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The influence of copolymerization and plasticization on the $\alpha\beta$ splitting behaviour of the glass transition in poly(n-alkylmethacrylate)s

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The dielectric function was determined in the $\alpha\beta$ splitting region of a series of amorphous random copolymers of n-propylmethacrylate (nPrMA) with n-pentylmethacrylate (nPeMA). The intensity of the α process decreases with increasing temperature in all copolymers investigated. The onset temperature of the α process intensity decreases with increasing nPeMA content. The splitting behaviour continuously changes with composition. These results were confirmed by dynamic shear modulus measurements in the $\alpha\beta$ splitting region. The shift of the PnBMA splitting region due to addition of plasticizer © 1997 Elsevier Science Ltd.

(Keywords: glass transition; dielectric relaxation; copolymerization)

INTRODUCTION

Poly(alkylmethacrylate)s are gaining increased technical interest as advanced materials for applications in non-linear optics[1,2], holographic data handling and energy storage[3]. Many practical problems are related to the dynamic glass transition (α process), which is still poorly understood[4]. Many relaxation details in the frequency and temperature region where a simple high-temperature process (a or $\alpha\beta$ process) splits up into two low-temperature processes (α or cooperative process, and local β or Johari–Goldstein process[5]) are still unclear.

The splitting region of several poly(n-alkylmethacrylate)s is in a frequency and temperature range which is accessible for many relaxation methods such as shear[6], dielectric[7] and heat spectroscopy, and ^{13}C two-dimensional magic angle spinning (2D MAS) exchange n.m.r.[8]. Dynamic scattering experiments, such as photon correlation spectroscopy (p.c.s.)[9,10], are also applicable in this region.

Further experimental advantages of poly(alkylmethacrylate)s are the relatively large dielectric β intensity and the comparable width of the α and β relaxations. There is only one essential dipole moment in the monomeric unit of the poly(alkylmethacrylate)s: the carboxyl group. The signals of the dielectric spectroscopy can, therefore, be assigned to the dynamics of these groups in neighbour monomeric units. The carboxyl group is situated between the main chain and the side-group and, in a sense, the dynamics of both the main chain and the side group can dielectrically be investigated.

The original aim of this work was to test the possibility of enlarging the frequency window of the relaxation measurements around the splitting region by using a compositional shift from statistical copolymers by means of a systematic composition variation. Copolymers of n-propylmethacrylate (nPrMA) and n-pentylmethacrylate (nPeMA) were used because an overall behaviour similar to poly(n-butylmethacrylate) was expected[7].

This paper shows, however, that there are detectable changes in the splitting behaviour of our copolymer series ('splitting scenario'[7]). The aim of this paper is, therefore, to investigate also the influence of molecular details on the splitting behaviour in our polymers.

The addition of plasticizer lowers the glass transition temperature of a polymer. This effect, known as 'external plasticization'[11], was examined in the splitting region of

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the dioctyl phthalate (DOP) and poly(n-butylmethacrylate) (PnBMA) system.

EXPERIMENTAL

Polymer preparation

Statistical copolymers of poly(nPrMA-*stat*-nPeMA) were obtained by radical polymerization in toluene solution using α,α'-azoisobutyronitrile (AIBN) as an initiator. The total monomer concentration was 7 mol l^{-1}, and the initiator concentration was 0.005 mol l^{-1}. The polymers were prepared with 0, 12.5, 25.5, ..., 100% nPeMA content (11 samples in total). All compositions are reported in units of mole per cent.

An aliquot of the solution was preserved before each reaction. The copolymerization temperature was 50°C. After 4 h a conversion of 10% was reached, and the reaction was stopped by adding 4-methoxyphenol. The polymer was precipitated by pouring the reaction product into a large amount of methanol. After standing overnight, a further aliquot was taken to perform the analysis of the copolymer content. The polymer was collected by filtration, washed several times with methanol, and dried in a vacuum at 50°C to constant weight.

The composition of the copolymers was determined by gas chromatographic analysis of the aliquots. Solutions with known fractions of the monomers nPeMA and nPrMA were produced and analysed for the calibration procedure. *Table 1* lists the experimental conditions for the analysis. The monomer peaks were integrated (areas A_1, A_2) and the nPeMA fraction y was calculated from the fraction of the A_1 pentyl peak area on the total area:

$$y = A_1/(A_1 + A_2) \qquad (1)$$

Figure 1 shows y as a function of the known mole fraction x of nPeMA in the monomer mixture of nPeMA and nPrMA in solution. As expected, a straight line for calibration is obtained.

Table 1 Conditions used for gas chromatographic analysis

Device	Chromatron GCHF18
Column	20% Apiezon on Chromatron DMCS
Integrator	Shimadzu C-R6A
Flushing gas	Hydrogen, 3 l h^{-1}
Detector	Heat conductivity detector
Temperature	150°C
Injection volume	4 μl

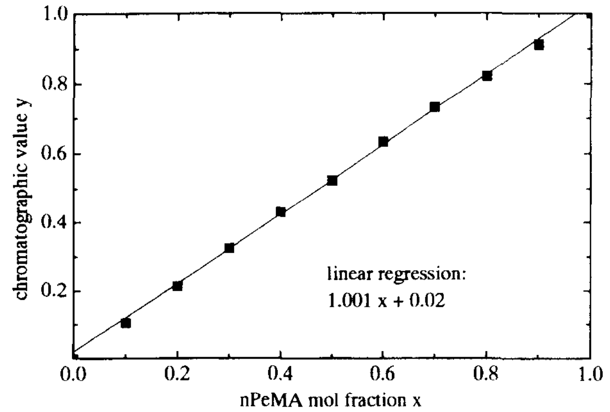

Figure 1 Calibration diagram for gas chromatographic analysis: monomer peak fraction y for nPeMA as a function of known mole fraction x of nPeMA in the monomer mixture of nPeMA and nPrMA

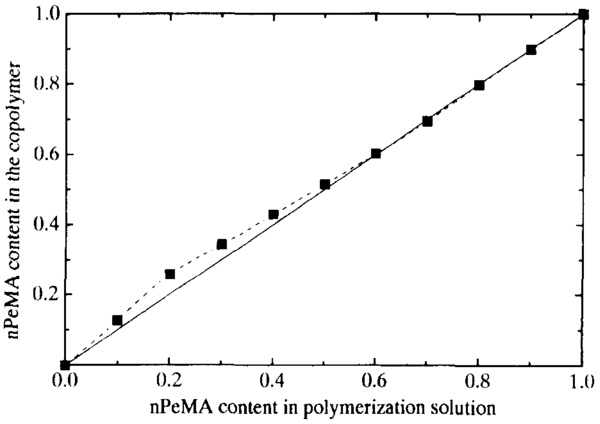

Figure 2 Copolymerization diagram for the different nPeMA-*stat*-nPrMA copolymers

The aliquots from the polymerization were analysed in the same manner. The copolymer composition was calculated from the remaining monomer content. The copolymerization diagram is shown in *Figure 2*. From this diagram the copolymerization parameters ($r1_{\mathrm{nPeMA}} = 0.909$, $r2_{\mathrm{nPrMA}} = 0.7$) were determined considering the conversion by the Kelen–Tüdös method[12]. The r values show that the monomers are nearly statistically distributed in the copolymer. Because of the very similar structure of nPrMA and nPeMA, high-resolution n.m.r. measurements in solution gave no information about the sequence distribution of nPrMA and nPeMA in the copolymer.

The tacticity of all samples (dissolved in non-deuterated tetrahydrofuran, THF) was obtained by ^{13}C n.m.r. with a Varian 400 spectrometer. In all samples, 75 ± 4% syndiotactic sequences (corresponding to 60% syndio triads) were recorded. The molecular weights M_w, estimated by gel permeation chromatography with polystyrene standards, of all samples were above 500 kg mol^{-1}. The M_w/M_n ratios were 1.9 ± 0.2.

In a further experiment the homopolymer PnBMA was mixed with different amounts (1, 3, 5, 15, 20% w/w) of DOP. Both components were dissolved in THF and thoroughly stirred. The solution was slowly evaporated, and the polymer film obtained was dried at 60°C in a vacuum until a constant sample weight was achieved.

Preparation of the samples

Gold-plated stainless steel electrodes of 20 mm diameter were used for the dielectric measurements. The samples were pressed between them at 80°C to a thickness of 250 μm. Analogously, the samples for the shear measurements were pressed to strips of 1.5 mm thickness, 10 mm width and 25 mm length.

Measurements

The complex dielectric function $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ (ε' real part, ε'' loss part, f frequency) was investigated with a Schlumberger frequency response analyser (FRA 1260) supplemented with a buffer amplifier of variable gain (frequency range 10^{-2} to 10^6 Hz). The sample temperature was controlled by a nitrogen gas jet heating system covering a broad temperature range from 173 to 493 K with a resolution of 0.05 K. The equilibration time for each temperature was 10 min.

The dielectric relaxation at a given temperature T was characterized by the frequency at maximal loss, $\omega_{\max} = 2\pi f_{\max}$, and the relaxation strength $\Delta\varepsilon$. The data in the frequency domain were analysed by means of one or a sum of two Havriliak–Negami (HN) model functions[13] using a Gaussian least squares method[7]. The HN function reads

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (\mathrm{i}\omega/\omega_0)^b]^g} \qquad (2)$$

where $\omega_0 = 2\pi f_0$ is the characteristic HN frequency, closely related (but not identical) to the loss peak frequency $\omega_{\max}$, and $\varepsilon_\infty = \varepsilon(\omega = \infty)$ is the real part for high frequencies compared to $\omega_{\max}$. The shape parameters b and $b \cdot g$ $(0 < b < 1, 0 < b \cdot g < 1)$ describe the slopes of the log $\varepsilon''(\log \omega)$ curve below and above the peak frequency, respectively. It depended on the temperature whether one or a sum of two HN functions was fitted to each isothermal data set.

A spectrometer, RDAII from Rheometrics Scientific, was used for the mechanical shear measurements. All experiments were performed in torsion on specimens of rectangular cross-section. The strain amplitude of 0.2% was well within the limits of linear response. The temperature stability was ±0.2 K. All experiments were realized in the same manner[14]: The sample was equilibrated for 10 min at a temperature T about 50 K above T_g. Then the sample was rapidly cooled down to the measuring temperature of 10°C with a cooling rate of $0.9 \pm 0.2\,\mathrm{K\,s^{-1}}$. The sample remained at this temperature for another 10 min without shear measurements. Within this time period the temperature inside the sample was assumed to be equalized. Subsequently, dynamic shear measurements were started. Frequency sweeps in the range from 100 to $0.001\,\mathrm{rad\,s^{-1}}$ were continuously performed, beginning at high frequencies. To suppress possible ageing effects[14], only data after an ageing time of $t_e = 9\,\mathrm{h}$ are considered in the following.

The thermal analysis was performed with a Perkin Elmer differential scanning calorimeter (DSC 7) using a heating rate of $10\,\mathrm{K\,min^{-1}}$ and sample weights of about 10 mg. The glass transition temperature T_g was calculated by an equal area construction regarding the difference areas between the measured curves and an idealized T_g jump between the tangents on the temperature-dependent c_p values above and below the glass transition.

RESULTS AND DISCUSSION

Statistical copolymers

The d.s.c. results for the thermal glass transition of the statistical copolymers with different nPeMA content are shown in *Figures 3* and *4*. The glass transition temperature T_g continuously decreases with increasing nPeMA content, as expected (*Figure 3*). This shift of glass temperatures with increasing nPeMA content is known as internal plasticization[11]. The values of T_g for the statistical copolymer with 51.5% nPeMA and for the homopolymers PnPrMA and PnPeMA from this series agree satisfactorily also with the corresponding results on the homopolymers in another methacrylate polymer series[15].

The step height Δc_p at the glass transition becomes smaller with increasing nPeMA content (*Figure 4*). This will be discussed below in connection with the shift of the splitting region.

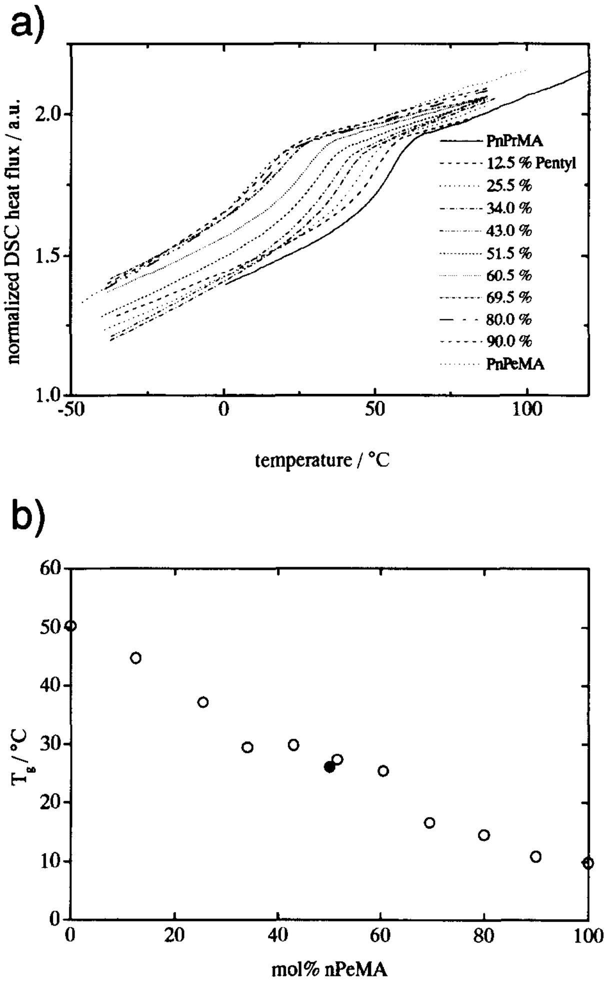

Figure 3 (a) D.s.c. heating runs and (b) glass transition temperatures T_g of the statistical copolymers as a function of nPeMA content. Also shown is the T_g value for the homopolymer PnBMA (solid circle)

In addition to the Δc_p values, the mean temperature fluctuations δT of functional α subsystems are depicted in *Figure 4*. The δT values were estimated from the transformation interval ΔT of the heating run c_p steps according to the equation $\delta T = \Delta T/2.5$. ΔT is the temperature interval between 16 and 84% of the Δc_p step. The latter equation was obtained from a rough summary of the detailed methods of Schneider *et al.*[16]. This is only a crude approximation for the structural-relaxation corrections for obtaining an equilibrium δT dispersion from the d.s.c. transformation interval.

From these data a characteristic volume V_α for the cooperatively rearranging regions (CRRs) in the statistical copolymers was calculated according to[17,18]

$$V_\alpha = kT_g^2\,\Delta c_p/\rho(\delta T)^2\bar{c}_p^2 \qquad (3)$$

with ρ the density, $\bar{c}_p$ the average of the extrapolated c_p values at T_g, $\bar{c}_p = (c_{p\,\mathrm{liquid}} + c_{p\,\mathrm{glass}})/2$. The densities at T_g were linearly interpolated between the values for the homopolymers taken from the literature[19].

With the known volume of one monomer unit, the number N_α of monomer units per CRR was estimated from the V_α value. The quantity decreases with increasing pentyl methacrylate content, in agreement with the behaviour of the methacrylate homopolymer series[15]. Analogously to the homopolymer series in Hempel

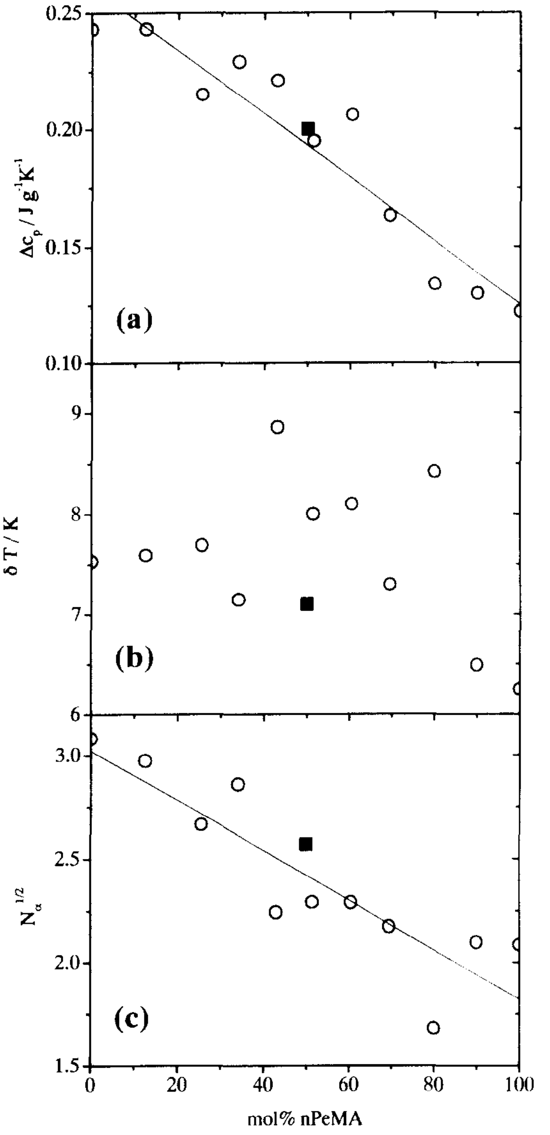

Figure 4 (a) Step height Δc_p of the specific heat, (b) temperature fluctuation δT, and (c) square root of particle number N_α per cooperatively rearranging region at the glass transition as a function of nPeMA content in the statistical copolymers. Also shown are the values for the homopolymer PnBMA (solid symbols)

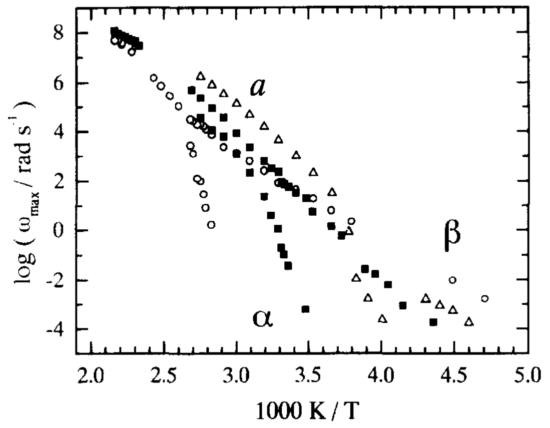

Figure 5 Arrhenius diagram (log ω_{max} as a function of $1/T$) from the dielectric results on some homopolymers of the methacrylate series (O, PEMA; ■, PnBMA; Δ, PnHMA)

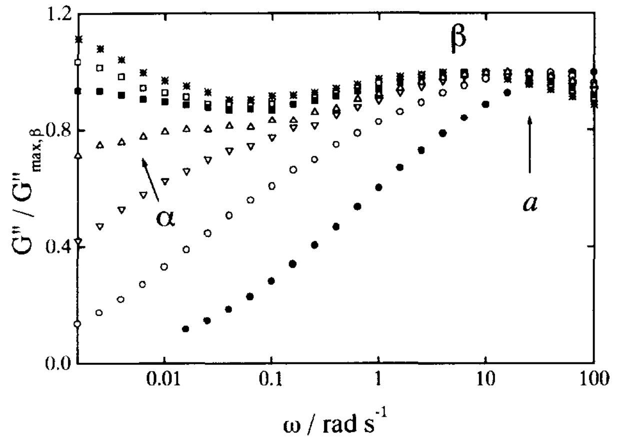

Figure 6 Normalized loss part of the dynamic shear modulus as a function of frequency for the different statistical copolymers (nPeMA content: ●, 100 mol%; O, 90 mol%; ∇, 80 mol%; Δ, 69.5 mol%; ■, 60.5 mol%; □, 51.5 mol%; *, 43 mol%) at the same temperature $T = 10°C$

et al.[15] the square root $N_\alpha^{1/2}$ as a function of composition is depicted in *Figure 4*.

From preceding dielectric investigations on the homopolymers PeMA, PnBMA and PnHMA[7] it is known that the splitting region shifts to lower frequencies and temperatures in an Arrhenius diagram with increasing length of the polymer side-group. This is shown in *Figure 5* for the homopolymers. The α process intensity decreases with increasing temperatures in all the polymers investigated. At the α onset point the intensity becomes zero. The details of the $\alpha\beta$ splitting behaviour ('splitting scenario'), however, differ in the homopolymer series[7].

Below the onset, the separation between α and β relaxation increases with decreasing frequency, and so their separate analysis is favoured. Frequencies lower than 0.01 Hz can be reached by means of dynamic shear experiments. *Figure 6* shows the normalized shear modulus $G''(\omega)$ after 9 h ageing time for a series of statistical copolymers at a temperature of 10°C. With decreasing content of nPeMA the low-frequency flank of the high-temperature a process becomes broader, until a second process (α process) of low-intensity emerges. The α process shifts continuously to lower frequencies and becomes more pronounced. The β process changes only slightly, so that the splitting between α and β gets larger.

The shear measurements in the RDAII instrument are limited to frequencies lower than 100 rad s^{-1}. To get a more comprehensive picture of the whole splitting region, dielectric measurements were performed on all samples. In *Figure 7* the dielectric loss of the 51.5% nPeMA statistical copolymer is presented in a three-dimensional diagram. Besides a conductivity flank at high temperatures, two relaxation processes can be recognized which seem to merge with increasing temperature. A comparison between samples with different nPeMA content shows differences in the shape of the dielectric function. But further details are not seen in this representation.

An individual evaluation of each dielectric isotherm was accomplished by adjustment of HN functions to the loss part $\varepsilon''(\omega)$. *Figures 8* and *9*, for instance, show the adjustment for the copolymer with 25.5% nPeMA at two different temperatures. At high temperatures, the

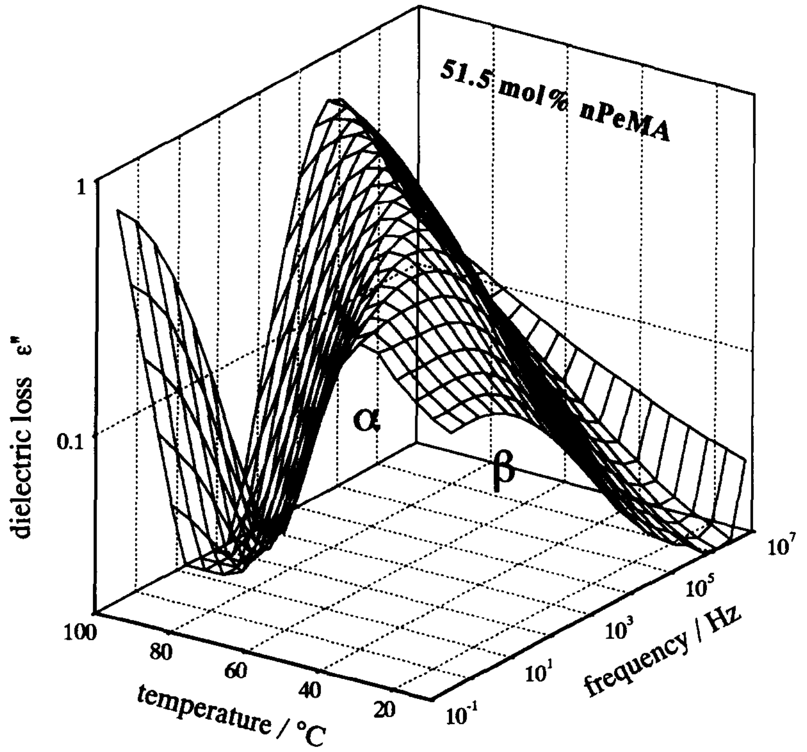

Figure 7 Three-dimensional plot of the frequency and temperature dependence of the dielectric loss part ε'' for the copolymer with 51.5 mol% nPeMA

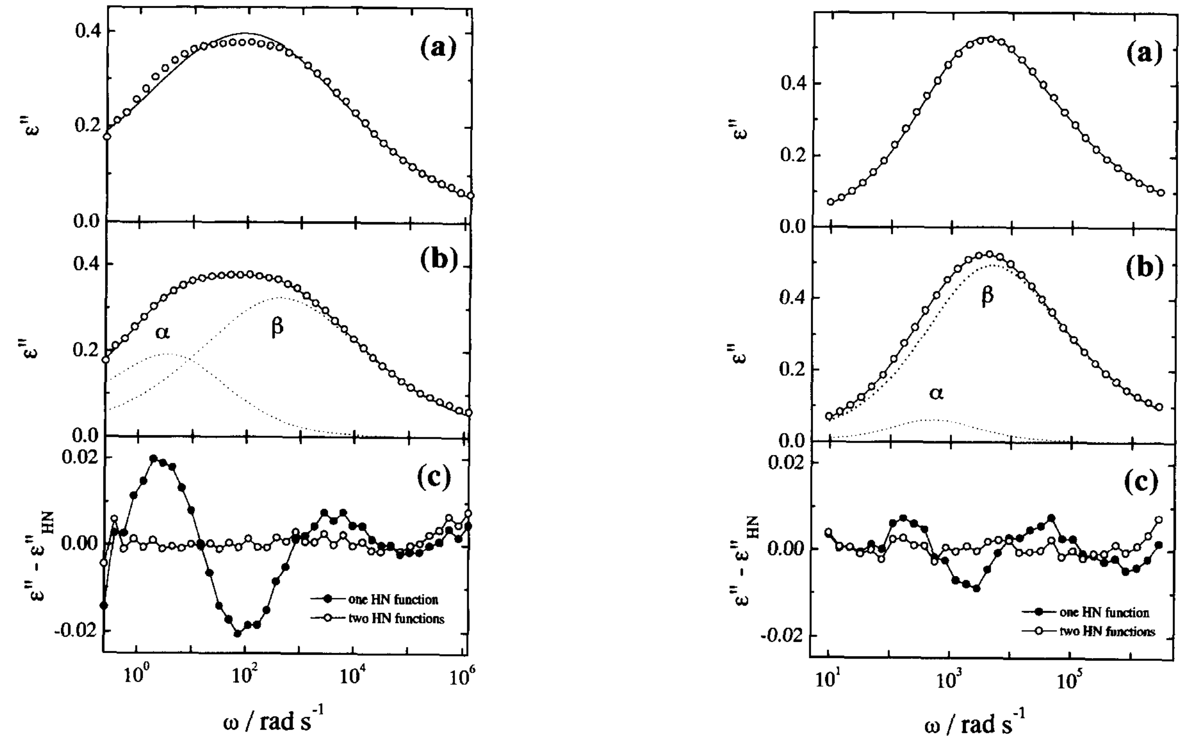

Figure 8 Example of the fit of individual isotherms with HN functions for the copolymer with 25.5 mol% nPeMA at a temperature of 50°C: (a) one HN function, (b) sum of two HN functions and (c) deviation plot

Figure 9 Fits for the same copolymer with 25.5 mol% nPeMA at a temperature of 70°C: (a) fit with a single HN function, (b) fit with the sum of two HN functions and (c) deviation plot

relaxation curves for the *a* process can always be fitted by one single HN function. At lower temperatures, small systematic deviations appear (see the deviation plots in *Figures 8* and *9*). A better fit can then be achieved by using the superposition of two HN functions. The intensity and width relationships of the two processes in our copolymers allow an evaluation also in the overlap case of the α and β relaxations.

The dielectric α relaxation is only investigated at such temperatures above the thermal glass transition T_g where, therefore, ageing effects are absent.

The temperature dependence of the maxima frequencies

Table 2 Activation energy E_A and pre-exponential factor ω_∞ of local β and high-temperature a processes

nPeMA content (%)	0	12.5	25.5	34	43	51.5	60.5	100
$E_{A\beta}$	65	69	81	[a]				
$\log \omega_{\infty\beta}$	11.4	12.3	14.3					
E_{Aa}	141	135	125	135	130	128	125	114[b]
$\log \omega_{\infty a}$	22.8	22.2	21.1	22.6	21.9	21.8	21.5	20.6

[a] β relaxation outside the low-frequency measurement range
[b] This is only a mean value because the trace in the Arrhenius diagram is curved

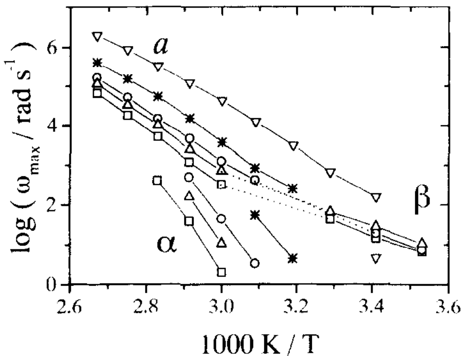

Figure 10 Arrhenius diagram from dielectric experiments for the statistical copolymers with different nPeMA contents (□, 0 mol%; △, 12.5 mol%; ○, 25.5 mol%; * 51.5 mol%; ▽, 100 mol%)

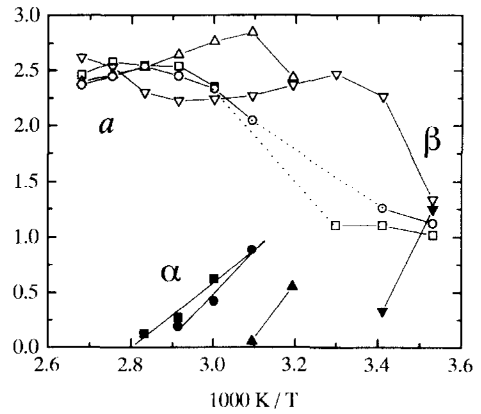

Figure 11 Temperature dependence of the dielectric intensity of the different relaxation processes in the splitting region of copolymers with different compositions (□, 0 mol%; ○, 25.5 mol%; △, 51.5 mol%; ▽, 100 mol% nPeMA). The solid symbols are for the α relaxation

ω_{max} obtained from the HN fits for different copolymers are collected in the Arrhenius diagram (*Figure 10*). We observe a systematic shift of the α and also of the high-temperature a relaxation, and altogether a shift of the whole splitting region to lower temperatures. For PnPrMA the activation energy of the continuous $a\beta$ process changes near the α onset. This change of the activation energy diminishes with increasing nPeMA content and disappears at about 50% nPeMA content, similar to the homopolymer PnBMA. This indicates a change of the splitting behaviour from PEMA-like to PnHMA-like[7].

The activation parameters of the a and β relaxations are collected in *Table 2*. At high nPeMA contents the trace of the a process in *Figure 10* is curved, and the (apparent) activation energy quoted is a mean value estimation. The large values of the extrapolated high-frequency asymptote for the a process in *Table 2* (pre-exponential factor) can be interpreted as an indication of a certain cooperativity of the high-temperature process a in our polymers.

The statistical copolymer with 51.5% nPeMA was expected to correspond nearly to the homopolymer PnBMA (for PnBMA see *Figure 5*). The ω_{max} traces for the a, α and β processes outside the splitting region are really very similar. But within the splitting region they are significantly different. The a process of the statistical copolymer can be fitted above 50°C with a single HN function (see *Figure 5*) whereas the a process of PnBMA can be fitted only above 80°C with one HN function (*Figure 10*). This indicates a strong difference in the α onset temperature ($T_{ons} \approx 110°C$ for the homopolymer[7], $T_{ons} \approx 50°C$ for the copolymer). In the statistical copolymer the long parallel course of the PnBMA ω_{max} traces for α and β is not observed. This means that small variations in molecular details, here the random variations of the side-group length, have a considerable influence on the splitting behaviour. Sensitivity to molecular details was observed even for the homopolymer PnBMA[7].

The temperature dependence of the dielectric intensities in several statistical copolymers is shown in *Figure 11*. The experimental values can directly be compared, because PnPeMA and PnPrMA differ only slightly in mass density and dielectric polarization. All copolymers behave similarly. The intensity of the a process increases slightly with decreasing temperature. Below the α onset temperature the intensity of the local process (β process) decreases. But the intensity of the cooperative α process increases strongly with decreasing temperature (increasing $1000\,K/T$).

The dotted lines in *Figure 11* are to indicate that no statements about the intensity of the β process were possible in this temperature range because the maximum of the α process was no longer in the frequency window of measurements. The fitted parameters of the α process influence the estimated intensity of the β process in such a way that it was not possible to determine reliable values of $\Delta\varepsilon$. Experiments on a broader frequency scale would be necessary for more precise statements in this temperature range.

It should be mentioned that the α relaxation process is not only associated with the main chain movements. As n.m.r. results[8,20] show, at least the dynamics of the carboxyl group in the side-chain (which contains the dielectric dipole) is intimately connected to the main chain dynamics. The estimated characteristic volume V_α for the α relaxation, of the order of cubic nanometres, also contains side-chains. Nevertheless the caloric (c_p) activity is only sensitive to the cooperative aspect of the motions. The Δc_p decrease is, therefore,

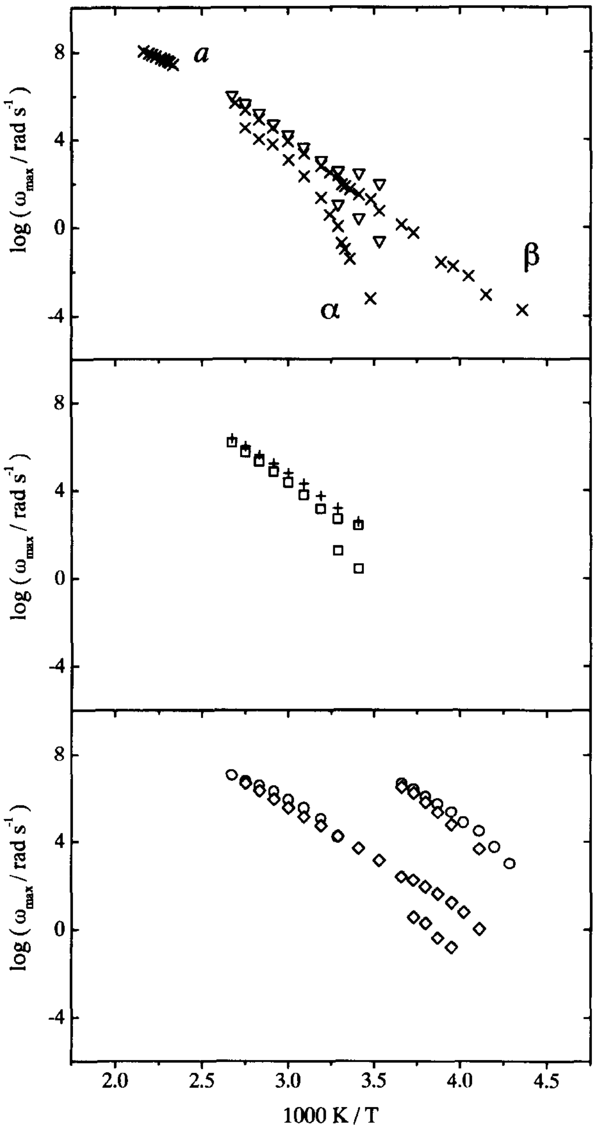

Figure 12 Arrhenius diagrams from dielectric measurements for the homopolymer PnBMA with different contents of the plasticizer DOP (×, 0%; ∇, 1%; □, 3%; +, 5%; ◇, 15%; O, 20%)

connected with a decrease of cooperativity, cf. equation (3).

We can now explain the decreasing step height Δc_p at the thermal glass transition with increasing pentyl copolymer content (see *Figure 4*). The typical d.s.c. heating rates of 10 K min^{-1} can be associated with low frequencies of dynamic measurements, about 10^{-3} Hz, well below the splitting region in the Arrhenius diagram (*Figure 10*). The splitting region is shifted to lower frequencies with increasing nPeMA content, which means that it approaches more and more this d.s.c. frequency. This frequency shift can thus be translated to a composition shift that connects the observed decrease in the step height Δc_p at the thermal glass transition with approach to the splitting region. This corresponds to the observation of a vanishing Δc_p step height for poly(n-alkyl methacrylate)s when the octyl side-group is approached[15].

Addition of DOP to PnBMA

Besides the variation of the nPeMA content in statistical copolymers, a shift of the splitting region can be achieved by an addition of DOP to the homopolymer PnBMA. DOP has two carboxyl groups defining two dipole moments in this molecule. *Figure 12* shows how the log $\omega_{\max}$ values for the *a* process are shifted to higher frequencies by addition of DOP. The activation energy does not change appreciably. For 20% DOP the trace of the *a* process in the Arrhenius diagram (*Figure 12*) is curved. The $\varepsilon''(\omega)$ dispersion curves of this sample can be fitted with a single HN function at all the temperatures measured.

The log $\omega_{\max}$ values of the α process shift to lower temperatures with increasing DOP content. At 15% DOP a further, separate process emerges at high frequencies. The trace of this new relaxation is slightly curved in the Arrhenius diagram. It is interpreted as the α process of the 'pure' DOP. At 20% DOP content this process shifts to slightly lower temperatures, and its intensity increases. The addition of DOP to PnBMA does not alter the parallel course of the log $\omega_{\max}$ values of the α and β processes in the splitting region.

CONCLUSIONS

It is shown in this study that the glass transition temperature T_g and the $\alpha\beta$ splitting region can continuously be shifted by variation of the composition of statistical copolymers of nPrMA with nPeMA. This shift is observed in both mechanical shear and dielectric experiments. In a way the copolymers behave like the homologous series of poly(n-alkyl methacrylate)s[7,15]. This means that a possible molecular ordering in the homopolymers is not responsible for the splitting scenario observed.

The evaluation of the dielectric experiments by means of a sum of two HN fitting functions shows, however, that the details of the $\alpha\beta$ splitting behaviour in statistical copolymers are more complex than previously expected. Besides a shift of the whole splitting region to lower temperatures, fine differences for increasing pentyl contents are detected. The splitting behaviour of statistical copolymers is changed from the PEMA-like behaviour[7] on the propyl side to a PnHMA-like behaviour on the pentyl side.

The log $\omega_{\max}$ values, the activation energy, the shape, and the temperature dependence of the local process intensity ($a\beta$ process) continuously change with the variation of nPeMA content in the statistical copolymers. In each copolymer the intensity of the α process decreases with increasing temperature in the vicinity of the splitting region. The Δc_p step height decreases with increasing nPeMA content. A parallel course of the log $\omega_{\max}$ values for the α and β processes in the splitting region (such as observed for the homopolymer PnBMA) was not observed for the 51.5% nPeMA copolymer. By addition of DOP to PnBMA, however, the parallel course of both processes is maintained.

The results of this study confirm the statement[7] that the details of the $\alpha\beta$ splitting region are rather sensitive to molecular details.

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