Macromolecules **1999,** *32,* 5701−5703 **5701**

Notes

Effect of Molecular Weight on αβ Splitting Region of Dynamic Glass Transition in Poly(ethyl methacrylate)

S. Reissig,[†] M. Beiner,[†] S. Zeeb,[‡] S. Höring,[‡] and E. Donth*,[†]

Fachbereich Physik and Fachbereich Chemie,
Universität Halle, D-06099 Halle (Saale), Germany

Received August 26, 1998

Introduction

The relaxation behavior of glasses is characterized by multiple relaxation processes that can be detected by different experimental methods. It is well-established that many glasses, e.g., amorphous polymers[1] and small-molecule glass formers,[2] exhibit a main or α process and a secondary *β* or Johari−Goldstein[2] process. In an Arrhenius plot (logarithm of frequency vs inverse temperature) relaxation frequencies of the main process α show a curved trace that can usually be parametrized by a WLF equation,[3] whereas the *β* process follows an Arrhenius law linear in this plot. The α process is generally attributed to cooperative motions of many particles, whereas the *β* process is associated with more local motions. Both relaxation processes approach each other with increasing temperature and frequency in the so-called crossover region. Above this region, only one process, the "high-temperature process" *a* (sometimes called α*β*) can be observed.

The crossover region in poly(*n* -alkyl methacrylate)s was extensively investigated by different linear-response methods.[4−9] A typical scenario[6] was observed in poly(*n* -butyl methacrylate), P*n*BMA: The *a* and *β* traces are continuously connected, whereas the α trace sets in separately about 1 frequency decade below the continuous *aβ* trace, with linearly increasing α intensities $\Delta\epsilon_\alpha$ and Δc_p. In general, we have two scenarios, I and II. (I) The scenario as described above, i.e., with a separate α onset, will be called the splitting scenario. (II) A second scenario,[10−12] with a seemingly continuous *a*α trace, will be called the merging scenario.

We asked whether the splitting scenario is specific for P*n*BMA or typical for a more general system class. P*n*BMA was therefore chemically disturbed by (i) the variation of the *n* -alkyl side chain length inclusive of random copolymerization with respect for different side-chain lengths, (ii) external plasticization with DOP, and (iii) random copolymerization of *n* -BMA with styrene.[13] The change of the crossover was always the same: We remain in the splitting scenario. The details correspond to an old conjecture of Williams concerning the pressure dependence:[5] Both relaxation processes, *a* and α, move to lower temperatures (higher mobilities) when the disturbance can be interpreted as an increase of free volume, whereas the *β* process position in the Arrhenius plot approximately remains unchanged. Although the splitting scenario remains unchanged, the details seem to be different for different disturbances.[13] This means that the influence of free volume on the splitting can not be parameterized by one parameter.

It is well-known that lower molecular weights also correspond to larger free volumes.[14] The aim of this paper is to investigate if the α*β* splitting behavior for poly(ethyl methacrylate) (PEMA) depends on molecular weight in a way similar to those described for the other free-volume disturbances.

Experimental Section

The molecular characteristics of the poly(ethyl methacrylate)s investigated are listed in Table 1. Samples I and IV were purchased from Polysciences, Inc., and Polymer Standards Service, respectively. Samples II and III are synthesized by group transfer polymerization.[15] The tacticity of all the samples as determined by NMR is comparable (see Table 1); i.e., the influence of tacticity on the relaxation behavior is small. Specific heat of the samples was measured in a Perkin-Elmer DSC 7 at a heating rate $\dot{T} = +10$ K/min after a cooling run with $\dot{T} = -10$ K/min. The glass temperatures in Table 1 were calculated from the thermograms using an equal-area construction. All samples were carefully dried at a temperature between 100 and 130 °C for 12 hours under vacuum to remove moisture, residual solvent, or monomer.

The dielectric function $\epsilon^*(\omega,T)$ was measured using a BDS 4000 system from Novocontrol. Isothermal frequency scans were performed at temperatures between −40 and 150 °C. The frequency ranges from $\omega = 2\pi \times 10^{-2}$ to $\omega = 2\pi \times 10^{6}$ rad/s.

One, or a sum of two Havriliak Negami (HN) functions,[16]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega/\omega_0)^b]^g} = \epsilon' - i\epsilon'' \tag{1}$$

and an additional conductivity term ($\sim\omega^{-1}$) were used to fit the isothermal ϵ'' data. The details of the fitting procedure are described in Kahle et al.[17] The exponents b and g ($0 < b, g \leq 1$) in eq 2 describe the shape of the ϵ'' peak: b and $-bg$ are the slopes of low- and high-frequency wing in a double logarithmic plot log ϵ'' vs ϵ'' log ω. The parameter ϵ_∞ gives the real part of permittivity at very high frequencies outside the dispersion zone, and $\Delta\epsilon$ is the intensity or relaxation strength of the relaxation process. The HN frequency, ω_0, is connected with frequency of maximum loss, $\omega_{\max}$, used for the representation in the Arrhenius plot, by the equation

$$\omega_{\max} = \omega_0 \left\{ \frac{\sin[\pi g b/(2g + 2)]}{\sin[\pi b/(2g + 2)]} \right\}^{-1/b} \tag{2}$$

Results and Discussion

The dielectric isotherms at $T = 70$ and 80 °C for poly(ethyl methacrylate)s with different molecular weights illustrate different stages of the α*β* splitting process (Figure 1): At high temperature and low molecular

---

* E-mail: donth@physik.uni-halle.de.

[†] Fachbereich Physik.

[‡] Fachbereich Chemie.

10.1021/ma9813441 CCC: $18.00

Table 1. Molecular Characteristics of the Poly(ethyl methacrylate) Samples

sample	symbol	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	tacticity (% synd. diads)	T_g (°C)	T_{on} (°C)	log ω_{on}[a] (rad/s)
I	□	154	1.90	78	74	107	3.6
II	●	21	1.26	78	55	84	2.8
III	△	7.1	1.37	78	42	72	2.6
IV	♦	1.65	1.08	80	10	39	2.3

[a] Obtained at the onset temperatures of Figure 2b from the WLF parameters for the α process. In this paper, log means $\log_{10}$.

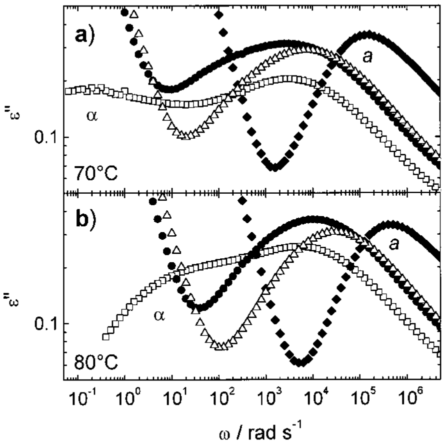

Figure 1. Double-logarithmic plot of dielectric loss vs frequency at 70 (a) and 80 °C (b) for poly(ethyl methacrylate)s with different molecular weights. The symbols are explained in Table 1.

weight, only one relaxation process, the high-temperature process *a*, was observed. The corresponding isotherms can be fitted with one HN function and the additional conductivity term without systematic deviations. With decreasing temperature or increasing molecular weight, a slight shoulder appears on the low-frequency wing of the loss peak, indicating the emerging α relaxation. These isotherms cannot be approximated by only one HN function. An additive superposition of two HN functions, representing α and β relaxation, was used. At low temperature and high molecular weight, two well-separated relaxation processes (α and β) can be detected. At least in the frequency−temperature range investigated, this separation process is accompanied by a decrease of the maximal dielectric loss under isothermal conditions. Similar behavior in this region was previously observed for poly(*n*-alkyl methacrylate)s with different side-chain lengths.[6,7] In a way, the isotherms in Figure 1 indicate that the changes in *M* and T^{-1} affect the dielectric relaxation behavior in a similar way; i.e., for a certain distance from the αβ splitting, the shape of the isotherms seems comparable.

In the Arrhenius plot (Figure 2a), the complete αβ splitting region shifts along the β trace to lower temperatures and frequencies with decreasing molecular weight *M*. In other words, the β process is practically independent on molecular weight while α and *a* shift to lower temperature and frequency. The topology of the αβ splitting region is not affected by molecular weight. A quasicontinuous *a*β trace was observed for all samples by HN fits to the dielectric data. The α trace is well-separated and starts about 1 frequency decade below. Below the onset, the relaxation strength of the α process increases linearly for all molecular weights, $\Delta\epsilon_\alpha \sim (T^{-1} - T_{on}^{-1})$ (Figure 2b). The slope $d\Delta\epsilon_\alpha/dT^{-1}$ does not significantly depend on *M*. The α onset temperature T_{on} (Table 1) can be linearly extrapolated for temperatures where $\Delta\epsilon_\alpha \rightarrow 0$. The corresponding onset frequency, ω_{on}, is calculated using the WLF parameters of the α trace. The frequency−temperature position of the α onset in the Arrhenius plot is indicated by crosses in Figure 2a. The onset shifts to lower frequencies and temperatures with decreasing molecular weight, as does the whole αβ splitting region. The variation of *M* does not change the scenario; we remain in the splitting scenario.

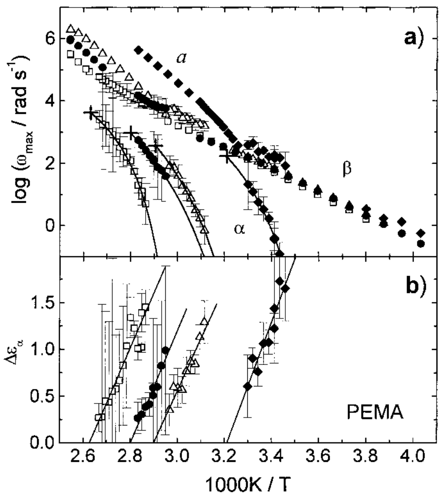

Figure 2. (a) Arrhenius plot for poly(ethyl methacrylate)s with different molecular weights (for explanation of symbols, see Table 1; *a* = high-temperature process above the crossover, α = cooperative process below the crossover, β= local Johari−Goldstein process). The error bars indicate the uncertainty of the fitting procedure in the αβ splitting region. The crosses mark the α process onsets. (b) Dielectric intensity of the α relaxation vs inverse temperature. The straight lines are linear fits used for the extrapolation $\Delta\epsilon_\alpha \rightarrow 0$ to the α onset temperatures T_{on}.

As shown previously for poly(*n*-hexyl methacrylate),[7] all three relaxation processes α,β, and *a* behave qualitatively differently; i.e. there are three distinct, relatively independent relaxation processes.[5−7] Regarding the dielectric behavior, the influences of molecular weight, internal or external plasticization, and pressure[5] on the *a* and α processes are similar. We think, therefore, that both processes are similarly affected by free volume.

The separateness of the α onset, however, points to a property that is only typical for α but not for *a*. This new element for α is expected to be the intermolecular cooperativity of the molecular environment. This was concluded from the determination of the size of cooperatively rearranging regions (CRR)[18] for several poly(*n* -alkyl methacrylate)s using a fluctuation formula.[19] The interpretation is that the *a* process is connected with localized cage escape motions in a material that is dynamically homogeneous. The α relaxation is characterized by a slower cooperativity shell around these cages assisting the escape. The material becomes dynamically heterogeneous with a characteristic length of 1...3 nm. The details of this empirical picture are discussed elsewhere.[20]

As mentioned above, the β trace is not significantly affected by molecular weight (and pressure); i.e., the effect of free volume on the underlying motions is small. This finding is consistent with the picture given by Kuebler et al.[21] They conclude from NMR experiments that a stepwise side-chain rotation accompanied by a reorientation of the backbone is responsible for the β process in PEMA.

We conclude that our PEMA series behaves similarly to other methacrylate polymers: Decreasing molecular weights corresponds to larger free volumes, which does not change the crossover scenario. Both *a* and α relaxations shift to lower temperatures. This proves that the P*n*BMA splitting scenario is stable against many chemical disturbances. It represents, therefore, a distinct and independent crossover scenario that may also be representative for a certain class of other substances.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft DFG (Graduiertenkolleg "Heterogeneous Polymers") and the Fonds Chemische Industrie FCI for financial support. We are grateful to C. Schicktanz and Prof. K. Schlothauer (Merseburg) for the determination of the tacticities by NMR.

References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967 (reprint 1991).
(2) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.
(3) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(4) Ishida, Y.; Yamafuji, K. *Kolloid-Z.* **1961**, *177*, 98.
(5) Williams, G. *Trans. Faraday Soc.* **1966**, *62*, 2091.
(6) Garwe, F.; Schönhals, A.; Lockwenz, H.; Beiner, M.; Schröter, K.; Donth, E. *Macromolecules* **1996**, *29*, 247.
(7) Beiner, M.; Kahle, S.; Hempel, E.; Schröter, K.; Donth, E. *Europhys. Lett.* **1998**, *44*, 321; *Macromolecules* **1998**, *31*, 8973.
(8) Bergman, R.; Alvarez, F.; Alegria, A.; Colmenero, J. *J. Chem. Phys.* **1998**, *109*, 7546; *J. Non-Cryst. Solids* **1998**, *235−237*, 580.
(9) Floudas, G.; Stepanek, P. *Macromolecules* **1998**, *31*, 6951. Meier, G.; Kremer, F.; Fytas, G.; Rizos, A. *J. Polym. Sci.: Polym. Phys. Ed.* **1996**, *34*, 1391.
(10) Kahle, S.; Schröter, K.; Hempel, E.; Donth, E. *J. Chem. Phys.*, in press.
(11) Alvarez, F.; Hoffmann, A.; Alegria, A.; Colmenero, J. *J. Chem. Phys.* **1996**, *105*, 432.
(12) Arbe, A.; Richter, D.; Colmenero, J.; Farago, B. *Phys. Rev. E* **1996**, *54*, 3853.
(13) Beiner, M. Review on the "Crossover Region of Dynamic Glass Transition in Poly(*n* -alkyl methacrylate)s" In preparation.
(14) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950** , *21*, 581.
(15) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(16) Havriliak, S.; Negami, S. *J. Polym. Sci. Part C: Polym. Symp.* **1966**, *14*, 99.
(17) Kahle, S.; Korus, J.; Hempel, E.; Unger, R.; Höring, S.; Schröter, K.; Donth, E. *Macromolecules* **1997**, *30*, 7214.
(18) Adam, G.; Gibbs, H. J. *J. Chem. Phys.* **1965**, *43*, 139.
(19) Donth, E. *J. Non-Cryst. Solids* **1982**, *53*, 325.
(20) Kahle, S.; Hempel, E.; Beiner, M.; Unger, R.; Schröter, K.; Donth, E. *J. Mol. Struct.* **1999**, *479*, 149.
(21) Kuebler, S. C.; Schaefer, D. J.; Boeffel, C.; Pawelzik, U.; Spiess, H. W. *Macromolecules* **1997**, *30*, 6597.

MA9813441