume fraction of the alkyl groups can be large enough to have a situation with two bi-continuous phases. Independent on that the occurrence of additional free volume can be explained at least qualitatively by the simple empirical picture discussed above because solid-like and liquid-like regions will coexist below $T_g(\alpha)$ in all cases. Simulations on amorphous alkanes containing five to eight carbons in relatively small boxes with fixed volume have shown that cavities can be formed in such systems. The formation of cavities and the existence of chains which are aligned preferentially perpendicular to the cavity-liquid interfaces have been observed in molecular dynamic simulations on n-octane-like molecules with an attractive interaction [20]. More recent simulations on n-pentane-like molecules [21] have shown that cavities with mesoscopic dimensions are only formed below a certain critical density $\rho_c$, called Sastry density [22]. In all these cases the density of CH$_3$ end groups in the cavity-liquid interface is large. In a simple view this is a consequence of the fact that the van der Waals distance between non-bonded carbons of about 0.45nm is large compared to the distance between two bonded carbons of about 0.15nm. The system can
minimizes the energy by reducing the number of carbons in the interface. This produces finally a high CH₃ density in the interface and chains aligned perpendicular to the interfaces. Note, that formation of large mesoscopic cavities in the alkyl nanodomains of side chain polymers seems unlikely since the alkyl groups are initially interdigitated, not to far from an extended chain conformation and connected by chemical bonds at (more or less) fixed positions to the immobile main chain cages (Fig.1a). The contraction of the "alkyl liquid" within the cages must occur under these conditions, i.e. there are much more constraints compared to the situation in the simulations discussed above. Somehow the alkyl groups in our side chain polymers can be understood as frustrated alkanes. In order to get large mesoscopic cavities the main chains must move. A common aspect of all the pictures discussed above is, however, that heterogeneously distributed free volume is produced during cooling short chains in a cage with fixed volume. Note, that heterogeneously distributed free volume will be accompanied by the occurrence of inhomogeneously distributed internal stresses in the alkyl nanodomains. Theoretical studies aimed to describe liquid crystalline side chain polymers with a molecular architecture which is similar to that of our polymers have shown that the occurrence of internal stresses can influence the dynamics of such systems [23, 24]. The application of such models, however, is complicated since the details of the distribution of internal stresses and free volume in the alkyl nanodomains are basically unknown.

That additional free volume amplifies the localized dynamics seems to be intuitively clear. As long small parts of the alkyl groups have space enough to move without assistance by the environment no cooperativity is required. That these localized motions occur just in that frequency range where the βPE process in PnBMA is remarkable and supports the idea that the same type of motions is detected in both cases. This may indicate that localized motions (βPE) will survive in PnHepMA and PnDMA samples which show in addition an αPE process with typical features of a dynamic glass transition. In general this finding supports the idea that there is a transition from localized to more cooperative motions within the alkyl nanodomains with increasing side chain length and increasing alkyl nanodomain size. There seem to be good reasons to assume that the localized motions - indicated by the βPE process found for PnBMA - also exist in higher members apart from the cooperative motions reflected by the αPE process. Thus, the relaxation behavior in alkyl nanodomains shows probably all typical features of the dynamics of ordinary glass-forming liquids. There is not only a dynamic glass transition (αPE) indicating the solid-to-liquid transition but also a localized dynamics (βPE) which is an intrinsic feature of glassy state according to Johari [25].

The discussion above shows that one can possibly learn a lot about the dynamics of glasses based on studies of self-assembled systems with domains having mesoscopic dimensions. The advantage here is that the number of "particles" in a "box" is quite small and that one can really study the transition from localized to cooperative motions. Free volume is produced in such two component systems in a special way and aging effects seem to be more pronounced. Otherwise, the findings in these complex systems can also be compared with findings in conventional one-component glass-forming liquids. Similarities in both cases may be a hint for the existence of fluctuating density pattern in glass-forming liquids (dynamic heterogeneities = cooperatively rearranging regions [26, 27]) which freeze in at Tg and survive in form of spacial heterogeneities in the glassy state at lower temperatures. Some approaches predict that such patterns are a general feature of glasses characterized by the existence of less densely packed regions ("islands of mobility" [25]) surrounded by regions with a higher density [26, 28]. Although the density contrast might be tiny, the differences in mobility can be huge. The size of a representative subsystem of this pattern at Tg is assumed to be 1-3nm [26, 29]. Although there are only indirect proofs for the existence of dynamic heterogeneities in glasses [30, 31] and several controversially debated topics in this field [26, 32] it is worth mentioning that the situation in nanophase-separated side chain polymers below Tg is not too different from the situation which is assumed
in the framework of such models for chemically homogeneous glasses.

Apart from this discussion about basic questions of glass transition and physical aging the investigation of the equilibration process of nanophase-separated side chain polymers in different temperature ranges might be important in order to understand and to predict the properties of modern nano-structured materials used in the glassy state. Significant changes due to physical aging are expected in such materials combining two or more components with quite different properties ($T_g$'s). From our point of view this will cause more relevant problems with the long term stability due to the amplification of non-equilibrium effects during preparation and processing. In nano-structured materials it is naturally a two step procedure incorporating a lot of non-equilibrium aspects which brings the system from the molten to the glassy state.

4. Conclusions
We have presented in this paper first experiments showing the influence of quenching and physical aging on the relaxation behavior of nanophase-separated side chain polymers. An amplification of the localized dynamics within small alkyl nanodomains and weak additional relaxation peaks in dielectric spectra at high frequencies are observed for quenched samples. The frequency-temperature position of these peaks is similar like that of the $\beta_{PE}$ process in poly(n-butyl methacrylate) with very small alkyl nanodomains. Such localized motions seem to survive also in larger alkyl nanodomains of higher poly(n-alkyl methacrylates) where cooperative motions within these domains are indicated by an $\alpha_{PE}$ process with typical features of a dynamic glass transition. The additional peaks in the spectra of quenched samples disappear after longer periods of isothermal annealing slightly below the conventional glass temperature $T_g(\alpha)$ where the main chains soften. This finding is discussed to be a consequence of additional free volume produced in the alkyl nanodomains of nanophase-separated side chain polymers by quenching. The importance of these findings for an understanding of physical aging effects in glasses and for the long term stability of nano-structured materials is considered.

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6. References
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