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Dynamic shear modulus in the splitting region of poly(alkyl methacrylates*)

M. Beiner, F. Garwe, K. Schröter, and E. Donth

Fachbereich Physik, Universität Halle, Halle (Saale), FRG

*) *Dedicated to Prof. E. W. Fischer at the occasion of his 65th Birthday*
Lieber Herr Fischer, die Hallenser Polymerphysiker danken Ihnen aufrichtig für die warmherzige und effektive Förderung der Polymerwissenschaften im Raum Halle-Merseburg.

Abstract: A systematic study of the dynamic shear modulus $G^* = G' + G''$ in three poly(alkyl methacrylates) (PEMA, PnPMA, PnBMA) at frequencies between 0.001 and 500 rad/s is presented. As the $\alpha\beta$ splitting frequencies ω_s are low, aging effects can be observed in the splitting region. There is a systematic shift of the splitting frequency ω_s to lower values with increasing length of the alkyl side group. In PnBMA a separate shear α appearance is observed about two frequency decades below the local mode β. This is discussed in terms of the concept of minimal cooperativity. Aging effects are: Shift of the maximum loss frequency ω_α to lower values, peak sharpening of the α relaxation, and intensity changes of α and β. These effects are discussed in terms of the sequential aging concept. Aging leads to a pronounced bending of the α traces upwards from the equilibrium line in the Arrhenius diagram. These non-equilibrium phenomena are promoted by the small slope $m_\alpha = d(\log \omega_\alpha)/dT$ of the α trace in the splitting region.

Key words: Splitting region – physical aging – glass transition – shear modulus – poly(ethyl methacrylate) – poly(*n*-propyl methacrylate) – poly(*n*-butyl methacrylate)

1. Introduction

Studies in the splitting region, where the high-temperature-relaxation (a) splits into the main transition (α) and the ordinary secondary relaxation (β), are assumed to give some ideas about the molecular cooperativity of the developing dynamic glass transition α, and possible interrelations between α and the local mode β [1, 2]. Interesting questions are, for example, the behavior of the characteristic length ξ_a for the dynamic glass transition [3–5] and the thermokinetic heterogeneity [6, 7] there.

Physical aging is a well known phenomenon in polymer glasses [8–10]. There are some theoretical approaches for the explanation of some details of the aging process, such as shape and intensity variation of α and β relaxation [11–14]. Nevertheless, a generally accepted treatment for the quantitative description has not existed up to now.

Time-dependent measurements in the splitting region S are necessary in our substances because the glass transition temperature T_g and the splitting temperature T_S are close to each other [15, 16] so that aging is unavoidable. A second peculiarity is that the slope $m_\alpha = d(\log \omega_\alpha)/dT$ of the α trace in the splitting region is small (Fig. 1).

The interrelation of splitting and physical aging should give some information about a possible fine structure in the α relaxation and in the region between α and β because the cooperativity is assumed to be low near the α onset [6].

Poly(alkyl methacrylates) were used because the splitting region in these polymers is in the Hz. . . kHz frequency range accessible for precise

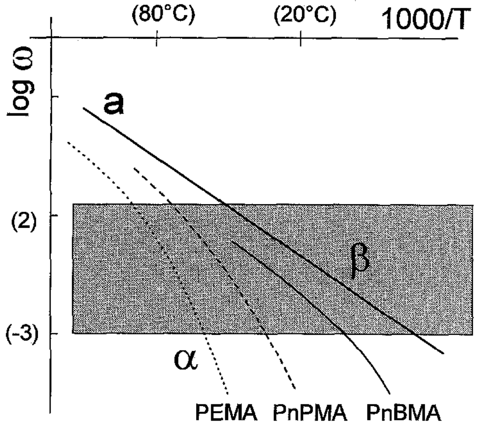

Fig. 1. Schematic Arrhenius diagram of the splitting region in a series of poly(alkyl methacrylates) (ethyl, *n* propyl, *n* butyl). The gray region is the frequency window of our dynamic shear measurements

dynamic shear measurements. Furthermore, the α onset frequency depends systematically on the length of the alkyl side group while the β relaxation is nearly independent from the alkyl group (see [17–19] and the schematic Arrhenius diagram in Fig. 1).

The aim of this paper is a systematic study of the shear response in the splitting region of poly(ethyl methacrylate), PEMA, poly(*n*-propyl methacrylate), PnPMA, and poly(*n*-butyl methacrylate), PnBMA.

2 Experimental

2.1 Samples

The polymer samples were purchased by Polyscience Inc. and measured as received. Several repeating measurements at the end gave the same results so that the measurements are thermoreversible. The polymers have an average molecular weight M_w of 72 ± 3 kg/mol (PEMA), 292 ± 10 kg/mol (PnPMA) and 330 ± 8 kg/mol (PnBMA). The M_w/M_n ratios are 1.9 ± 0.1 (PEMA), 5.0 ± 0.3 (PnPMA) and 2.35 + 0.1 (PnBMA). The molecular weight distribution of PnPMA is slightly bimodal with a main peak at $M = 76 \pm 5$ kg/mol and a second peak at $M = 340 \pm 20$ kg/mol. The M_w and M_w/M_n values are determined by gel permeation chromatography (GPC). The glass transition temperatures T_g were calculated by an equal area construction from DSC measurements ($\dot{T} = +10$ K/min). The T_g values are: 72 ± 1 °C for PEMA, 46 ± 1 °C for PnPMA and 24 ± 2 °C for PnBMA. NMR experiments show that our poly(alkyl methacrylates) are atactic, with 78 ± 4% syndiotactic sequences (corresponding to 60% syndio triads).

2.2 Mechanical measurements

Two different mechanical spectrometers RDA II from Rheometrics Inc. were used. All measurements were performed in torsion on specimen of rectangular cross-section (width 10 mm, thickness 1.5 mm, length 25 mm). The strain amplitude of 0.2% was well within the limits of linear response. The temperature stability was ± 0.2 K.

All the time-dependent shear measurements are realized in the same manner. The time-temperature program is schematically shown in Fig. 2. The different stages are labelled by arabic numbers: 1) The sample was held for 10 min at a temperature T_i (PEMA: 105 °C, PnPMA: 65 °C, PnBMA: 50 °C) above T_g. The "memory" of the glass transition is deleted by means of this procedure. 2) The sample was rapidly cooled down to the measuring temperature T_e with a cooling rate of 0.9 ± 0.2 *K*/s. 3) The sample was held at T_e for 5 min without shear measurement. Within this time the main temperature gradients inside the sample are assumed to be equilibrated. 4) The isothermal dynamic shear measurements labelled by $t_e = 5$ min are started. Frequency sweeps in the

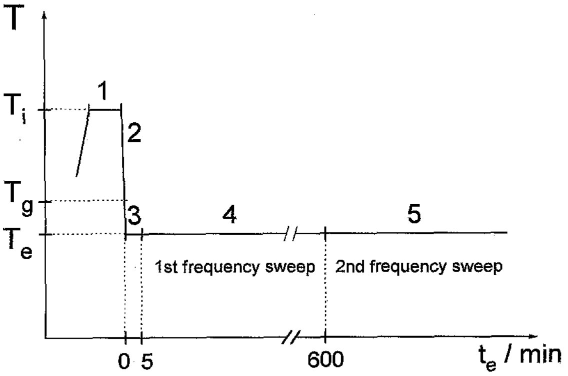

Fig. 2. Time-temperature program used for the measurements of the dynamic shear modulus $G^*(\omega, T_e, t_e)$; T_e = experimental temperature; t_e = nominal aging time. It should be mentioned that the aging time really runs during the isothermal frequency sweeps

range from 500 to 0.001 rad/s were performed continuously beginning at high frequencies. 5) The second frequency sweep starts after an aging time $t_e = 600$ min, counted from stage 3.

3. Results

Figure 3 shows the time-dependent measurements of the shear loss modulus G'' (ω, t_e) in PEMA at temperatures between 57 and 80 °C. Figure 3a shows G'' as a function of frequency for $t_e = 5$ min. The parameter is the aging = measuring temperature T_e. The frequency window of shear measurements is far below the α onset in poly(ethyl methacrylate). Therefore, the G'' peaks for α and β relaxation are clearly separated at all the temperatures T_e. The G'' data after $t_e = 10$ h isothermal aging are shown in Fig. 3b.

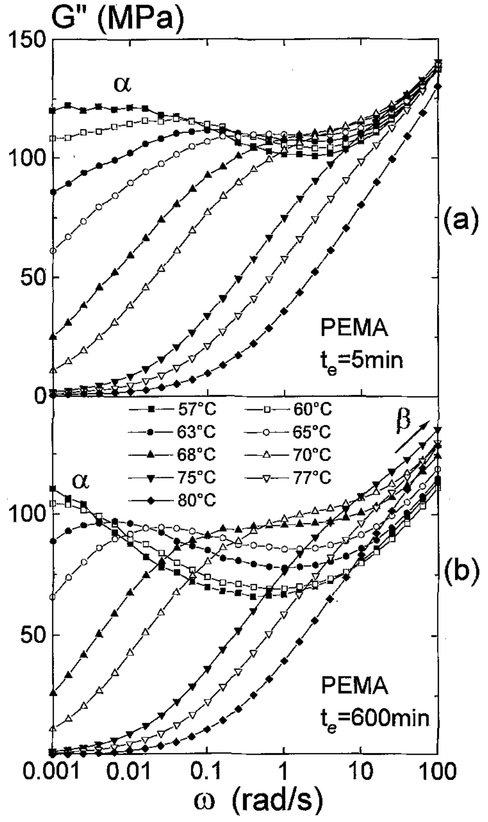

Fig. 3. Shear loss modulus $G''(\omega)$ in PEMA for $t_e = 5$ min (a) and $t_e = 600$ min (b) at different temperatures T_e around the DSC glass transition temperature T_g. The lines are only guides for the eyes

Physical aging leads to an increasing separation of the relaxation maxima for α and β at temperatures below T_g. This is a consequence of a time-dependent shift of the maximum loss frequency ω_α to lower values, a typical effect of the physical aging in glasses. This effect is especially pronounced in the temperature range from 57 to 65 °C. The shift of the α relaxation to lower frequencies is accompanied by intensity changes of (or intensity exchanges between) the main relaxation α and the local mode β (see Fig. 4). This affects mainly the low frequency wing of the β and the valley between α and local relaxation. While the α intensity seems to increase, the β intensity tends to decrease. Apart from these changes in position and intensity, a sharpening of the α peak is also observed. This will be discussed in more detail in a forthcoming paper [29].

The next poly(alkyl methacrylate) in our series is poly(n-propyl methacrylate), see Fig. 5. The shift of the splitting region to lower frequencies (and temperatures) is indicated by an approaching of the α and β relaxations in the frequency sweeps. At short aging times (Fig. 5a) no clearly separated G''-maxima of the two relaxations can be seen. At temperatures below 37 °C the main transition is indicated as an α shoulder at the low frequency wing of β. At higher temperatures ($T_e > 37$ °C) both relaxations seem to form a common relaxation process. But they are explicitly separated after the 600 min aging, cf. Fig. 5b and Fig. 6: At temperatures $T_e > 37$ °C independent α shoulders are observed caused by a shift of the ω_α frequency

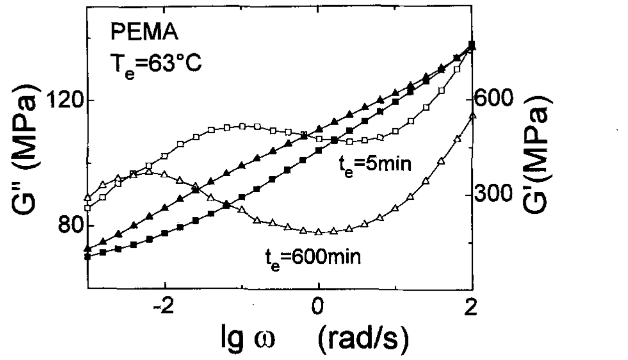

Fig. 4. Aging effects on storage (full symbols) and loss shear modulus (open symbols) for PEMA at $T = 63$ °C. The squares are the $G^*(\omega)$ for $t_e = 5$ min while the triangles are the values after $t_e = 600$ min. The curves are not vertically shifted

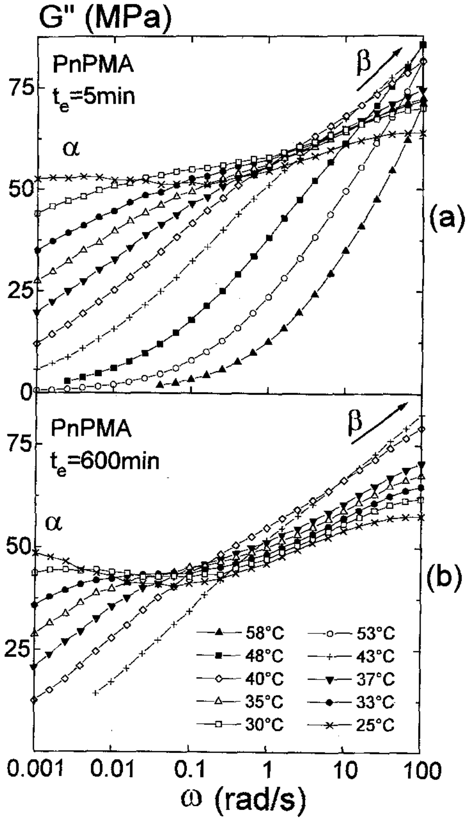

Fig. 5. Shear loss modulus G'' in PnPMA for $t_e = 5$ min (a) and $t_e = 600$ min (b) at temperatures between 25° and 58 °C

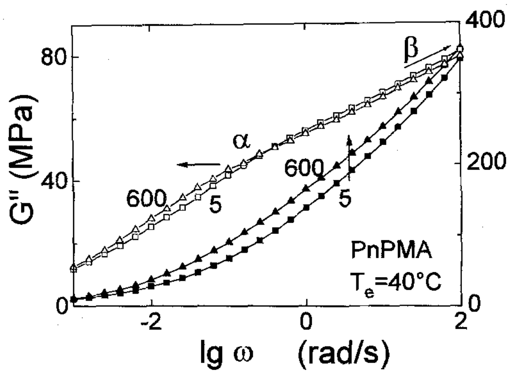

Fig. 6. Time dependent shift of the α relaxation in the real (full symbols) and imaginary (open symbols) part of the shear modulus for PnPMA at $T = 40\,°C$. The squares are the $G^*(\omega)$ values for $t_e = 5$ min while the triangles are the values after $t_e = 600$ min isothermal aging

to lower values. Below $T_e = 37\,°C$ a valley between α and β relaxation is observed. We conclude that the splitting region of PnPMA is still above the frequency window of our dynamic shear measurements. Figure 6 demonstrates explicitly the aging effect: There is a time-dependent shift (arrow) of the underlying maximum loss frequency ω_α to lower values and a percent range increase of the storage modulus $G'(\omega)$ in the frequency window.

The results in PnBMA after the short aging time are presented in Fig. 7a. The G''-data seem to indicate only one relaxation process at all temperatures T_e. The existence of an α relaxation is only detectable as a change of the slope for the low frequency wing of the β relaxation, corresponding to a seeming broadening of this process below 20 °C. The measurements after $t_e = 600$ min isothermal aging show that the G''-data at higher temperatures ($T_e > 12\,°C$) are hardly affected by the physical aging, while the other sweeps ($T_e < 12\,°C$), however, are dramatically modified over long times (see Fig. 7b and Fig. 8). At temperatures below 12 °C the development of the α relaxation is clearly detectable as a shoulder, or at

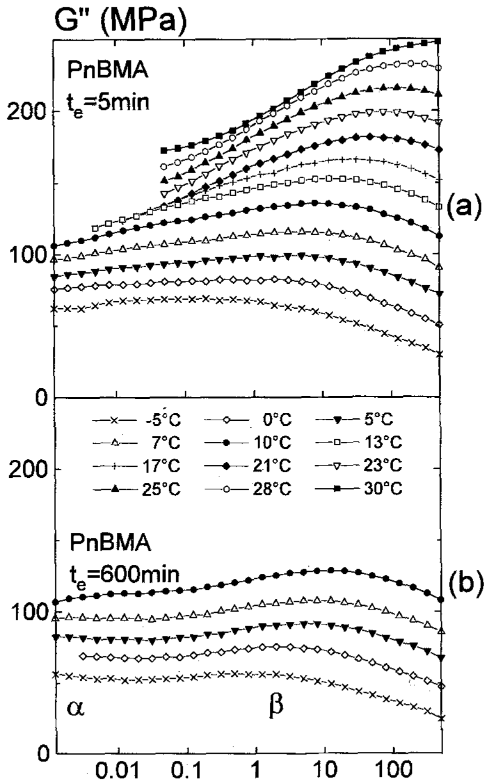

Fig. 7. Shear loss modulus $G''(\omega)$ near the α onset in PnBMA for $t_e = 5$ min (a) and after $t_e = 600$ min (b) isothermal aging. The G'' curves are vertically shifted by an amount of 15.4 MPa per data set ($T_{ref} = -5\,°C$)

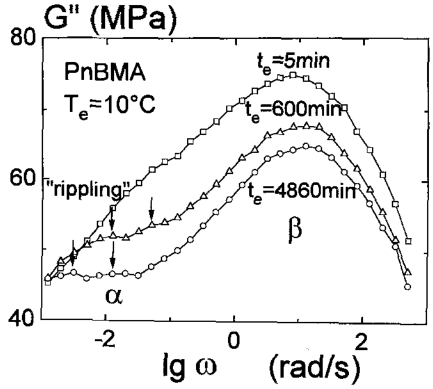

Fig. 8. Shear loss modulus $G''(\omega)$ for PnBMA at $T_e = 10\,°C$ with parameter aging time t_e. The arrows label some significant rippling in the G'' curves near the α maximum in $G''(\omega)$

lower temperatures ($T_e < 7\,°C$), as a separate relaxation peak. The absence of a shoulder in the low-frequency wing at temperatures $T_e > 20\,°C$ is a hint that the α appearance in PnBMA is practically inside the frequency window of our shear measurements. A check of this statement by different numerical fitting procedures is discussed below.

A fine structure (rippling) in the G''-data between α and β relaxation was observed in all three poly(alkyl methacrylates) (see for example Fig. 8). Such an effect was never reported before. (Some rippling was detected in the plateau zone of PMMA by Bartenev et al. [20, 21]). We think that this effect is especially pronounced in the splitting region S. Possible explanations of the ripples will be discussed in a short form below, and in detail elsewhere [22].

4. Discussion

The storage and loss modulus data were simultaneously fitted by numerical procedures to find the frequencies of maximum loss, ω_α and ω_β, as a function of temperature T_e. These calculations are difficult because of the relatively narrow mechanical frequency window and the superposition of two relaxation peaks of unknown shape. These problems are discussed in more detail in [22]. We used two independent models for the determination of the maximum loss frequencies. For a first approximation without any discussion of the relaxation intensities we fitted only the $G''(\omega)$-data with two logarithmic Gaussian functions, with no regard of any basis line. The observed curves fit the experimental data well (solid lines in Fig. 9). For PEMA and PnPMA only the low-frequency flank of the β-process could be observed in the frequency window of the apparatus. The outside maxima are extrapolated using the best fit to the G''- data in the window. Their position is more uncertain, as

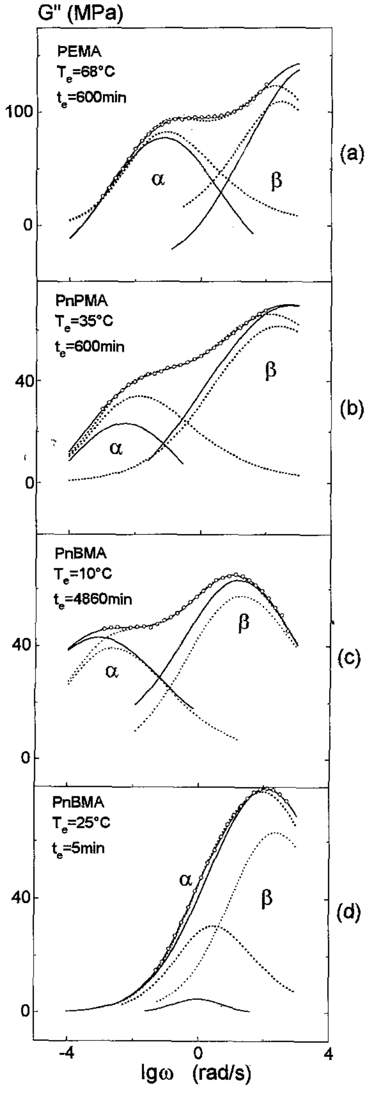

Fig. 9. Shear loss modulus as a function of logarithm frequency ω fitted by two logarithmic Gaussian functions (solid lines) or two MHN-functions (dotted lines) in PEMA at 68 °C for $t_e = 600$ min (a), in PnPMA at 35 °C for $t_e = 600$ min (b), and in PnBMA at 10 °C for $t_e = 4860$ min (c) and at 25 °C for $t_e = 5$ min (d)

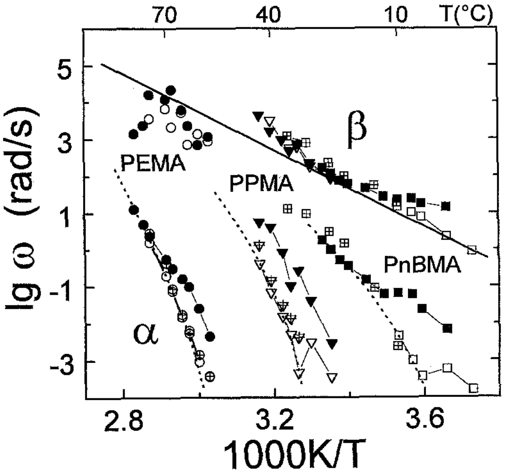

Fig. 10. Arrhenius diagram of the α and β traces in PEMA (circles), PnPMA (triangles) and PnBMA (squares) with parameter aging time t_e (full symbols: $t_e = 5$ min, Gaussian fit; open symbols: $t_e = 600$ min, Gaussian fit; cross at center: MHN-fit for equilibrium data)

can be seen from Fig. 10, but they fit well into the general trend of the β- trace.

In a second step, we used two Modulus-Havriliak–Negami (MHN)-functions [23]

$$G^*(\omega) - G_\infty = \Delta G[1 + (-i\omega_c/\omega)^\beta]^{-\gamma} \qquad (1)$$

for the adjustment of both parts of the modulus, $G'(\omega)$ and $G''(\omega)$. Some results for the shear loss modulus $G''(\omega)$ are also shown in Fig. 9 (dotted lines). While the Gaussian functions give a good approximation for all $G''(\omega, T)$ curves, it was impossible to get a satisfactory fit for several non-equilibrium $G^*(\omega, T)$-curves by two MHN-functions.

The common Arrhenius diagram (Fig. 10) shows that the obtained values for the maximum frequencies, ω_α and ω_β, are relatively independent from the fitting function used.

4.1 Splitting behavior

4.1.1 Shift by larger side groups

With regard to the frequency-temperature position of the splitting region in the different polyalkylmethacrylates, our dynamic shear measurements confirm the results of the single-frequency experiments by Heijboer and others [17, 15]: While the Arrhenius line for the β relaxation is nearly the same for all the poly(alkyl methacrylates), the main transition α shifts to lower temperatures and frequencies with increasing side chain length.

Heijboer et al. [17], Ishida et al. [24], and Gomez et al. [19] concluded from mechanical and dielectric measurements that the reason for the β relaxation is a rotation of the –COOR group. Spiess et al. observed, using special NMR-methods, 180°-flips of the –COOR group in PEMA [25] and PnBMA [26]. This motion is near T_g coupled with a small-angle rocking of the backbone. It seems that the local β mode in all the poly(*n*-alkyl methacrylates) is similar. This correlates with the finding that the β relaxation in shear measurements is, if at all, only weakly influenced by the length of the *n*-alkyl side group –*R*.

In contrast to the behavior of the local mode β, the main transition α depends strongly on the length of the side group. There is a major influence of the alkyl group on the frequency-temperature position of the splitting region. The longer side groups lead to a lower frequency and lower temperatures where the first G'' signal for α can be detected. Roughly, we see a shift of about two frequency decades per additional CH_2 unit in the side group (at given tacticity). This offers the extraordinary possibility to study the region around the α appearance by low frequency ($10^{-3} \ldots 10^3$ Hz) methods such as dynamic shear and calorimetric measurements, and to make some progress in the understanding of the relation between α and β [1].

4.1.2 α appearance in PnBMA

By analyzing the $G^*(\omega, T_e)$ data for PnBMA in Fig. 10, a *separate* α appearance is observed nearly two frequency decades below the local mode β. Both fitting procedures give, in the finite temperature range 25 °C < T_e < 40 °C, a nearly constant frequency gap of about two logarithmic decades between ω_α and ω_β.

At higher temperature no α peak with detectable intensity could be found. At a crossover temperature $T_{co} \approx 22$ °C and $\omega_{co} \approx 1$ rad/s, α reaches a considerable intensity, and the curvature of the α trace increases with lower temperature.

Let us discuss this finding in terms of the minimal cooperativity concept [6]. This is based on the idea that a cooperative phenomenon cannot smoothly be extrapolated to a few-particle motion, $N_a \to 1$. The secondary relaxation peak β marks local motions of only a very few particles (momomeric units of chains here) and is assumed here to be the "local element" of the cooperative motion. A cooperative process (like the α relaxation) with such local elements cannot smoothly transmute into its own local element. The concept predicts some minimal cooperativity, estimated [27] to involve $N_a = 10 \ldots 30$ particles, that cannot be diminished in the α regime. A separate α onset ($\alpha - \beta$ gap) was also found in numerical simulations by a modified Fredrickson model for a two-dimensional system [28].

From an extrapolation of the α intensities I_α from MHN-fits to zero, $I_\alpha(T) \to 0$ we calculated a "first shear appearance" in PnBMA: $T^s = 55 \pm 15\,^\circ\mathrm{C}$ and $\log \omega^s/(\mathrm{rad/s}) = 2 \pm 1$. The details will be published elsewhere [29].

4.2 Physical aging

4.2.1 Analysis of the G''-maxima position

Strong non-equilibrium effects are observed in all three samples. The non equilibrium α curves are bent from the assumed (dotted in Fig. 10) α equilibrium lines. The equilibrium times $t_\infty(T_e)$ determined from the bending points of the α traces are in good agreement with a prediction by Struik [8] suggesting a general relation between the equilibrium time $t_\infty(T_e)$, the difference between aging and glass transition temperature, $T_e - T_g$, and the slope of the α trace $m_\alpha = d(\log \omega_\alpha)/dT)$ at T_g.

The bending of the α traces seems to be much more pronounced when the frequency ratio to the splitting frequency decreases, i.e., in the sequence PEMA, PnPMA, PnBMA (Fig. 10). This may be a direct consequence of the distance from the α onset: The local slope of the α trace in a $\log\omega - 1/T$-representation near the α onset is small, corresponding to that of the β slope, while it is greater far below the splitting region. Ordinarily, as for polystyrene, the "mechanical frequencies" are $6 \ldots 9$ decades below the splitting region, and the slope $m_\alpha = d(\log \omega_\alpha)/dT)$ of the α trace is high (≈ 0.3 decades/K). Therefore, a few degrees Kelvin below the DSC glass transition temperature T_g the equilibrium α maximum in G'' is outside the mechanical frequency window, and deviations of the $G''(\omega)$ maximum from the equilibrium α trace of order decades ("strong" bending) are usually not detectable in such glasses. In our substances, however, the slope m_α of the α trace is small ($0.1 \ldots 0.2$ decades/K) and the α maximum remains inside the mechanical frequency window also about 20 K below T_g. Consequently, strong bending effects are detectable in such glasses (see PnBMA).

4.2.2 Analysis of $G''(\omega)$-curves

Figures 4 and 8 show intensity changes of (or exchanges between) α and β relaxation and connected changes of the peak shapes. Furthermore, some rippling between the α and β peak is observed in all samples below T_g (see, e.g., Fig. 8).

These effects can be discussed in terms of the concept of sequential aging. This approach was developed for the time domain by McCrum [30], and later enlarged to space [31]. The concept assumes a successive freezing-in of molecular motions during the quench of a sample from $T > T_g$ to $T < T_g$. It predicts a successive thawing of the frozen modes during the aging process at $T_e < T_g$, the longer modes need more time.

Under isothermal conditions at $T_e < T_g$ a shift of the modes to lower frequencies, and finally a shift of the G'' maximum frequency ω_α, is expected. Such time-dependent changes should lead to pronounced shape changes at the low frequency wing of the β relaxation. The short time modes should thaw first.

The concept of sequential aging may also give a *possible* explanation for the ripples in our G''-data. The ripples could be a hint to some discreteness in the small modes between α and β which are initially frozen and then come successively to equilibrium during isothermal aging below T_g (see [22]). A rippling maximum occurs when a special and frequent mode comes to the thawing. The rippling effect will be the scope of further G^*-measurements with a better time resolution.

5. Conclusions

Dynamic shear measurements in a series of poly(alkyl methacrylates) show a systematic shift of the α appearance (splitting region S) to lower frequency values with increasing length of the alkyl side group (≈ two frequency decades per additional CH_2-unit). Since the local mode β remains nearly unchanged by a variation of the size of the alkyl group the effect is mainly the result of a modification of the main transition α.

A separate α onset about two frequency decades below the local β mode is directly observed for PnBMA, practically inside the frequency window of our dynamic shear measurements. This result is obtained by two independent fitting procedures. The frequency gap points to the existence of a minimal number of particles which can perform a cooperative motion (concept of minimal cooperativity).

A strong bending of the α trace from the equilibrium line is detected near the α onset in PnBMA. The deviations from the equilibrium line decrease with increasing length of the linear alkyl side group. Intensity and shape of α and β relaxation were influenced by physical aging in all three samples. Some rippling in the G''-intensity valley between α and β peak was observed for all the three poly(alkyl methacrylates). The effects of physical aging on peak position, intensity and shape can be discussed in terms of the concept of sequential aging in time and space.

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References

1. Johari GP, Goldstein MJ (1970) J Chem Phys 53:2372
2. Mc Crum NG, Read BE, Williams G (1991) Anelastic and Dielectric Effects in Polymeric Solids. Dover Publications Inc, New York
3. Donth E (1982) J Non-Cryst Solids 53:325
4. Beiner M, Garwe F, Hempel E, Schawe J, Schröter K, Schönhals A, Donth E (1993) Physica A201:72; F. Garwe et. al. submitted to J Non-Cryst Solids
5. Fischer EW, Donth E, Steffen W (1992) Phys Rev Lett 68:2344
6. Donth E (1981) Glasübergang. Akademie Verlag, Berlin; Donth E (1992) Relaxation and Thermodynamics in Polymers. Glass transition. Akademie Verlag, Berlin
7. Schmidt-Rohr K, Spiess HW (1991) Phys Rev Lett 66:3020
8. Struik LCE (1978) Physical Aging in Amorphous Polymers and other Materials. Elsevier, Amsterdam
9. Kovacs AJ, Stratton RA, Ferry JD (1963) J Phys Chem 67:152
10. Read BE, Tomlins PE, Dean GD (1990) Polymer 31:1204
11. Kovacs AJ, Aklonis JJ, Hutchinson JM, Ramos AR (1979) J Polym Sci, Polym Phys Eds 17:1097; Kovacs AJ (1981) Ann NY Acad Sci 371:38
12. Narayanaswamy OS (1971) J Amer Ceram Soc 54:491; Gardon R, Narayanaswamy OS (1970) Amer Ceram Soc 53:380
13. Hodge IM (1987) Macromolecules 20:2897; Hodge IM, Berens AB (1981) Macromolecules 14:1598
14. DeBolt MA, Easteal AJ, Macedo PB, Moynihan CT (1976) J Amer Ceram Soc 59:16
15. Meyer HH, Mangin PMF, Ferry JD (1965) J Polym Sci A3:1785
16. Patterson GD, Jue PK, Stevens JR (1990) J Polym Sci, Polym Phys Ed 28:481
17. Heijboer J (1965) In: Prins JA (ed) Physics of Noncrystalline Solids. North Holland, Amsterdam, p 231
18. Tetsutani T, Kakizaki M, Hideshima T (1982) Polym J 14:305
19. Gomez Ribelles JL, Diaz Calleja R (1985) J Polym Sci, Polym Phys Ed 23:1297
20. Bartenev GM, Sanditov DS (1986) Relaksacionnye Processy v Stekloo-braznych Sistemach. Nauka, Novosibirsk (in Russian)
21. Yanovsky YG (1993) Polymer Rheology: Theory and Practice. Chapman & Hall, London
22. Beiner M, Garwe F, Schröter K, Donth E Polymer (in press)
23. Schlosser E, Schönhals A, Carius HE, Goering H (1993) Macromolecules 26:6027
24. Ishida Y, Yamafuji K (1961) Kolloid Z 177:97
25. Kulik AS, Beckham HW, Schmidt-Rohr K, Radloff D, Pawelzik Y, Boeffel C, Spiess HW submitted to Macromolecules
26. Spiess HW personal communication
27. Donth E (1991) J Non-Cryst solids 131–133:204
28. Schulz M, Donth E (1994) J Non-Cryst Solids 168:186
29. Garwe F, Schönhals A, Beiner M, Schröter K, Donth E, J Phys, Condens Matter (in press)
30. Mc Crum NG (1984) Polymer Communications 25:2
31. Schönhals A, Donth E (1986) Acta Polymerica 37:475

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Authors' address:

M. Beiner
Fachbereich Physik
Universität Halle
06099 Halle (Saale), FRG