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ORIGINAL CONTRIBUTION

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Struik law for enthalpy retardation at the glass transition in poly(*n*-alkylmethacrylates) measured by DSC aging experiments

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Abstract Results of calorimetric (DSC) experiments on a series of poly (*n*-alkylmethacrylates), from methyl to pentyl, after different aging times t_e at different aging temperatures T_e are presented. The aging behavior is quite different from that in other polymers, for example PS. For all poly(*n*-alkylmethacrylates) investigated the aging peak temperature T_{max} is shifted parallel to the aging temperature T_e in a large temperature interval below the glass temperature. The results are discussed with respect to shear and entropy response in the $\alpha\beta$ splitting region.

Key words DSC – Struik law – physical aging – $\alpha\beta$ splitting region – poly(*n*-alkylmethacrylates)

Introduction

Poly(*n*-alkylmethacrylates) are of interest because the $\alpha\beta$ splitting region, where α and β traces are close together in the Arrhenius diagram (Fig. 1), is at low frequencies that are accessible for dynamic calorimetric and shear experiments [1, 2].

The position of the α and β traces in the Arrhenius diagram of poly(ethylmethacrylate) (PEMA), poly(*n*-propylmethacrylate) (PnPrMA) and poly(*n*-butylmethacrylate) (PnBMA) was the subject of recent experimental work using photon correlation spectroscopy [3], dielectric and dynamic shear methods [4–7]. The β traces (local relaxation) of the poly(*n*-alkylmethacrylates) are quite similar, whereas the α traces (cooperative relaxation) shift towards lower frequencies with increasing number of the C atoms in the side chain [8]. The shear compliance J^* (Fig. 2B) and the shear retardation spectrum L (Fig. 2A) for PMMA show that the shear compliance in the frequency range of the splitting region ($\log\omega/s^{-1} > 3$) is higher than for polystyrene, PS (see also [9]). This is a hint for intensified relaxation processes between α and β relaxation.

Physical aging experiments for shear in PEMA and PnBMA shift the α relaxation in an Arrhenius diagram to higher temperatures. This corresponds qualitatively, after temperature time superposition, to the Struik law [10] in the Andrade zone between α and β for many polymers, e.g., PS far below the splitting, describing some parallelism between the time shift of response (t_{meas}) and the aging time (t_e), $\mu_{Struik} = d\log t_{meas}/d\log t_e \approx$ const (≈ 1). The high shear activity in the splitting region of the poly(*n*-alkylmethacrylates) suggests the question of if a similar behavior as observed in shear can, for these polymers, also be observed by calorimetry. If the material is "enthalpy active," or because of $\Delta H \approx T\Delta S$ for isobaric experiments in condensed matter, "entropy active" in the splitting region – which means that aging varies the entropic state there – then we expect, similarly to shear, that the peak (partly called the overshoot in DSC experiments) is shifted with the aging time t_e and aging temperature, T_e.

The aim of this paper is a systematic experimental study of the DSC peak shift due to aging. Calorimetric aging experiments are described in the literature for PMMA [11] and recently for PEMA [12]. In this paper we include PnPrMA, PnBMA and poly(*n*-pentylmethacrylate)

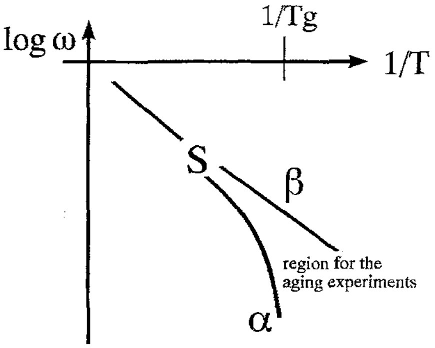
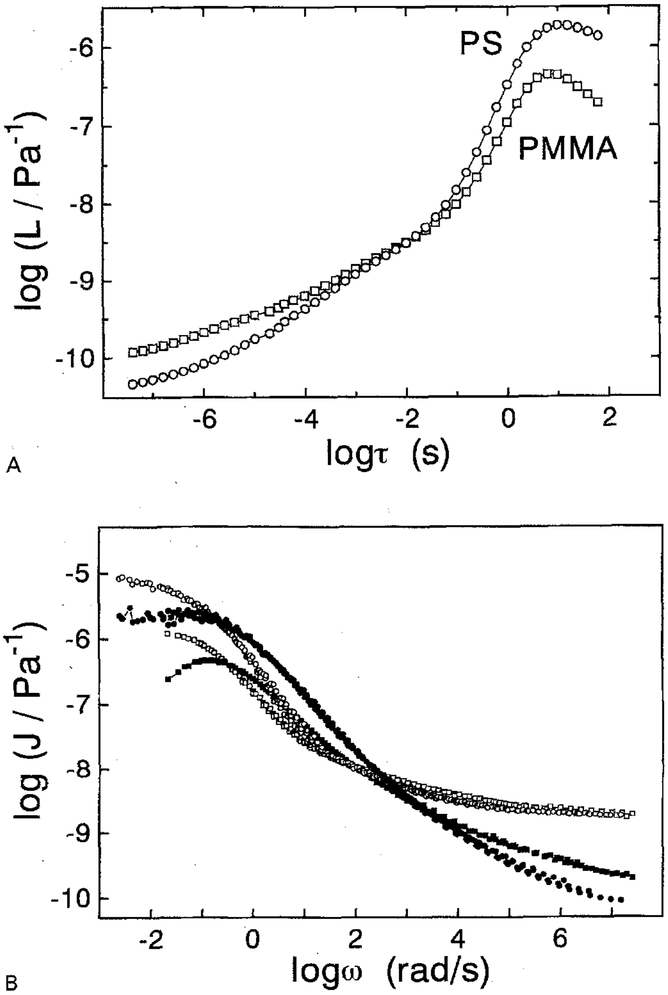


Fig. 1 Region for the aging experiments near the splitting region S of the Arrhenius diagram (schematically)

Fig. 2A Shear retardation spectrum L for PMMA (reduced to 117 °C) and PS (reduced to 100 °C), calculated by a nonlinear regularization method [13]. The symbol log always means the logarithm on a base 10, $\log_{10}$ and $\omega\tau = 1$. **B** Mastered shear compliance J' and J'' data for PMMA (reduced to 117 °C) and PS (reduced to 100 °C) from which the spectra are calculated (○ J', ● J'' for PS; □ J', ■ J'' for PMMA)



PnPMA. The results will be discussed in the framework of a modified Struik law, transferring μ_{Struik} from the time dependence to a $\tilde{\mu}$ for the temperature dependence.

Experimental

The polymers PEMA, PnPrMA, PnBMA and the monomer *n*-pentylmethacrylate were purchased from Polyscience, Inc. They were prepared in the same way as described in [4] and [5]. PnPMA was obtained by radicalic polymerization. PS is a commercial product from Buna AG (formerly VEB Chemische Werke Buna)

The DSC glass transition temperatures T_g (heating rate 10 K/min), the molecular weights M_w and the M_w/M_n values (determined by GPC) for the poly(*n*-alkylmethacrylates) are listed in Table 1. The PS sample has a molecular weight of $M_w = 360$ kg/mol. All poly(*n*-alkylmethacrylates) are atactic (78% syndio sequences in the average).

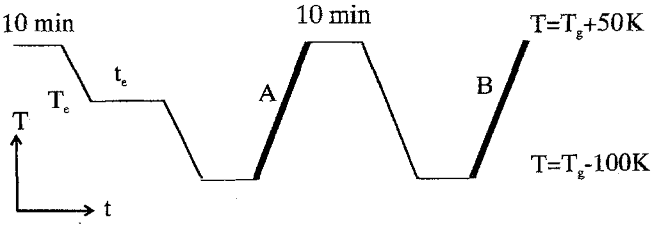
Calorimetric experiments were made in a DSC-7 instrument from Perkin Elmer. The sample weights were 10 ... 15 mg, and the temperature time program is shown in Fig. 3. The cooling and heating rates were always 10 K/min. Dynamic shear compliance for PMMA and PS was measured in a RDA II instrument from Rheometrics Scientific using a stripe ($1.5 \times 10 \times 25$ mm^3) as sample. The shear retardation spectrum was calculated using an algorithm according to [13]. The time dependent creep

Table I Molecular weight and glass transition temperature T_g for poly(*n*-alkylmethacrylates)

	$M_w/\text{kg}\cdot\text{mol}^{-1}$	M_w/M_n	$T_g/°\text{C}$
PMMA	≈ 6700	1.8 ± 0.1	100 ± 1
PEMA	72.3 ± 3.0 76 ± 5	1.9 ± 0.1	74 ± 1
PnPrMA[a]	340 ± 20	5.0 ± 0.3	46 ± 1
PnBMA	330 ± 8	2.35 ± 0.1	24 ± 2
PnPMA	570 ± 30	1.8 ± 0.1	13 ± 2

[a] bimodal

Fig. 3 Temperature time program. T_e aging temperature, t_e aging time, A measuring run, B comparison run



experiments on PEMA were performed in a DSR instrument from Rheometrics Scientific. The PEMA sample had a diameter of 8 mm and a thickness of about 3 mm.

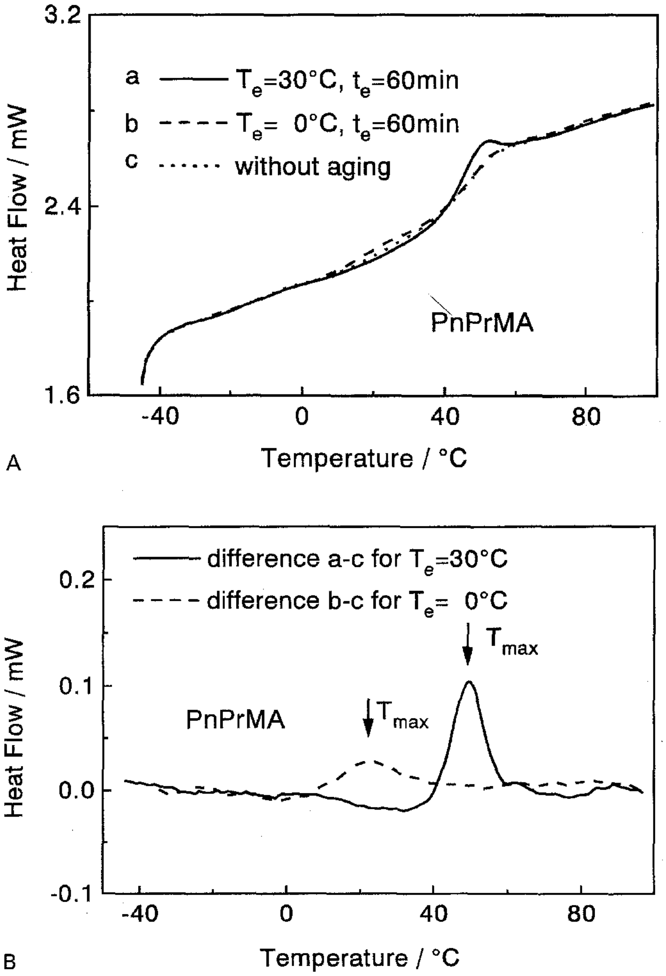
The polymers are measured as purchased or polymerized, respectively. The water content is small ($< 1\%$) and without detectable influence on the dynamic shear properties [4].

Results

Figure 4A shows two examples for DSC runs after aging (curve $a + b$) with different aging temperatures T_e, and a comparison run (curve c) without aging for PnPrMA. The $(a - c)$ and $(b - c)$ difference curves have a peak with a maximum temperature T_{max} (Fig. 4B). In Fig. 5 the shift of T_{max} is shown as function of the aging temperature T_e for an aging time $t_e = 60$ min. The accuracy of T_{max} is about ± 1 K.

Normally [14–19] the shift of the overshoot with varying aging temperature is comparatively small (10 Kelvins), see for example the experimental points for PS in Fig. 5. But for the poly(n-alkylmethacrylates) the shift of T_{max} is large. The relation between the maximum T_{max} and the aging temperature T_e (for a given aging time $t_e \ll t_{equil}$) is similar for all the poly(n-alkylmethacrylates) in a temperature range $0 < T_g - T_e < 50$ K (Fig. 5).

Fig. 4A DSC curves (a, b) for two different aging temperatures T_e and aging time $t_e = 60$ min, and without aging (c) for PnPrMA. **B** Differences between the scans of Fig. 4A for the aged and unaged sample for PnPrMA



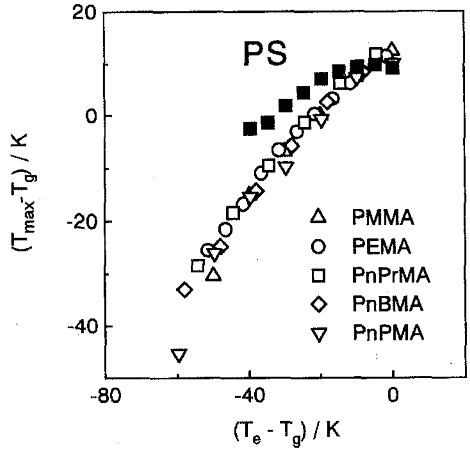
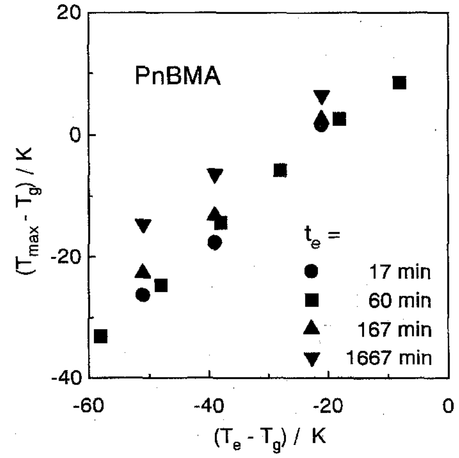


Fig. 5 Peak temperature T_{max} as a function of aging temperature T_e for an aging time $t_e = 60$ min. The slopes $\bar{\mu}$ in the upper part of the diagram for PMMA, PEMA, PnPrMA, PnBMA and PnPMA are 0.83 ± 0.08; 0.76 ± 0.04; 0.81 ± 0.04; 0.85 ± 0.03 and 0.88 ± 0.09, respectively

Fig. 6 Peak temperature T_{max} as a function of aging temperature T_e for different aging times t_e in PnBMA. The slopes $\bar{\mu}$ for $t_e = 17$ min, 60 min, 167 min and 1667 min are 0.90 ± 0.09; 0.85 ± 0.05; 0.84 ± 0.05 and 0.70 ± 0.05, respectively



The slope of the upper linear part,

$$\tilde{\mu} \equiv dT_{\max}/dT_e = 0.85 \pm 0.10 \qquad (t_e = 60\ \mathrm{min}) \tag{1}$$

is nearly the same for all the poly(n-alkylmethacrylates) investigated. The slope increases slightly for decreasing aging temperature T_e. The shift of the annealing peaks with the aging time is shown in Fig. 6 for PnBMA. The slope $\tilde{\mu}$ decreases with increasing annealing time t_e. This finding confirms the result for PEMA given in [12]. The other poly(n-alkylmethacrylates) show a similar decrease of the slope with increasing annealing time.

Discussion and conclusion

The reason for the $T_{\max}$ shift is probably similar to that of the general shear-compliance shift reported by Struik [10], when translated from the time to the temperature variable by means of temperature time superposition. The compliance measurements shown in Fig. 2A + B indicate that the Andrade part in the compliance spectrum (slope of 0.3 for PMMA) corresponds to the frequency interval of the splitting region. In the temperature region between T_α and T_β usually the Struik law [10] is valid (t_e is the annealing time, t_{meas} a characteristic relaxation time of the shear compliance, $t_{\mathrm{meas}}(t_e)$):

$$\mu_{\mathrm{Struik}} \equiv \frac{d\log t_{\mathrm{meas}}}{d\log t_e} \approx 1\ . \tag{2}$$

Equation (2) means that annealing time t_e and the time t_{meas} are scaled in the same way.

Comparing Eq. (1) and Eq. (2), the μ ratio can be expressed by the ratio of the differential time-temperature (superposition) slopes

$$\frac{\mu_{\mathrm{Struik}}}{\tilde{\mu}} = \left(\frac{d\log t_{\mathrm{meas}}}{dT_{\max}}\right) \Big/ \left(\frac{d\log t_e}{dT_e}\right)\ . \tag{3}$$

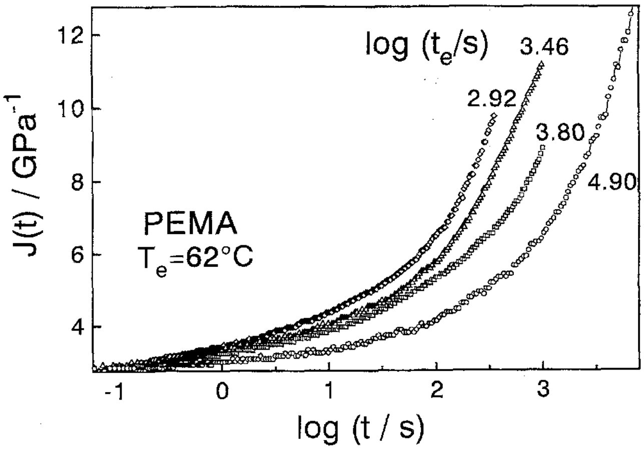


Fig. 7 Shift of shear compliance during physical aging for PEMA at $T_e = 62\,°\mathrm{C}$. The parameter is the aging time, t_e. The curves are slightly shifted in vertical direction to correct some rippling [4] between α and β

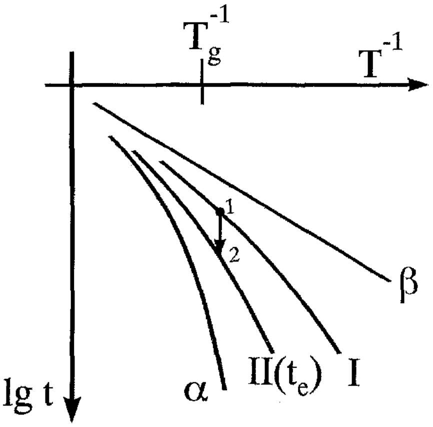


Fig. 8 Annealing 1 → 2 in the splitting region between α and β-traces [22] (schematically). The details are explained in the text

According to Eq. 3, the equality $\tilde{\mu} = \mu_{\mathrm{Struik}}$ would mean that the temperature dependence of the (actual) relaxation time is equal to that of the annealing time, compared at a given aging state. Shear compliance experiments on PEMA (Fig. 7) result, however, in a somewhat different exponent,

$$\mu_{\mathrm{Struik}} \approx 0.5 \pm 0.1\ , \tag{4}$$

i.e., for PEMA at 62 °C we have $\mu_{\mathrm{Struik}}/\tilde{\mu} \approx 0.66 \pm 0.11 < 1$. This means that the actual and the aging time-temperature slope are not the same. This will be explained in Fig. 8 showing the equilibrium Arrhenius diagram for two selected processes (modes I, II) between β and α in the splitting region. It is assumed that such processes can be defined (e.g., by sequential aging [20, 21]), and that there is a certain continuity of the slopes between α and β (i.e., the curves are not parallel). Point 1 in Fig. 8 means [22] an actual state (T_{meas}, $\lg t_{\mathrm{meas}}$), see also Eq. (3). Point 2 means a state reached after isothermal aging ($T_e = T_{\mathrm{meas}}$, $t_e > t_{\mathrm{meas}}$). We see that the slope dt/dT – mediating the time-temperature superposition – is really larger in point 2 than in point 1, which means, according to Eq. (3), $\mu_{\mathrm{Struik}}/\tilde{\mu} < 1$, as observed (under the condition that shear and entropy relaxes with the same rate).

It was also tried to reproduce the DSC traces by simulation with a Narayanaswamy program. Strong peak shifts can be simulated because of the small slopes of the traces in the splitting region of Fig. 8 [23]. But it is still an open question if the details of the DSC curves in the splitting region can be reproduced by such a program.

In summary, DSC aging experiments in the splitting region of poly(*n*-alkylmethacrylates) show pronounced peak shifts that can be explained by a temperature version of the Struik law originally formulated for shear in the time domain. Such an entropy activity indicates that molecular order observed by exchange NMR [24, 25] is also important for calorimetry in the splitting region of these polymers.

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