Nanophase separation in side chain polymers: new evidence from structure and dynamics

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Abstract. New evidence for a nanophase separation of incompatible main and side chain parts in amorphous poly-(n-alkyl methacrylates) with long alkyl groups are presented. Independent indications for the existence of alkyl nanodomains with a typical dimension in the 1 nm range from studies on dynamics and structure are reported. Results from nuclear magnetic resonance (NMR) experiments are compared with data from different relaxation spectroscopy methods on poly-(n-decyl methacrylate). The NMR results in combination with relaxation spectroscopy data support the existence of an independent polyethylene-like glass transition, \(\alpha_{PE}\), within the alkyl nanodomains in addition to the conventional glass transition \(\alpha\) at higher temperatures. X-ray scattering data show that the situation in homopolymers is similar to that for random poly-(n-alkyl methacrylate) copolymers with the same average length of the alkyl group in the side chains. Scattering data for a series of \(n\)-butyl methacrylate samples with polymerization degrees reaching from \(P = 1\) to 405 indicate that nanophase separation is chain-length independent above \(P = 25\), while the nanophase separation tends to disappear below \(P = 6\). Insensitivity of structural aspects in nanophase-separated poly-(n-alkyl methacrylates) to changes in the molecular microstructure and consistency of NMR results with independent conclusions from relaxation spectroscopy underline the general importance of nanophase separation effects in a broad class of side chain polymers.

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1. Introduction

In a recent paper [1], we have shown that a nanophase separation of incompatible main and side chain parts on a length scale of about 1 nm is a common feature of several series of side chain polymers with long alkyl groups. Structural data from x-ray scattering indicate that alkyl nanodomains with a typical size of 0.5–2 nm are formed in the amorphous melt by aggregation of alkyl groups from different monomeric units, which can belong to one and the same or different polymer chains. Within these alkyl nanodomains an independent relaxation process with the typical features of a dynamic glass transition—called polyethylene-like glass transition $\alpha_{\text{PE}}$—has been observed. In calorimetric data, this second glass transition can be seen at low temperatures, in addition to the conventional glass transition at higher temperatures related to the softening of the entire system [2]–[4]. As in the case of microphase-separated block copolymers, the co-existence of two glass transitions is a strong indication for a demixing of incompatible components.

A comparison of data for different series of polymers with long alkyl groups shows that the main features of nanophase-separated side chain polymers do not depend significantly on the microstructure, flexibility and glass temperature of the main chain: (i) two glass transitions have been observed for poly($n$-alkyl methacrylates) [2], poly(di-$n$-alkyl itaconates) [3], hairy rod polyimides [4] and poly($n$-alkyl acrylates) [1]. For all these series, the glass temperature for the polyethylene-like glass transition $T_g(\alpha_{\text{PE}})$ increases with increasing side chain length and depends mainly on the number of alkyl carbons per side chain $C$ or equivalently on the alkyl nanodomain size. For a given $C$ number, $T_g(\alpha_{\text{PE}})$ is basically main-chain-independent [1], although the difference in the conventional $T_g$ is up to 200 K. (ii) A prepeak in x-ray scattering data—being the structural reflection of the nanophase separation in side chain polymers—shifts systematically with the number of alkyl carbons per side chain $C$. Qualitatively, the scattering curves of poly($n$-alkyl methacrylates), poly($n$-alkyl acrylates) [1], hairy rod polyimides [4] and poly(di-$n$-alkyl itaconates) [5] show the same behaviour. Quantitatively, the prepeak shift for different polymer series is at least similar [1]: clear indications for a prepeak are observed,
Figure 1. Different views on the nanophase separation in side chain polymers. Quasi-one-dimensional (l.h.s.) and three-dimensional (r.h.s.) pictures are compared. The alkyl nanodomains are shown in grey. The small red beads represent the carboxyl groups (COO) where the dipole moment of the monomeric units is located.

beginning with the butyl members \((C = 4)\) where the prepeak maximum corresponds to an equivalent Bragg spacing of about 1.2 nm. For the decyl members \((C = 10)\), equivalent Bragg spacings of about 1.8–2.0 nm are reported. Different pictures for an understanding of the scattering behaviour can be considered. One can think about a more local, quasi-one-dimensional picture starting from two single-polymer chains or, on a more abstract level, in three dimensions consider approximately the average distance of alkyl nanodomains in the melt (figure 1). Both pictures do not exclude each other and certain aspects of both views might be relevant. Although details of the morphology of nanophase-separated side chain polymers are not yet clear, the common aspect of both views is the aggregation of alkyl groups in alkyl nanodomains.

The results described for different series of side chain polymers support the idea [6] that nanophase separation is a general phenomenon in materials that consist of molecules with incompatible parts. Nanophase-separation effects have been reported for small molecule liquids [6], metallic glasses as well as semi-crystalline, liquid–crystalline [7]–[9] and amorphous [2, 3] polymers.

An interesting point is the interrelation between structure and dynamics in nanophase-separated polymers. The polyethylene-like glass transition \(\alpha_{PE}\) in these polymers can be understood as a hindered glass transition in self-assembled confinements [1, 10]. The small dimensions of these domains in the 1 nm range are attractive for the background of the ongoing discussion regarding the existence and size of dynamic heterogeneities in glass-forming materials [11, 12]. The dependence of the polyethylene-like glass transition \(\alpha_{PE}\) on the alkyl nanodomain size gives interesting information about the influence of spatial restrictions on the co-operative dynamics similar to experiments on liquids constrained in external confinements such as nanoporous glasses [13, 14] or zeolites [15].

The aim of this paper is to support the interpretation that the dynamics of nanophase-separated poly\((n\)-alkyl methacrylates) is characterized by two co-existing glass transitions \(\alpha\) and \(\alpha_{PE}\) based on NMR experiments, which can detect selectively the mobility of different
main and side chain carbons in poly(n-decyl methacrylate). Random poly(n-alkyl methacrylate) copolymers and a series of n-butyl methacrylates reaching from the monomer to long polymer chains are studied by different x-ray scattering techniques to learn more about the influence of other molecular parameters on the nanophase separation in side chain polymers.

2. Experimental

2.1. Samples

Poly(n-alkyl methacrylates) (PnAMA) with various side chain lengths were studied. The pentyl (PnPMA, C = 5), heptyl (PnHepMA, C = 7) and decyl (PnDMA, C = 10) members, a random ethyl-hexyl copolymer (P(EMA-nPrMA)) containing 50% EMA (C = 2.5) and random butyl-hexyl copolymers (P(nBMA-nHexMA)) containing 75, 54 and 25% BMA (C = 4.5, 4.9 and 5.5) were synthesized by free radical polymerization using α,α′-isobutyronitrile as the initiator. The poly(n-hexyl methacrylate) (PnHexMA, C = 6) sample was kindly provided by Dr G Meier (MPI-P, Mainz/FZ, Jülich) and poly (n-octyl methacrylate) (PnOMA, C = 8) by Dr Th Wagner and Dr W Steffen (MPI-P, Mainz). Further details of the PnHexMA sample are described in [16]. The methyl (PMMA, C = 1), ethyl (PEMA, C = 2) and propyl (PnPrMA, C = 3) members were purchased from Polysciences Inc. Poly(n-butyl methacrylate)s (PnBMA, C = 4) with different degrees of polymerization were purchased from PSS GmbH (Mainz). The n-butyl methacrylate monomer (nBMA) was received from Sigma–Aldrich Corp. The dibutyl ester of 2,4-dimethyl glutaric acid being a dimer analogue (DinBMA) was synthesized by Dr U Dümichen (Merseburg). Molecular weight parameters and conventional Tg values from DSC (dT/dt = ±10 K min⁻¹) for all samples are summarized in table 1.

2.2. Methods

2.2.1. Scattering methods. Wide angle x-ray scattering (WAXS) measurements in the range 3.5 nm⁻¹ < q < 32 nm⁻¹ for the scattering vector q = 4π/λ sin(θ/2) were performed using the Guinier method with a film camera (Huber diffraction equipment). X-ray scattering data in the range 2 nm⁻¹ < q < 16 nm⁻¹ were obtained from measurements with a two-dimensional (2D) detector (SIEMENS HI star) installed on a rotating anode. An Anton Paar Kratky camera was used for SAXS experiments (0.06 nm⁻¹ < q < 7.44 nm⁻¹) in combination with an x-ray generator Seiffert ID 3000 having a sealed x-ray tube operating at 40 kV and 30 mA. Cu Kα radiation with a wavelength of 0.145 nm⁻¹ was selected with a Ni filter (20 µm) combined with the pulse-height-discrimination method. The intensity was recorded with a proportional counter in the step-scanning mode. The beam intensity was controlled by measuring a LUPOLEN standard. The variation in transmission factor was ≤ 20%. The entrance slit had a width of 100 µm and the height-determining slit length was 16 mm. Peak maxima and peak widths were taken from curves after correcting the error due to the slit-like cross-section of the primary beam in the Kratky system using a home-made desmearing program. All x-ray measurements were carried out at 298 ± 1 K. Samples are polymer films with a thickness of about 1.5 mm prepared using a hydraulic press at T ≈ Tg + 50 K. Monomer, dimer and oligomers with very low viscosity are measured in thin-walled glass capillaries (Hilgenberg glass no. 140, wall thickness 0.01 mm and diameter 1 mm).
Table 1. Molecular weight parameters and glass temperatures.

| Sample                      | C number | P  | $M_w/M_n$ | $T_g/K$ |
|-----------------------------|----------|----|-----------|---------|
| PMMA                        | 1        | 860| 2.6       | 379     |
| PEMA                        | 2        | 1350| 1.9       | 343     |
| P(EMA-nPrMA) 50% EMA        | 2.5      | 3100| 1.6       | 336     |
| PhPrA                       | 3        | 2210| 4.6       | 324     |
| P(nBMA-HexMA) 75% BMA       | 4.5      | 1610| 1.8       | 296     |
| P(nBMA-HexMA) 54% BMA       | 4.9      | 2130| 1.5       | 289     |
| P(nBMA-HexMA) 25% BMA       | 5.5      | 3530| 1.4       | 281     |
| PnPenMA                     | 5        | 2090| 2.2       | 283     |
| PnHepMA                     | 6        | 1050| 2.1       | 253     |
| PnHepMA                     | 7        | 3700| 2.2       | 256     |
| PnDMA                       | 10       | 3270| 2.2       | 228     |
| nBMA                        | 4        | 1   | 1         | 133     |
| DinBMA                      | 4        | 2   | 1         | 158     |
| PnBMA 6                     | 4        | 6   | 1.2       | 216     |
| PnBMA 10                    | 4        | 10  | 1.1       | 252     |
| PnBMA 25                    | 4        | 25  | 1.08      | 281     |
| PnBMA 52                    | 4        | 52  | 1.07      | 295     |
| PnBMA 405                   | 4        | 405 | 1.04      | 303     |

a Significant contributions from $a$ and $\alpha_{PE}$ glass transitions overlap [2].
b From TMDSC measurements with a period $t_p = 60$ s.

2.2.2. Nuclear magnetic resonance. NMR experiments were performed on a UNITY 200 spectrometer equipped with a 7 mm Super-Sonic DOTY CPMAS probe. For $T < 300$ K, spectra were obtained by Standard CPMAS experiments with constant radiofrequency amplitudes of 32 kHz and CW proton decoupling (33 kHz), whereas for $T > 300$ K, single-pulse excitation rather than CP was applied. The MAS spin rates were set at 2 kHz and controlled by a standard DOTY controller. The temperature was carefully calibrated for each temperature and spinning rate by a standard procedure [17]. The uncertainties in temperature and spin rate are 1 K and 2 Hz, respectively. At temperatures lower than 220 K, the temperature uncertainty is about 5 K. Broad signals between 100 and 200 ppm in the low-temperature MAS spectra are artifact signals from the low-temperature rotor caps.

The MAS spectrum (magic-angle spinning) of an $I = 1/2$ nucleus (e.g. $^{13}$C) in a rigid solid, spinning with a MAS rate $v_{ROT}$, consists of spinning side bands (ssb), centred around the isotropic chemical shift of the nucleus and separated by $v_{ROT}$. The periodicity of the time-domain MAS–NMR signal, imposed by the macroscopic rotation of the sample, is transformed into ssb in the spectral dimension. In the time-domain signal, the so-called rotational echoes are formed at multiples of $T_R = 1/v_{ROT}$ that transform into the narrow ssb of the MAS–NMR spectrum. Ssb of observable intensity appear in the spectral range that is approximately equal to the span of the powder pattern owing to the anisotropy of the chemical shift (CSA) $\Delta \sigma$ in a non-spinning sample. The relative intensities of the ssb carry information about the elements of the CSA tensor, which can be obtained by standard procedures [18].

The occurrence of a dynamic process with a characteristic time $\tau_c$ of the order of $T_R$ disturbs the MAS periodicity of the NMR signal, leading to the so-called dynamic broadening.
of the ssb [19]–[21]. Starting from low temperatures where the correlation time of the relevant motions $\tau_c$ is much larger than the MAS period $T_R$, the line widths of the individual ssb start to increase and reach a maximum value for $\tau_c \approx T_R$, followed by a decrease in the line widths at shorter $\tau_c$ (high temperatures). Thus, the information about the relaxation dynamics can be taken from the temperature of the maximum dynamic broadening and the relation between the MAS rate and the correlation time of the dynamic process [21]. NMR results are compared with relaxation spectroscopy data at $\omega_{\text{max}} = 2\pi v_{\text{ROT}}$. Since a MAS rate of $v_{\text{ROT}} = 2 \text{kHz}$ was used, the temperatures at which the maximum dynamic broadening occurs corresponds to $\log(\omega/\text{rad s}^{-1}) = 4.1$.

2.2.3. Relaxation spectroscopy. A commercial Novocontrol setup based on a Schlumberger SI1260 response analyser was used to measure the complex dielectric function $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ in the frequency range from 0.1 Hz to 1 MHz. Relaxation frequencies are taken from Havriliak Negami (HN) fits ($\varepsilon^*(\omega) = \Delta \varepsilon \cdot (1 + (i\omega/\omega_c)^\beta)^{-\gamma} + \varepsilon_{\infty}$) to the data. If required, an additional conductivity term $\sigma \sim \omega^{-1}$ was included.

The complex shear modulus $G^*(\omega) = G' + iG''$ of PnDMA was measured in the frequency range from 1 to 100 rad s$^{-1}$ with a Rheometrics Scientific RDAII instrument. The experiments were performed in stripe geometry ($1.5 \times 10 \times 25 \text{mm}^3$). The uncertainty of the absolute values for $G^*$ is large in this case ($\sim \pm 30\%$) owing to uncertainties concerning the sample geometry. $T_g$ for PnDMA is far below room temperature. Undercooled samples were quickly mounted at room temperature. Afterwards, the sample was cooled down step by step ($\Delta T = -3 \text{ K}$) and equilibrated at each temperature for 100 s before the isothermal frequency sweep was started.

Heat capacity measurements were performed using a non-commercial setup of the $3\omega$ method. Two different heater sizes were used: in the low-frequency range (0.2–20 Hz), large heaters ($5 \times 10 \text{ mm}^2$) were used to obey the boundary conditions (heater size > thermal wavelength); in the high-frequency range (20–2000 Hz), small heaters ($1.5 \times 5 \text{ mm}^2$) were used to get sufficient signals. TMDSC data were used to calculate dynamic heat capacities $c_p^*(\omega, T)$ from the originally measured effusivities $\rho \kappa c_p^*(\omega, T)$ where $\rho$ is the mass density and $\kappa$ the heat conductivity. Details of the experimental setup and data evaluation are described elsewhere [22].

3. Results

3.1. Dynamic aspects

Data from dielectric, shear and heat capacity spectroscopy for poly(n-decyl methacrylate) ($C = 10$) are shown in figure 2 as a representative example for the relaxation behaviour of nanophase-separated homopolymers. Temperature-dependent shear data ($G''(T)$) measured at a frequency of 10 rad s$^{-1}$ indicate the occurrence of two relaxation processes in the relaxation spectrum (figure 2(a)). The dielectric loss $\varepsilon''(T)$ at the same frequency indicates that only the conventional glass transition $a$ at higher temperatures is observed with a significant intensity (figure 2(a)). Measurements with the $3\omega$ method of heat capacity spectroscopy (at slightly higher frequencies) show that there are two co-existing processes in calorimetric data $c_p^*(\omega, T)$. There is a very broad step in the real part and two well-separated peaks in the imaginary part.
Figure 2. Relaxation behaviour of poly(n-decyl methacrylate). Temperature dependence of (a) shear loss modulus $G''$ (■) and dielectric loss $\varepsilon''$ (▴) for $\omega = 100 \text{ rad s}^{-1}$ as well as (b) the imaginary part of the heat capacity $c_p''$ (○) at $\omega = 3800 \text{ rad s}^{-1}$ are shown. The dashed lines in (b) correspond to $a$ and $\alpha_{\text{PE}}$ components as obtained from a fit to the $c_p''(T)$ data with a sum of two Gaussian functions. (c) Arrhenius plot with relaxation frequencies from shear (□, ⊙), dielectrics (□, ○) [23] and heat capacity spectroscopy (■, ○). The temperatures for which the mobility of carbons C5–C12 in the alkyl group (○) and COO carbons (□) is maximal in NMR cross-polarization experiments (cf text and figure 3) are indicated. The dashed line indicates the relevant NMR frequency.

The imaginary part can be fitted to a sum of two Gaussian functions. This function approximates usually the dynamic glass transition peak in $c_p''(T)$ quite well. The dispersion width of both peaks is about $\delta T = 20 \text{ K}$, similar to the values observed for other strong glasses. The relaxation strengths $\Delta c_p(a)$ and $\Delta c_p(\alpha_{\text{PE}})$ are similar. Although the uncertainty of the peak temperatures for both processes is relatively large, it is clear from an Arrhenius plot (figure 2(c)) containing data from shear, dielectrics and heat capacity spectroscopy that the two peaks in $c_p''(T)$ correspond to the processes observed in the shear modulus $G''$. The high-temperature process is related to the conventional main transition $a$, where the material softens dramatically and undergoes a glass-to-rubber transition. It is calorimetrically active and can also be observed in dielectric data, since the complete monomeric unit—including the carboxyl group where the main dipole moment is located—will move. The second process at lower temperatures is obviously also a dynamic glass transition, since it can be detected in calorimetric data, which is a typical feature of glass transitions in contrast to the behaviour of secondary relaxations in glasses showing only a tiny response in calorimetric signals [24]. This view is supported by the temperature dependence of the relaxation frequencies in the Arrhenius plot. In an Arrhenius approximation $\log \omega = \log \Omega \cdot \exp(-E_A/RT)$, one obtains unrealistic prefactors $\log(\Omega/\text{rad s}^{-1}) \approx 38$, which is much larger than $\log(\Omega/\text{rad s}^{-1}) \approx 14$ as expected for secondary relaxations in glasses. The temperature dependence of the relaxation frequency of the $\alpha_{\text{PE}}$ process indicates non-Arrhenius behaviour and corresponds to the situation in a strong glass with a fragility (steepness index) of $m \approx 37$ [10]. The missing signal in the dielectric response shows that the carboxyl group with
Figure 3. NMR results for poly(n-decyl methacrylate). (a) MAS spectra at different temperatures. All spectra are from CP (cross-polarization) experiments, except those at 315 K for which direct $^{13}$C excitations are used. The recycle delays were of the order of 1–5 s. The wide lines between the COO ssb are artifacts from the special caps of the MAS rotor that have to be used at lower temperatures. (b) Experimental full width-at-half-maximum height (fwhmh) for the main chain CH$_2$ carbon C1 (○) as well as for the COO carbon (□) and the side chain carbons C5–C12 (▲). Note that the open symbols represent the widths of individual resonances, whereas the full symbols, at least for temperatures below 300 K, represent the widths of multiple overlapping resonance lines.

Figure 3(a) shows MAS spectra of PnDMA for different temperatures. The line assignment is given at the $T = 223$ K spectrum; asterisks mark the ssb. The non-resolved lines between 20 and 40 ppm are resonances belonging to the side chain aliphatic carbons. Dynamic broadening of the carboxyl ssb at high temperatures is most obvious; however, a careful inspection of the resonances C5–C12 reveals a temperature-dependent line width for all carbons, but at different temperatures. Figure 2(b) shows the temperature dependence of the full width-at-half-maximum height (fwhmh) for the main chain CH$_2$-carbon (C1) as well as for the carboxyl group (COO) and the alkyl carbons (C5–C12). Since the individual side chain aliphatic lines cannot be resolved, the total widths of the overlapping resonances is plotted for the latter. The rather different temperature dependences of the line widths of the main chain carbons and carboxyl group on the one hand and of the alkyl carbons on the other hand is obvious: while the former broaden at temperatures higher

the main dipole moment of the monomeric units is not involved in the motions relevant for the $\alpha_{PE}$ process. All findings are consistent with the idea that the $\alpha_{PE}$ process is a ‘polyethylene-like glass transition’ in alkyl nanodomains formed by self-assembling in the melt. To prove this interpretation of the dynamics of side chain polymers with long alkyl groups, selective NMR measurements to detect the mobility of the different carbons in the monomeric units were performed.
than 300 K, the latter exhibit a maximum line width at $T \approx 230$ K. The dynamic broadening of the side chain resonances is close to the limit of detection and can hardly be realized from the spectra in figure 2(a). This is probably owing to the unfavourable $v_{\text{ROT}}/\Delta \sigma$ ratio and/or small amplitudes of the molecular reorientations that constitute the dynamic process. Lowering the MAS rate will probably increase the dynamic broadening effect but in turn would result in line overlap, making the interpretation of the spectra rather difficult. However, the effect is outside the margins of error and thus an important experimental finding supporting and complementing the relaxation spectroscopy data. Using $\omega = 2\pi v_{\text{ROT}}$ and inserting the NMR data in the Arrhenius plot (figure 2(c)) reveals that the broadening of the main chain and carboxyl resonances is due to the conventional glass transition $\alpha$, whereas those of the alkyl carbons must be due to the polyethylene-like glass transition $\alpha_{\text{PE}}$.

It is worthwhile to note that the maximum line widths for the main chain and carboxyl carbon seem to appear at slightly different temperatures. Subsequently, a more mobile carboxyl group as compared with the main chain may be anticipated. Unfortunately, low signal-to-noise ratio and the merging of the resonances of the carbon C1 with the O-CH$_2$ carbon C4 of the side chain do not permit a closer evaluation (see spectra for $T > 300$ K in figure 3(a)).

3.2. Structural aspects

X-ray scattering curves for representative poly(n-alkyl methacrylate) homopolymers (PnBMA, PnHexMA, PnHepMA, PnDMA) are shown in figure 4. The scattering intensity shows two significant peaks. The peak at large scattering vectors $q_l \approx 13$ nm$^{-1}$ corresponds to the van der Waals’ peak (I), which is related to the average distance of non-bonded atoms in the melt. In a Bragg approximation ($d = 2\pi/q_{\text{max}}$), one obtains for the homopolymers repeating distances in the range $d_l = 0.48$–0.495 nm, e.g. $d_l$ values which are nearly independent of the side chain.

Figure 4. X-ray scattering data for amorphous poly(n-alkyl methacrylates). Scattering intensity versus scattering vector $q$ for PnBMA 405 (a), PnHexMA (b), PnHepMA (c) and PnDMA (d) as obtained from Guinier method (lines) and measurements with a 2D detector (○). Prepeak (II) and van der Waals’ peak (I) are indicated. Scattering pattern from the 2D detector are shown in the insets.
Figure 5. X-ray scattering data for poly(n-alkyl methacrylate) copolymers and homopolymers. (a) SAXS raw data for random P(EMA-nPrMA) (■) and P(nBMA-nHexMA) (●, ⊙, ◦) copolymers. Homopolymers are shown for comparison. The labels give the average number of carbons per alkyl group. (b) Equivalent Bragg spacings \( d_{II} \) (large symbols) and \( d_I \) (small symbols), (c) full width of the prepeak taken at 85\% of the maximum height from desmeared SAXS curves and (d) scattering intensity at \( q = 0.5 \text{ nm}^{-1} \) as a function of the (average) number of alkyl carbons per side chain \( C \) for homopolymers (■) and random copolymers (□) from SAXS. WAXS data are shown in (b) for comparison (●, from figure 4; ▲, from [26]).

length \( C \). The second peak in the scattering curves at low \( q \) values indicates an additional repeating unit in our side chain polymers (\( d_{II} \)). The position of this prepeak (II) depends significantly on the side chain length (figure 4) and is interpreted as a structural indication for a nanophase separation of incompatible main and side chain parts. As expected, the samples are fully isotropic and continuous rings in the 2D intensity patterns (insets in figure 4) are observed.

Representative curves for several random PnAMA copolymers are shown in figure 5(a). The shift of the prepeak (II) with the number of alkyl carbons per side chain \( C \) is clearly visible. Seemingly random copolymers made from comonomers with not too different side chain lengths
Waals’ peak (I) is nearly independent of the chain length for all samples with 6 increasing 
the peak starts to decrease significantly below C = 5. For example, the scattering 
per side chain and d\(_{II}(C)\) corresponds to the behaviour of the homopolymers (figure 5(b)). The width of the 
prepeak \(\Delta q\) for the copolymers seems to be also similar to those for the homopolymers. 
The general trend in the amorphous PnAMAs is obviously a broadening of the prepeak with 
increasing C number (figure 5(c)).

A detailed analysis of the scattering data for amorphous PnAMAs below decyl (C < 10) 
indicates that the \(d_{II}\) values have a slightly non-linear dependence on the number of alkyl carbons 
per side chain (figure 5(b)). Obviously, the slope in the \(d_{II}\) versus C dependence is significantly 
different from the behaviour expected for alkyl groups in an all-\textit{trans} configuration, which is 
indicated by the dashed line in figure 5(b). A simple linear approximation [5], 
d\(_{lin} = 0.8\) nm for the ‘main chain diameter’ and d\(_{lin} = 0.105\) nm for the slope (average 
length per CH\(_2\) unit). An alternative equation [23], 
d\(_{II} = d_{0}^{\text{Gauss}} + C/2 \cdot d_{0}^{\text{Gauss}}\), implying that 
the alkyl groups behave like Gaussian chains, yields d\(_{0}^{\text{Gauss}} \approx 0.2\) nm and d\(_{0}^{\text{Gauss}} \approx 0.5\) nm. The 
‘main chain diameter’ d\(_{0}^{\text{Gauss}}\) is unrealistically small in this case, although the d\(_{Gauss}\) value 
is in reasonable agreement with Ferry’s structure length for various vinyl polymers of about 
a\(_F\) \approx 0.5–0.8 nm. Generally, it is questionable whether one of these simple models can be used to 
approximate the C number dependence of \(d_{II}\) in a wide range.

Another interesting aspect is the C number dependence of the scattering intensity in the 
small angle range 0 \(\leq q \leq 1\) nm\(^{-1}\). The experimental finding is that the intensity in this 
plateau region increases systematically with the side chain length for the amorphous PnAMA 
with C \(\leq 10\) (figure 5(d)). Note that the scattering intensity in the region q < 0.3 nm\(^{-1}\) increases 
significantly for all the investigated polymers (figure 5(a)). A similar behaviour is reported 
for several other non-crystalline materials and discussed in the context of long-range density 
fluctuations [25] in glasses.

X-ray scattering curves for poly(n-butyl methacrylates) with different degrees of polymerization \(P\), including the butyl methacrylate monomer and the dibutyl ester of 2,4-dimethyl 
 glutaric acid as dimer analogues, are compared in figure 6. Wide-angle x-ray scattering measurements on polymers and oligomers with the 2D detector (figure 6(a)) show that the general features 
in the scattering curves are very similar down to PnBMA chains with only six monomeric 
units. Especially, the prepeak (II) indicating the nanophase separation is observed for all these 
samples. Its maximum position is nearly independent of the chain length in the range \(P \geq 25\). 
Looking in some more detail on the prepeak using SAXS, one observes that the intensity of the 
prepeak starts to decrease significantly below \(P \approx 25\). This tendency is accompanied by 
a slight shift of the peak maximum to larger q values related to smaller repeating units \(d_{II}\) (figure 6(b)). While \(d_{II} \approx 1.25\) nm is observed for all high-molecular-weight samples (\(P \geq 25\)), 
the scattering data for the hexamer (PnBMA 6) indicate a repeating unit of only \(d_{II} \approx 0.9\) nm. 
For the dimer and the monomer, no pronounced peak maximum could be observed in the SAXS 
data and the prepeak tends to disappear (figure 6(b)). The maximum position of the van der 
Waals’ peak (I) is nearly independent of the chain length for all samples with 6 < \(P < 405\), 
indicating a nearly constant average distance of the non-bounded neighbour atoms in the melt of about \(d_{l} = 0.495\) nm. Preliminary WAXS data for the dimer indicate that the prepeak intensity 
is indeed small and that the van der Waals’ peak shifts significantly to larger q values, i.e. the 
average distance \(d_{l}\) decreases in the small-molecule liquids.

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Figure 6. X-ray scattering data for a series of \textit{n}-butyl methacrylate samples with different degrees of polymerization. Scattering intensities as obtained from (a) WAXS measurements with the 2D detector and (b) SAXS measurements are shown. The curves in (a) are vertically shifted. Labels indicate the degrees of polymerization.

4. Discussion

The results reported here provide additional evidence for the demixing of incompatible main and side chain parts in polymers with long alkyl groups and they support the existence of alkyl nanodomains in the amorphous melt with an independent dynamics and a typical dimension of 0.5–2 nm.

Temperature-dependent NMR line widths for different carbons in PnDMA strongly support the concept—deduced previously from a comparison of dielectric data with shear and calorimetric data—that the backbone and carboxyl group are involved only in the conventional dynamic glass transition \(a\), whereas the dynamics of the side chain carbons C5–C12 is characterized by an independent relaxation process within the alkyl nanodomains at low temperatures, which is basically decoupled from the immobile main chain. In combination with the calorimetric activity and the non-Arrhenius behaviour, these results support the interpretation of this low temperature process as a polyethylene-like glass transition \(\alpha_{PE}\) in PnDMA. In this sense, the NMR results are also a confirmation of the nanophase separation picture for side chain polymers with alkyl groups. Co-operative motions within isolated alkyl groups are impossible and aggregated alkyl groups seem to be a natural assumption considering the lack of mobile main chain carbons and moving dipoles in the frequency–temperature range of the \(\alpha_{PE}\) process.

In an oversimplified picture, the situation in nanophase-separated side chain polymers at low temperatures \((T_{g}(\alpha_{PE}) < T \ll T_{g}(a))\) can be described as follows. There are already very mobile alkyl nanodomains interrupted by immobile main chains. Co-operative motions within these alkyl nanodomains are possible and give rise to the low-temperature glass transition \(\alpha_{PE}\). The continuous, relatively rigid ‘main chain phase’ causes the still relatively high modulus of
the material in this state \((G' \geq 10^8 \text{ Pa})\). The final glass-to-rubber transition occurs after the main chains become mobile and complete monomeric units can move. This happens in the region of the conventional dynamic glass transition \(\alpha\). The influence of the alkyl volume fraction on the main chains is reflected by a shift of the conventional \(T_g\) to low temperatures explained usually by internal plasticization [27]. However, several points are not clear, since details of the morphology are not yet understood. However, it is clear that there should also be changes in the morphology with side chain length or volume fraction \(\Phi\) of the alkyl groups. For short side chains, one would expect isolated alkyl nanodomains, whereas for really long alkyl groups, two continuous phases should occur. In comparison with block copolymers, the situation in nanophase-separated side chain polymers with a high degree of polymerization is \textit{a priori} asymmetric considering the volume fraction \(\Phi\), since the existence of long main chains causes the occurrence of at least one continuous phase for all \(\Phi\) values. Aggregates as discussed in the quasi-one-dimensional picture (figure 1, l.h.s.) appears to be a realistic approach on very-short-length scales, but extended layer-like structures with a large lateral dimension should not exist. This can be concluded from the absence of higher-order maxima belonging to the prepeak in the scattering curves of all side chain polymers investigated. This indicates less regular structures compared with the high degree of order observed in microphase-separated block copolymers [28]. The finding that neither a linear dependence nor the Gauss-like approximation describes the \(d_{II}(C)\) values for amorphous PnAMAs is understandable, since for short alkyl groups, Gauss behaviour is unexpected, whereas for longer alkyl groups in the amorphous state, an all-trans configuration is unlikely.

In any case, the existence of rigid main chains will be a restriction for the cooperative dynamics in small alkyl nanodomains at low temperatures. Since typical features of a dynamic glass transition are observed, one can discuss (at least for \(C > 6\)) the \(\alpha_{PE}\) process as a hindered glass transition in a self-assembled confinement [1]. The possibility to control the size of small nanodomains opens new perspectives and might allow more detailed answers to important questions about cooperativity and dynamic heterogeneities in glasses. The first, more traditional question might be: at which domain size the dynamic glass transition of the confined liquid will differ from the behaviour of the bulk liquid? For the investigated systems, the question is: at which alkyl domain size will the \(\alpha_{PE}\) process become similar (identical) to the glass transition in amorphous polyethylene? It was shown recently that there is at least a tendency in this direction. With increasing alkyl nanodomain size, \(T_g(\alpha_{PE})\) and steepness index \(m(\alpha_{PE})\) approach the values reported for amorphous polyethylene [1]. However, one should note that there are possibly additional complications because of orientation and finally crystallization effects in polyethylene-like materials. The second important question which one can address concerning the confined dynamics is: at which domain size will the relaxation process inside the domains become really a dynamic glass transition? It was shown that the \(\alpha_{PE}\) process in the butyl member, where clear indications for an additional \(\alpha_{PE}\) peak in shear data were observed first, is Arrhenius-like. With increasing side chain length, a strong-to-weak transition was observed [1], i.e. the non-Arrhenius character of the \(\alpha_{PE}\) process increases. An important experimental question is then whether the \(\alpha_{PE}\) process shows from the very beginning a significant calorimetric response or it is becoming calorimetrically active at a certain alkyl nanodomain size. This would add new experimental information to the discussion about early stages of cooperative motions and their relation to more localized secondary relaxations. Such relations are discussed in different approaches to understand the nature of the dynamic glass transition [29, 30]. Unfortunately, calorimetric experiments of this type are complicated, since the small volume fraction of small
alkyl nanodomains causes less pronounced signals in the relevant experiments. The hope is that the increasing sensitivity of newly developed calorimetric methods will help to solve this experimental problem.

The x-ray scattering data presented here suggest that nanophase separation effects are stable against significant variations in the molecular microstructure. Random PnAMA copolymers with a not too different side chain length behave in x-ray scattering experiments like homopolymers with the same average C number. All trends concerning the prepeak are similar to the trends observed for the homopolymers. There is also no dramatic peak broadening, indicating that short and long alkyl groups are mixed in most of the alkyl nanodomains. The number of alkyl groups and the intermixing of different lengths in each nanodomain are, at least for small C number differences, good enough to have mainly one nanodomain size. This does not mean that there is no distribution in the alkyl nanodomain sizes caused by copolymerization, but obviously this effect is not dominating for the investigated copolymers. The fact that the scattering curves are not dominated by one of the comonomers seems to be understandable in the case of amorphous systems having a strong tendency to maximize the density. A large degree of similarity between random PnAMA copolymers and homopolymers in the amorphous state is also observed concerning other physical properties like relaxation effects [31] and the typical low-temperature anomalies in the range below 1 K [32]. Otherwise, it is known that block copolymers made of two different poly(n-alkyl methacrylates) show, in many cases, microphase separation [33]. This suggests that there could also be a tendency in random copolymers with significantly different side chain lengths favouring the aggregation of only one type of alkyl groups in each nanodomain. First experiments on random butyl-lauryl methacrylate copolymers seem to support this idea [34].

Systematic increase in the scattering intensity with increasing side chain length in the plateau region \(0.3 \text{ nm}^{-1} \leq q \leq 1 \text{ nm}^{-1}\) might be an additional indication for the occurrence of a nanophase separation in amorphous PnAMAs. Although we have no absolute values for the scattering intensity so far, there seem to be strong indications for excess scattering in addition to the contributions from density fluctuations [35] in this \(q\) range. A possible explanation would be additional contributions due to concentration fluctuations [36] in nanophase-separated systems. A decrease in the scattering intensity in the same \(q\) range observed for PnAMAs with longer alkyl groups \((C \geq 12)\) seems to be related to side chain crystallization within the alkyl nanodomains, i.e. lack of contributions from fluctuation scattering if the alkyl nanodomains are partly crystalline. Further details of the scattering intensity at low \(q\) values seem to be also interesting in connection with the discussion about long-range density fluctuations [25] and dynamic heterogeneities [30] in glasses. Thus, more detailed information about different contributions to the scattering intensity and absolute scattering intensities would be important.

Scattering data for nBMA systems reaching from the nBMA monomer to long PnBMA chains with \(P = 405\) monomeric units underline the robustness of the nanophase separation phenomenon. Obviously, the main features of the nanophase structure are nearly identical for all polymers and oligomers with \(P > 25\) monomeric units. Note that these PnBMAs have glass temperatures between 303 K (close to the x-ray measurement temperature of 298 K) and 281 K, i.e. the structures in the melt and in the glassy state are comparable. The structure is significantly different for the shortest oligomers \((P \leq 10)\), especially for the monomer and the dimer. Typical indications for a nanophase separation in x-ray scattering curves, namely the prepeak, disappear systematically with decreasing polymerization degree of the system. This shows that the strong tendency of different parts of the molecule to demix is a common feature of all polymeric
systems, whereas for very short oligomers and small molecules, this tendency is reduced or at least very irregular structures are formed. For nBMA systems, the chain structure is obviously an important condition for well-pronounced nanophase-separation effects. Further details of the transition from polymer chains to small molecule liquids seem to be an interesting topic for further investigations.

5. Conclusions

In summary, we have shown in this paper that nanophase separation is a general feature of poly(n-alkyl methacrylates) independent of details of their molecular microstructure. Alkyl nanodomains formed in homopolymers are similar to those in random PnAMA copolymers with the same average number of alkyl carbons per side chain. The alkyl nanodomains in all poly(n-butyl methacrylates) with > 25 monomeric units are practically identical. Only at much lower degrees of polymerization, nanophase separation effects tend to disappear. NMR data for poly(n-decyl methacrylate) support the existence of an independent polyethylene-like glass transition \( \alpha_{PE} \) within alkyl nanodomains of size \( \sim 1 \) nm. Insensitivity of the main findings to significant changes in the molecular microstructure and consistency in the results from different dynamic methods strengthen our opinion that nanophase separation effects are important for an understanding of complex materials in nanoscience and nature.

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