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Multiple Glass Transition and Nanophase Separation in Poly(*n*-alkyl methacrylate) Homopolymers

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ABSTRACT: Shear data in the temperature range from −145 °C to the flow zone are presented for the poly(*n*-alkyl methacrylate)s from methyl ($C = 1$) to lauryl ($C = 12$). Three qualitatively different glass transitions are observed in the shear curves at 10 rad/s: (i) the conventional α process in the $C < 5$ members, (ii) the high temperature *a* process in the $C > 5$ members, and (iii) an additional polyethylene-like glass transition, α_{PE}, in the $C \geq 3$ members. All three processes depend systematically on side chain length. Two alternative empirical pictures for the coexistence of two glass transitions are discussed: (a) a static nanophase separation between main chains and side chains and (b) a dynamic heterogeneity with two different time and length scales.

1. Introduction

The relaxation behavior of a series of poly(*n*-alkyl methacrylate)s was first investigated in the ‘50s and ‘60s by different methods of relaxation spectroscopy[1−7] and dilatometry.[8,9] The dynamic mechanical properties of the members with shorter side chains from poly(methyl methacrylate) (≡methyl, $C = 1$) to poly(*n*-hexyl methacrylate) (≡hexyl, $C = 6$) were systematically studied by Heijboer.[6,11] The relaxation spectrum of the poly(*n*-alkyl methacrylate)s includes several relaxation processes whose frequency−temperature position depends systematically on the *C*-number of carbon atoms in the alkyl part of the side chain. Main topics of the early studies, summarized in ref 10, were the dynamic glass transition, α, and the secondary relaxations, β and γ. For the members above hexyl ($C > 6$), only the simple *a* process (sometimes called αβ) was observed, instead of α and β. A weak, additional relaxation process at lower temperatures was reported by Heijboer[11] for poly(*n*-hexyl methacrylate), at about −110 °C for 0.5 Hz. It was called the “polyethylene-like” glass transition, α_{PE},[12] and connected with the alkyl part of the side chain because of similarities to the glass transition in amorphous polyethylene ($T_g \approx -130$ °C[13]). A similar relaxation process in poly(di-*n*-alkyl itaconate)s was extensively studied by Cowie et al.[14] and discussed in the same way. In the ‘70s, ‘80s, and ‘90s the α relaxation of the lower poly(*n*-alkyl methacrylate)s ($C \leq 6$) has been the subject of many investigations by photon correlation spectroscopy (PCS)[15,16] and calorimetry.[17,18] Moreover the *a*αβ crossover region[19−22] and the molecular mechanisms of α and β relaxations[23] were studied in detail. More recently the relaxation behavior of some higher poly(*n*-alkyl methacrylate)s ($C = 12$ and $C = 10$) was investigated by Floudas et al. using PCS and other methods[24,25] in order to compare the relaxation behavior with that of the lower members.

The aim of this paper is to characterize the three different glass transitions (α, *a*, α_{PE}) in the homologous series of poly(*n*-alkyl methacrylate)s. In particular, the higher members above hexyl ($C > 6$) are included in the discussion of the polyethylene-like glass transition (α_{PE}) and the high temperature *a* process. Shear curves for the amorphous poly(*n*-alkyl methacrylate)s from methyl to lauryl ($C = 1$−$C = 12$) in the temperature range from −145 °C to the flow region are presented. Additional measurements by dielectric spectroscopy and temperature-modulated DSC in poly(*n*-decyl methacrylate) ($C = 10$) are shown for comparison. Wide-angle X-ray scattering (WAXS) results are included to correlate static and dynamic properties.

2. Experimental Section

The poly(*n*-alkyl methacrylate)s were synthesized by standard free-radical polymerization except the octyl and nonyl samples, which are prepared by living polymerization. All samples have high molecular weight ($M_w > 10^5$ g/mol) and similar tacticity (≈78% syndiotactic diades); i.e., the relative temperature shifts of the α-process due to tacticity[26,27] or molecular weight[26−28] are negligible. Dynamic shear modulus was measured at frequencies of 1, 10, and 100 rad/s using a Rheometrics Scientific RDAII in the temperature range from −145 to 150 °C. Strip geometry was used. For the low T_g samples above pentyl ($C > 5$), frozen strips were quickly mounted on the rheometer tools. Strip dimensions, and consequently the absolute modulus values, are relatively uncertain (50%). The temperature effects in the $G^*(T)$ curves are not influenced by this problem. The isothermal annealing time was 100 s at each temperature. Additionally, temperature modulated c_p^* measurements were made using a Perkin-Elmer DSC7 with Pyris software package. Dielectric properties of poly(*n*-decyl methacrylate) in the frequency range from 10 mHz to 1 MHz were studied using a Novocontrol dielectric analyzer. Wide-angle X-ray scattering (WAXS) measurements have been carried out with a Seifert XRD 3000 PTS diffractometer, using Cu Kα radiation ($\lambda = 0.154$ nm).

3. Results and Discussion

The shear loss modulus G'' versus temperature at 10 rad/s is shown in Figure 1 for different poly(*n*-alkyl methacrylate)s between methyl ($C = 1$) and lauryl ($C = 12$). For the members with short side chains ($C = 1$−4) the cooperative α relaxation shifts to lower temperatures with increasing CH_2 content. This behavior was explained[6] by “internal plasticization” of the mate-

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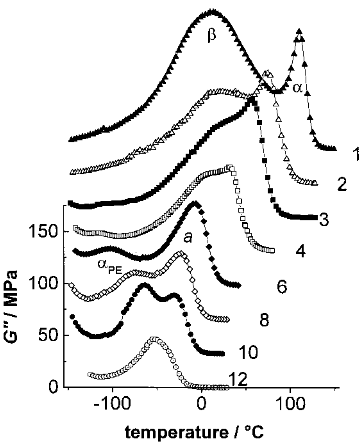

Figure 1. Shear loss modulus versus temperature for different poly(*n*-alkyl methacrylate)s from methyl ($C = 1$) to lauryl ($C = 12$). The shear curves are vertically shifted (33 MPa per curve). The scale is for $C = 12$. The frequency is 10 rad/s.

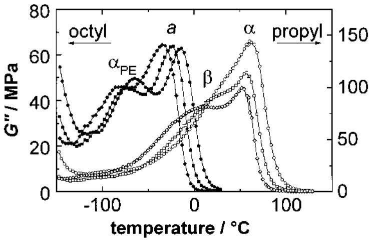

Figure 2. Shear loss modulus at three different frequencies (1 rad/s, diamonds; 10 rad/s, squares; 100 rad/s, circles) versus temperature for poly(*n*-propyl methacrylate) (open symbols) and poly(*n*-octcyl methacrylate) (full symbols). The different relaxation processes α, *β*, *a*, and α_{PE} are indicated.

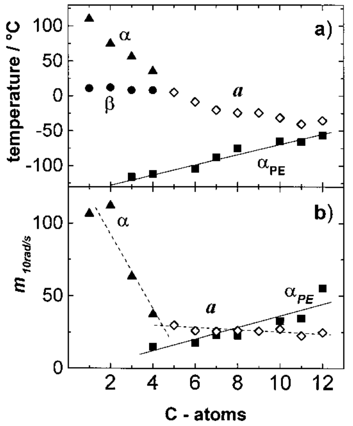

Figure 3. (a) Relaxation temperatures for different relaxation processes α, *β*, *a*, and α_{PE} as function of side chain length. The symbols correspond to the maxima positions in the shear curves at 10 rad/s. (b) Fragility of the α, *a*, and α_{PE} traces in the Arrhenius diagram at a frequency of 10 rad/s. The points were calculated from isochrones (Figure 2).

rial due to the CH_2 groups in the side chain. The temperature position of the loss peak for the secondary *β* relaxation, $T_{\beta,10\mathrm{rad/s}}$ remains nearly unaffected by side chain length (Figure 3a). This indicates the local character of the underling motions as typical for *β* processes.[29] The *β* relaxation in poly(*n*-alkyl methacrylate)s involves a stepwize rotation of the carboxyl group of the side chain accompanied by a main chain rearrangement.[23] A comparison of temperature sweeps for poly(*n*-propyl methacrylate) ($C = 3$) at different frequencies (Figure 2) shows that α and *β* relaxations converge at higher frequencies. The frequency−temperature range where α and *β* relaxation times become comparable is called α*β* splitting or *a*α*β* crossover region. Detailed studies of this region by broad band dielectric and shear spectroscopy were reported elsewhere.[5,7,10,20,22,30] It was shown[20,30] that the α*β* splitting frequency is lowered about one decade per additional CH_2 group in the side chain and that the cooperative α relaxation sets in with zero intensity in this region.

An alternative view on the α*β* splitting gives the relaxation temperature vs *C*-number diagram for the poly(*n*-alkyl methacrylate)s (Figure 3a). The relaxation temperatures of α and *β* processes merge near the pentyl member ($C \approx 5$) for the frequency selected (10 rad/s). Above hexyl ($C > 6$), only one relaxation process, the high temperature *a* relaxation, could be observed instead of separate α and *β* processes. Although the trace of the high-temperature process *a* is curved in an Arrhenius diagram[20,28] and shifts to lower temperatures with increasing side chain length, similar to the α trace, the behavior of both relaxation processes is qualitatively different (Figure 3b). While the fragility, $m = \mathrm{d}(\log T)/\mathrm{d}(\ln T)|_{T=T_\alpha}$,[31] for the members below pentyl (=the α process) depends strongly on side chain length and distance to *a*α*β* crossover region, the fragility for the higher members (=the *a* process) remains small and nearly constant.

A detailed investigation of the crossover substance poly(*n*-hexyl methacrylate) by means of dynamic calorimetric and dielectric methods in a wide frequency range is published in ref 21. The *a* relaxation above and the α relaxations below the *a*α*β* crossover region are two distinct, qualitatively different relaxation processes. A separate onset of the α relaxation at $T_{\mathrm{on}} \approx 8$ °C and $\omega_{\mathrm{on}} \approx 10$ rad/s, about one frequency decade below the *aβ* trace in the Arrhenius diagram, was observed for poly(*n*-hexyl methacrylate).

The analogy of our findings in the frequency dependence for a given substance and the *C*-number dependence for a given frequency indicates a certain degree of similarity of the relaxation behavior in different poly(*n*-alkyl methacrylate)s. The separateness of the α onset points to a property that is only typical for α and that is absent for *a*. This new element for α is expected to be molecular cooperativity.[32] This was concluded from the size of cooperatively rearranging regions (CRRs)[33] for several poly(*n*-alkyl methacrylate)s using a caloric fluctuation formula.[34] The cooperativity, N_α, i.e., the number of particles (monomeric units) per CRR, is small and constant for the *a* process ($N_a \leq 1$) while it strongly increases below the crossover for the α relaxation, up to typical values of $N_\alpha \approx 100$.[32]

Besides α, *β*, and *a*, an additional relaxation process at low temperatures was observed for all members above propyl ($C \geq 3$) (see Figure 1). This relaxation process was first reported by Heijboer for poly(*n*-hexyl methacrylate)[11] and discussed to be a polyethylene-like glass transition, α_{PE}.[12] Our measurements on the higher poly(*n*-alkyl methacrylate)s show that this process exists in all higher poly(*n*-alkyl methacrylate)s, contrary to a prediction by Cowie et al.[14] Its intensity increases systematically with increasing *C*-number. The relaxation temperature, $T_{\alpha_{PE},10\mathrm{rad/s}}$, increases with the *C*-number, contrary to the *a* process. Consequently, α_{PE} and *a* approach each other with increasing *C*-number. In poly(*n*-lauryl methacrylate) ($C = 12$), the relaxation temperatures are similar and a common relaxation process was observed at 10 rad/s. It seems to be an

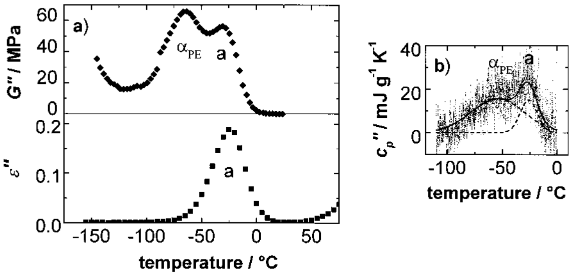

Figure 4. (a) Shear loss modulus, $G''(T)$, compared with dielectric loss function, ϵ'' (T), at a frequency of 10 rad/s for poly(*n*-decyl methacrylate). (b) Imaginary part of the complex heat capacity c_p'' (time period τ_p = 60 s) as function of temperature for decyl ($C = 10$). The dashed lines are Gaussian functions for the α and *a* component, respectively. The solid line gives the sum. The peak maxima for *a* and α_{PE} are at −25 and −54 °C, respectively.

interesting question to investigate *a* and α_{PE} in higher poly(*n*-alkyl methacrylate)s. We may ask whether the traces will intersect or only one of the processes survives.

The shear curves for poly(*n*-octyl methacrylate) ($C = 8$) in Figure 2 and the fragilities in Figure 3b indicate that the slopes in the Arrhenius diagram for α_{PE} and *a* are independent. In the members above nonyl ($C > 9$), the α_{PE} and *a* peaks seem to merge also when the frequency decreases. The fragility of both processes is significantly smaller than that of the cooperative α process far below the crossover (Figure 3b). The increase of the α_{PE} fragility (Figure 3b) and of α_{PE} intensity (Figure 7) with side chain length can be interpreted as the first hint to an increasing cooperativity of the polyethylene-like glass transition.

Experimental evidences assisting the α_{PE} cooperativity are assembled in Figure 4: The upper part shows the shear loss modulus and dielectric loss function versus temperature at comparable frequencies for poly(*n*-decyl methacrylate) ($C = 10$). It is obvious that only the *a* process is dielectrically active while α_{PE} is not active in the ϵ'' data (the intensity ratio for butyl is $\Delta\epsilon_{\alpha_{PE}}/\Delta\epsilon_a \leq 0.1$). This means that the carboxyl group of the side chain, where the main dipole moment of the monomeric unit is located, is not involved in the α_{PE} motion. This observation corresponds to the intensity increase of the α_{PE} loss peak with increasing *C*-number. The lower part of Figure 4 shows the $C_p''(T)$ curve for poly(*n*-decyl methacrylate). Two peaks are observed: The peak for the *a* process near −25 °C and an additional peak near −54 °C. The latter is considered as an important indication for the cooperativity of the α_{PE} process. Local secondary relaxations usually have not any significant calorimetric activity.[35]

We conclude that two calorimetrically active relaxation processes coexist in the members between propyl ($C = 3$) and lauryl ($C = 12$). The glassy material is not completely frozen below the glass transition temperature of the *a* (or α) process. Usually, there are local secondary relaxations that are operating in the glassy state. In our series, however, we have a second *cooperative* process, α_{PE}, which works also when the primary cooperative process is frozen. This is really unusual for homopolymers. We suggest two alternative ad hoc pictures to explain this behavior in our polymers: static and dynamic heterogeneities.

Static Picture. The coexistence of two cooperative α relaxations is typical for microphase-separated block copolymers,[36] while homopolymers, miscible copolymers, and plasticized homopolymers usually exibit one loss peak. This leads to the hypothesis that there may be some kind of microphase separation also in the poly(*n*-alkyl methacrylate)s with long side chains. Although our samples are homopolymers, we may expect a phase separation tendency between the main chain parts of the polymers and the alkyl side chain parts. A similar interpretation was given by Cowie et al.[14] for the higher poly(di-*n*-alkyl itaconate)s above di-*n*-heptyl showing also two glass transitions. The idea is that the side chains of different monomeric units (from the same or from different macromolecules) aggregate beause the polar methacrylate main chain and the nonpolar alkyl side chains are immiscible. This leads to a system which is (more or less) phase-separated, but only on very short length scales because the separation tendency is hindered by more local topological constraints than in block copolymers. A typical scale may be about 1 nm. We tend to call this effect *nanophase separation*.[45] At present we do not know a theoretical approach to this problem. We suppose that molecular aspects play a larger role than in the block copolymer morphology.[37] Results from wide-angle X-ray scattering (WAXS) on some samples are shown in Figure 5. Two pronounced peaks are detected in the higher poly(*n*-alkyl methacrylate)s (Figure 5a): (I) a main peak at $Q = 4\pi \sin \theta/\lambda \approx 13$ nm^{-1} which is nearly side chain independent and (II) a prepeak in the region 3.5 nm^{-1} ≤ Q ≤ 6 nm^{-1}, which shifts to lower angles with increasing side chain length. A third peak between the main peak and the prepeak at about $Q \approx 8$ nm^{-1} sometimes reported in the literature[25,39] will not be discussed here. Its intensity is only important in the ethyl to butyl members[39] and is very small in the higher members.

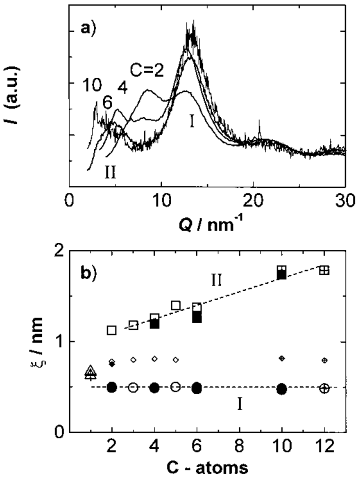

Figure 5. (a) Wide-angle X-ray scattering (WAXS) curves for some poly(*n*-alkyl methacrylate)s. Main peak and prepeak are indicated by I and II, respectively. (b) Equivalent Bragg spacings as function of *C*-number, i.e., the number of carbon atoms in the alkyl side chain. The spacings for an additional peak (diamonds) reported in the literature[25,39] are also given (open symbols, from ref 39, cross at center, from ref 25; filled symbols, this work). The lines are drawn to guide the eyes.

For the estimation of characteristic distances from the peak positions we used Bragg's law, $\xi = 2\pi/Q$, as an approximation. The corresponding distances are shown in Figure 5b: The main peak gives a nearly side chain independent periodicity of about 0.5 nm, while the prepeak indicates an additional length scale which increases from $\xi \approx 1$ nm in ethyl (*C* 2) to about $\xi \approx 1.8$

nm in lauryl ($C = 12$).[40] The interpretation may be that the main peak reflects the chain to chain or side chain to side chain distance, while the prepeak is an additional length scale in the nanometer range. In a first variant, the existence and position of the prepeak could be understood as an indication for a nanophase separation in the higher poly(*n*-alkyl methacrylate)s. In an other variant, it may be simply interpreted as a typical distance between dissolved backbones in the melt.[25,41] A decision between the two variants should be possible by a more detailed analysis of the prepeak position as a function of *C*-number. The details are the scope of further investigations.

As no sharp peak as typical for crystallinity was detected, our samples are considered amorphous. Nevertheless the increase of $T_{\alpha_{\mathrm{PE}},10\mathrm{rad/s}}$ with increasing side chain length could be an indication for an increasing molecular order[1] in the PE-like nanophase (Figure 3a).

Dynamic Picture. A completely different, alternative explanation for the coexistence of two glass transitions in higher poly(*n*-alkyl methacrylate)s would be the existence of a dynamic heterogeneity with characteristic length scales in these polymers, one upon the other.[42] The idea is to have a dynamic pattern which fluctuates in time and space with two inherent time and length scales. Such a picture was presumed[38] for the existence of a main glass (α) and a terminal transition (flow transition) in entangled polymers. Each part of the molecules would then be involved in two motions, but with different time scales. A similar picture was not a priori excluded for our poly(*n*-alkyl methacrylate)s. One cooperative relaxation process happens on small length scales in short times while a second one has to do with a cooperative motion on larger length scales in longer times.

Although the static picture seems more plausible, a final decision between the alternative explanations is impossible at the moment. An important point would be whether the *a* and α_{PE} traces in Figure 3a intersect or merge for *C*-numbers larger than 12. The interplay of a complex (static or dynamic) nanoscale heterogeneity and glass transition may be also interesting. The background is the long-standing question for the existence and size of cooperatively rearranging regions (CRRs)[33] as a basic feature of the dynamic glass transition.[34,43,44] Which minimal size of nanodomains is necessary for the existence of independent glass transitions seems to be interesting. Furthermore, the understanding of the complex relaxation behavior of poly(*n*-alkyl methacrylate)s and its derivatives is substantial for the optimization of material properties in a lot of applications.

4. Conclusion

Three qualitatively different dynamic glass transitions are observed in poly(*n*-alkyl methacrylate)s: *a*, α, and α_{PE} processes. It is shown that *a* and α glass transitions above and below the $a\alpha\beta$ crossover behave differently with respect to fragility. The additional low temperature glass transition in the members between propyl ($C = 3$) and lauryl ($C = 12$) is related to a polyethylene-like glass transition (α_{PE}). Two empirical pictures are suggested to explain the unusual coexistence of two glass transitions in the higher poly(*n*-alkyl methacrylate) homopolymers: A static nanophase separation or a dynamic heterogeneity with two intrinsic length scales.

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(12) Remark: In ref 1 the low-temperature peak at ≈ -125 °C and ≈ 300 cps for poly(stearyl methacrylate) was discussed as "segmental rearrangements in the 18 carbon atom alkyl side chains", i.e., as a kind of polyethylene-like glass transition. This assignment is not consistent with our understanding of the relaxation map for the poly(*n*-alkyl methacrylate)s. We think that this procress is the secondary relaxation (γ), which slightly shifts with side chain length or molecular order in the PE-like side chain phase ($T_\gamma(C{=}3) \approx -150$ °C and T_γ $(C{=}18) \approx -125$ °C). An additional loss peak at ≈ -50 °C was also observed by Hoff et al. in poly(stearyl methacrylate).
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