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Dynamical mechanical behavior of copolymers made of styrene and methyl methacrylate: Random, alternate and diblock copolymers

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Abstract

The dynamics of copolymers made of styrene and methyl methacrylate and of different architecture (three diblock, two random and one alternate) have been studied using a dynamic mechanical spectroscopy technique (DMTA). The scanning calorimetric results indicate that there is only one glass transition except for two of the diblock copolymers. In addition, only one broad mechanical relaxation is observed in all the copolymers studied in this work. However, it has not been possible to build master curves for the complex Young modulus E^* for the copolymers. In fact the relaxation spectra calculated from E^* are bimodal. In order to describe the relaxation functions of the samples, it has been necessary to use two Kohlrausch–Williams–Watts functions at each of the temperatures studied. The relaxation times of the two dynamic contributions can be described by Arrhenius laws, which is probably due to the relatively narrow temperature range for which the relaxation can be studied within the frequency range experimentally accessible. The stretching parameters increase linearly with T, which indicates that both dynamic transitions broaden as T is decreased.

Keywords: Dynamic mechanical spectroscopy; Block-copolymers; Random-copolymers

1. Introduction

Copolymers and blends have been used frequently to tune the properties of a material between those of the corresponding homopolymers [1,2]. In the case of copolymers, the final value of a given property, e.g. the melting or the glass transition temperature, T_g, does not only depend on the composition, but also on the architecture of the copolymer: random, alternate or block [2,3]. Also the morphology of the copolymers is strongly dependent on their architecture. In effect, random and alternate copolymers are one phase disordered materials, with concentration fluctuations of relatively short range [4]. On the other hand, block copolymers made of immiscible monomers have complex phase diagrams that may show micro-phase separation leading to different morphologies, depending on the copolymer composition and on the temperature [2]. In general, block copolymers present an ordered phase at low temperatures which becomes disordered above a composition dependent order–disorder temperature, T_{OD}. The equilibrium properties and phase diagram of diblock copolymers formed by styrene and an n-alkyl methacrylate (n being the number of carbon atoms of the lateral chain) have been studied in detail because of their departure from the classical behaviour [5–7]. While the copolymer with methyl methacrylate, and with $n>5$ show an order–disorder transition when the temperature is increased, those with $2 \leq n \leq 4$ are unusual because the transition takes place when the temperature is decreased. Copolymer composition and architecture have an important influence of the phase behaviour of blends [1,8], and thus in their use as compatibilizers.

Morphological complexity and concentration fluctuations have been found to have profound effects on the dynamics of the copolymers [9]. In the case of block copolymers, it has been found that the so-called normal mode of blocks such as poly(isoprene) or poly(propylene glycol) are different than in the corresponding homopolymers [10–12]. Also, the coexistence of an amorphous phase made of one of the co-monomers, and a glassy or a crystalline phase formed by the other one may lead to the appearance of a rigid amorphous phase, with well differentiated dynamic properties [13–15]. Finally, the existence of concentration fluctuations lead to

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Table 1
Characteristics of the different polymer samples

Sample	M_w (kDa)	M_w/M_n	M_w (PS) (kDa)	M_w (PMMA) (kDa)	Type	XMMA
PS	120	1.02	120	–	–	0.0
PMMA	135	1.05	–	135	–	1.0
A1	382	1.49	–	–	Alternate	0.50
R1	71.3	1.86	–	–	Random	0.40
R2	305	1.83	–	–	Random	0.75
D1	179.3	1.04	172	7.3	Diblock	0.04
D2	547.1	1.05	154.8	392.3	Diblock	0.73
D3	503	1.10	253	250	Diblock	0.51

M_w is the weight average molecular weight, M_w/M_n is the polydispersity index, and X_{MMA} is the mole fraction of methyl methacrylate groups.

a broadening of the dynamic relaxations, similar to the one described in polymer blends [16].

In a viscoelastic study of 1,4-poly(isoprene-*b*-vinylethylene) above the order–disorder temperature, Roovers and Wang showed that the block copolymer behaved as a thermorheologically simple material [17]. This behaviour was in contrast with that of the blends of the corresponding homopolymers. Similar conclusions were reached at by Ruzette et al. for diblock copolymers of styrene and *n*-alkyl methacrylates in the disordered state, for temperatures well separated from the order–disorder one [5]. However, Arendt et al. showed that the 1,4-poly(isoprene-*b*-vinylethylene) copolymers were thermorheologically complex materials when their rheo-optical properties were analyzed [18]. Thermorheologically complexity was also found when the copolymers approached the order–disorder transition from the disordered phase [5]. Pakula and Floudas [9] have shown that, for block copolymers in the ordered state, it is not possible to build master curves for the shear modulus at low frequencies.

The goal of the present work is to study the dynamics of copolymers made of styrene and methyl methacrylate using dynamic mechanical spectroscopy (DMTA). The results for diblock, random and alternate copolymers will be compared. Single phase and microphase separated samples have been studied. It will be shown that, regardless of their architecture and phase morphology, these copolymers show thermorheologically complex behaviour. Due to the proximity of the calorimetric T_g's of PS and PMMA, the analysis of the data in the frequency domain (loss modulus vs. frequency curves) does not allow one to resolve the contribution of two different dynamic modes near the glass transition. This is a problem usually found in this type of systems. However, we will show that the analysis of the data in the time domain (relaxation function vs. time curves), make such a task possible. More specifically, we will point out that to describe their relaxation functions it is necessary to use two Kohlrausch–Williams–Watts (KWW) functions over the whole temperature range studied.

2. Experimental section

The copolymers were purchased from Polymer Source (Canada). Gel permeation chromatography using tetrahydrofuran as solvent was used to determine the overall molecular weight, and the polydispersity index M_w/M_n. The relative content of the co-monomers was obtained by NMR. The characteristics of the different samples are given in Table 1. The calorimetric measurements reported were carried out at 10 K min^{-1} heating rate in a Mettler Star^e DSC instrument. The temperature scale was calibrated using 1-octane, indium and tin. The C_p scale was calibrated with sapphire. The second scan is reported for all the samples. T_g was obtained from the inflection point of the curves; the ΔC_p jump and the width of the transition ΔT were calculated according to Hempel et al. [19]. ΔQ was calculated from the integral under the peak of the thermogram.

The dynamic mechanical experiments were carried out on a DMTA V instrument from Rheometric Scientific. We have chosen the double cantilever geometry, and the experiments were carried out in the isothermal mode, which allowed the temperature to be constant within ±0.2 K. The measurements were carried out in the frequency range $0.01 \leq \omega/\text{Hz} \leq 100$. The probes were pressed in a Teflon mould under vacuum, and the temperature was kept 10° above the T_g of PMMA for 10 h in order to arise any previous thermal history. Afterwards the samples were allowed to reach room temperature while

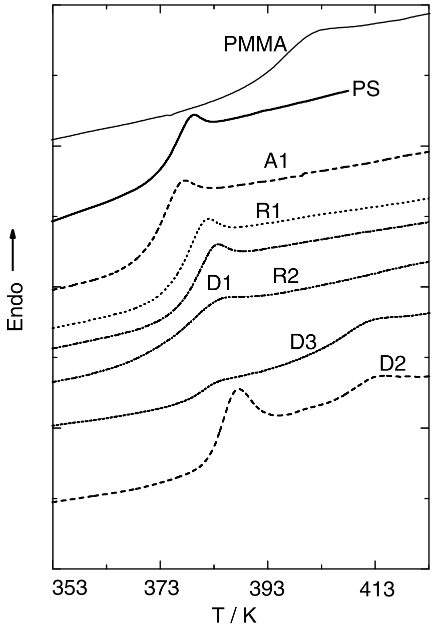

Fig. 1. Thermograms for the different polymer samples. The heating rate for all the samples was 10 K min^{-1}. The characteristics of the samples are given in Table 1.

Table 2
Calorimetric results for the different samples

Sample	$T_{g,1}$ (K)	$\Delta T_{g,1}$ (K)	ΔQ_1 (mW g^{-1})	$T_{g,2}$ (K)	$\Delta T_{g,2}$ (K)	$\Delta Q_{,2}$ (mW $^{g-1}$)
PS	375.5	12.1	0.32	–	–	–
PMMA	–	–	–	394.9	10.1	0.31
A1	372.5	11.9	0.30	–	–	–
R1	376.8	12.0	0.27	–	–	–
R2	385.8	21.5	0.30	–	–	–
D1	387.5	11.4	0.29	–	–	–
D2	391.8	13.4	0.36	408.4	9.2	0.12
D3	379.4	10.4	0.17	405.4	13.3	0.13

T_g is the calorimetric glass transition temperature, ΔT_g is the width of the glass transition region, and ΔQ is the height of the glass transition in the thermogram.

still under vacuum. Two probes were measured for each sample.

3. Results

Fig. 1 shows the thermograms obtained for the different copolymer samples, as well as for the PS and PMMA homopolymers. The values of the T_g's, the width of the transitions (measured as the difference between the onset and endset temperatures), and their intensities are given in Table 2. It can be observed that two of the diblock copolymers show two separate glass transitions, while the D1 diblock copolymer ($X_{MMA}=0.04$, X_{MMA} being the mole fraction of MMA) shows only one T_g. The TEM images taken for this sample (not shown) confirm that this sample is homogeneous at the level of a 10 nm scale, while the D2 and D3 diblock copolymers are in ordered states (microphase segregated, Fig. 2). The D2 sample presents an hexagonal packing of cilinders while the D3 seems to be in a lamellar morphology, in accordance to the conclusions of Russell et al. [20]. In spite of the width of the glass transitions, it can be observed that the T_g's for the diblock copolymers are slightly shifted with respect to that of the PS. Moreover, the high temperature glass transition for the D2 and D3 samples appear at temperatures higher than those of the pure PMMA homopolymer. As expected, the two random copolymers show values of the T_g intermediate between those of the homopolymers. While the width of the transition for the R1 sample ($X_{MMA}=0.40$) is similar to the values found for the diblock copolymers, for the R2 sample the width is much higher. Fox equation ($T_g^{-1}=w_1T_{g,1}^{-1}+w_2+w_2T_{g,2}^{-1}$ where w_1 and w_2 are the weight fraction of PS and PMMA, respectively, and the $T_{g,i}$ are their glass transition temperatures) is frequently used for predicting the glass transition temperature of random copolymers [21]. When applied to the two random copolymers studied in this work, the prediction is within the large experimental width for the R2 sample, while is too high for the R1 one. The results on Table 2 show that the content of MMA of a copolymer is not the factor that determines the shift of the T_g with respect to the homopolymers for the samples with one glass transition. In effect, for A1 ($X_{MMA}=0.50$) the T_g is lower than for R1 (random, $X_{MMA}=0.40$), and both have T_g's lower than the one of the one of D1 (diblock, $X_{MMA}=0.04$).

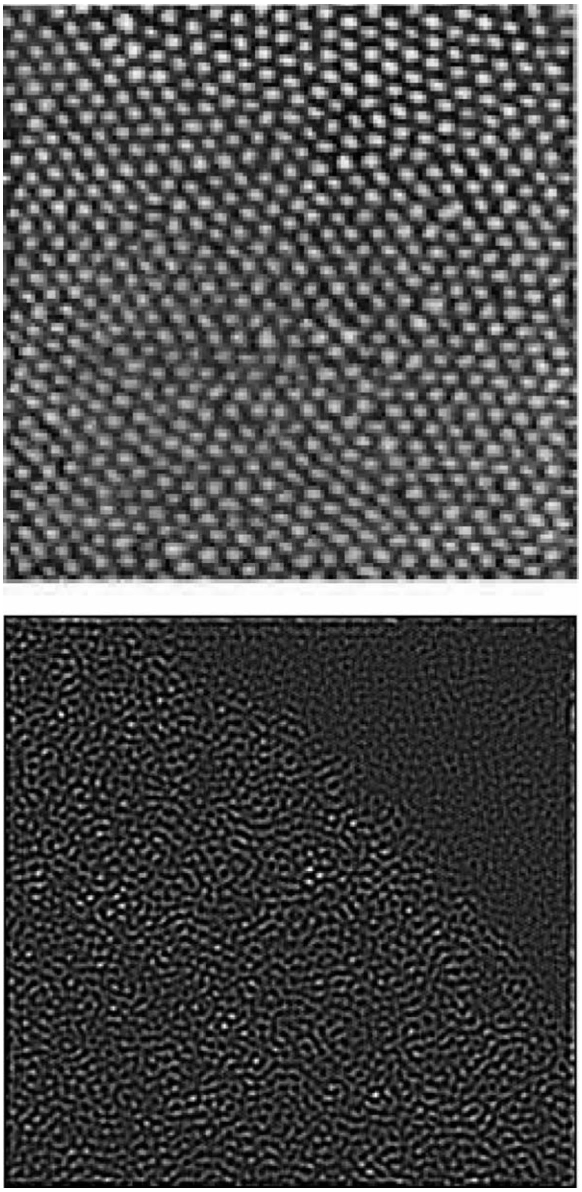

Fig. 2. TEM images of samples D2 (top) and D3 (bottom). While the morphology of the first is that of a hexagonal packing of cylinders, the second is compatible with a lamellar structure. The total width of the images correspond to 1 μm.

Fig. 3 shows the imaginary part of the complex Young modulus obtained from the DMTA experiments. Apparently all the samples studied show only one mechanical relaxation in the glass transition region. Previous studies of the viscoelastic properties of diblock copolymers in the homogeneous region (far from the order–disorder transition) have shown that these materials showed a thermorheologically simple behaviour, and that it was possible to build a master curve from the $G'(\omega)$ and $G''(\omega)$ curves obtained at different. Fig. 4 shows that it is not possible to build a master curve for the R16 and R2 random copolymers. Similar results are found for the other samples except for the D1 diblock copolymer where the different curves could be superimposed with a scattering smaller than for the other samples. The complex behaviour of the random and alternate copolymers is similar to the one found for blends of miscible homopolymers [17,22]. While the failure of

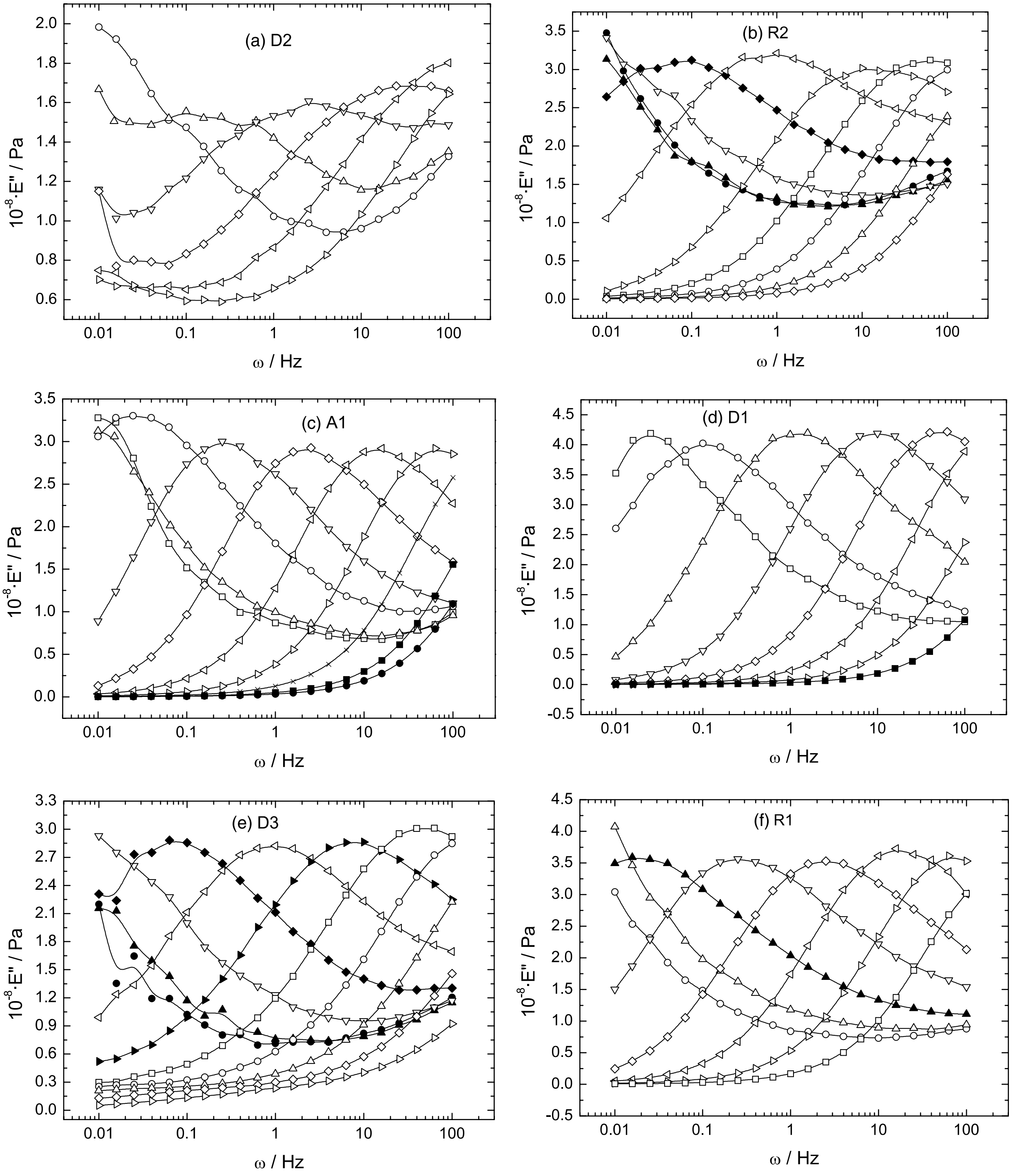

Fig. 3. Imaginary component of the Young modulus for the different copolymers. Only part of the experimental data have been plotted for clarity. The curves correspond to isotherms separated by 4°. The maximum and minimum temperatures plotted are: (a) 373, 393; (b) 373, 409; (c) 359, 493; (d) 373, 401; (e) 365, 405; (f) 363, 391 K.

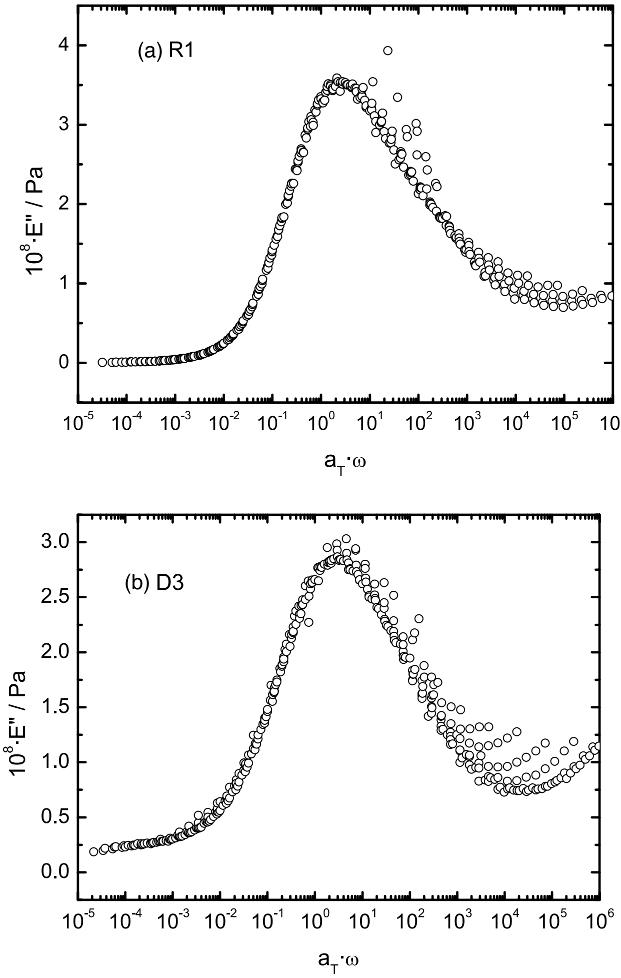

Fig. 4. Master curves obtained for the imaginary part of the Young modulus two of the copolymers. Similar results were obtained for the other samples. In general, it has not been possible to obtain a good superposition of the different isotherms in spite that shifts along both the frequency and the E'' axis were necessary to obtain the master curves.

the time–temperature superposition principle for the D2 and D3 samples is the expected behaviour for diblock copolymers in the ordered state, the behaviour of the D3 sample is in agreement with the behaviour described for block copolymers in the disordered state [17,18].

4. Discussion

In order to analyze the temperature dependence of the relaxation of the present copolymers it is necessary to fit each isotherm to a model because, as already shown, it is not possible to build master curves for them. The first option is to use the Coupling Model, which leads to a stretched exponential (or Kohlrausch–Williams–Watts, KWW) relaxation function

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\beta}\right] \tag{1}$$

where t is the time, $0 \leq \beta \leq 1$, and τ_{KWW} is related to the relaxation time through $\tau = (\tau_{\mathrm{KWW}}/\beta)\Gamma(1/\beta)$, $\Gamma(x)$ being the gamma function of x. Once $\phi(t)$ is known, the calculation of $E^*(\omega)$ is straightforward [23]

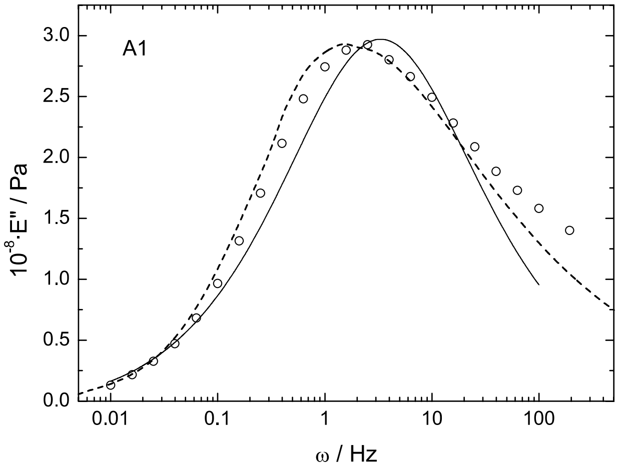

Fig. 5. Best fits obtained for one of the relaxation curves ($T = 375$ K) for the A1 copolymer. The symbols are experimental points, the continuous curve is the best fit obtained with the Havriliak–Negami function, and the dashed line is the best fit obtained with the Kohlrausch–Williams–Watts function.

$$\frac{E^*(\omega) - E_\infty}{E_0 - E_\infty} = \int_0^\infty \frac{\mathrm{d}\phi(t)}{\mathrm{d}t} \exp[-i\omega t]\mathrm{d}t \tag{2}$$

Fig. 4 shows the experimental and calculated values of E'' at 375 K for the A1630 copolymer for the optimum value $\beta = 0.40$. It can be observed that the KWW function is not able to reproduce the shape of the experimental data. The value of β increases with T. Similar results were obtained for the other samples.

A second possibility for describing the E^* results is to use an empirical function. This approach is frequently use in the analysis of the complex dielectric function ε^* [11–15]. Taking into account that in DMTA experiments the mechanical strain and the stress play roles equivalent to those of the electrical displacement and of the electric field in the dielectric relaxation measurements, it can be concluded that the compliance $D^* = 1/E^*$ is the mechanical equivalent of ε^* [24]. Therefore, one may

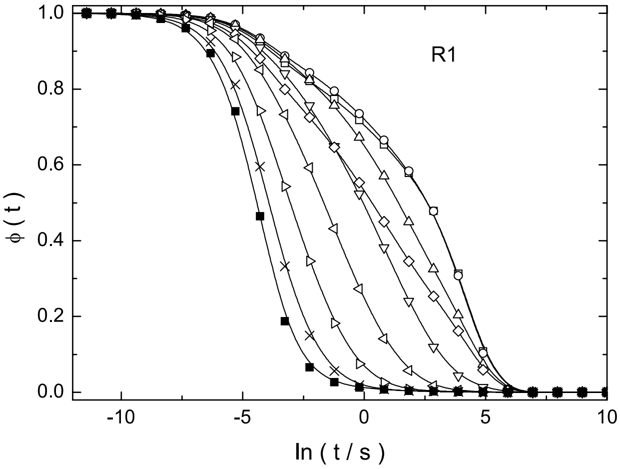

Fig. 6. Relaxation curves calculated from the relaxation spectra obtained from the experimental $E^*(\omega)$ curves for the R1 copolymer. The temperature interval is from 263 to 393 K (from right to left) with a 4° difference between two adjacent curves. Notice that the relaxations are clearly non-single exponentials.

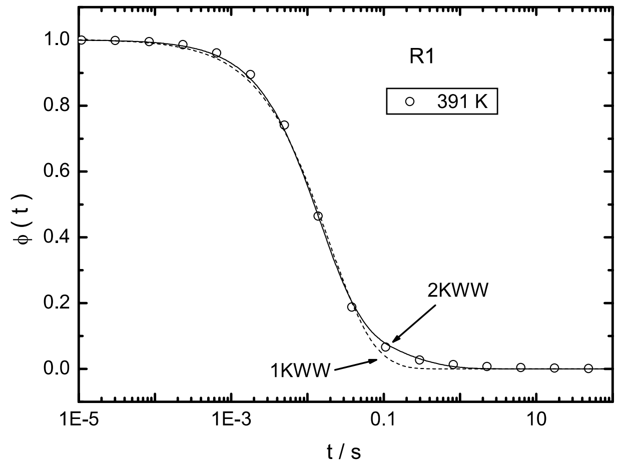

Fig. 7. Fit of the relaxation curve for the R1 sample at the highest temperature measured (393 K) using a single Kohlrausch–Williams–Watts (KWW) function (Eq. (1)), or the sum of two KWW functions (Eq. (5)).

write the following Havriliak–Negami (H–N) function [25]

$$\frac{1}{E^*} = D^*(\omega) - \frac{1}{\left[1 + i(\omega\tau_{\mathrm{HN}})^{\gamma}\right]^{\delta}} \tag{3}$$

where $0 \leq \gamma$, $\delta \leq 1$ are fitting parameters which account for the symmetrical and unsymmetrical broadening of the $E^*(\omega)$ curves, respectively. Fig. 5 shows the best fit obtained with Eq. (2) for the A1 copolymer at 375 °C. As in the case of the KWW function, the H–N function is not able to reproduce correctly the shape of the experimental curve. Similar results were obtained for the other temperatures and samples.

Due to the failure of Eqs. (1) and (3) in describing the experimental data, we have decided to calculate the relaxation spectra $H(\ln\tau)$ from the $E^*(\omega)$ curves. $H(\ln\tau)$ is given by

$$\phi(t) = \int_{-\infty}^{\infty} H(\ln\tau)\exp[-(t/\tau)]\mathrm{d}t \tag{4}$$

and it has been obtained using an algorithm based on Tikhonov's regularization method [26]. Fig. 6 shows the relaxation functions calculated from $H(\ln\tau)$ for R1 copolymer at different temperatures. They clearly reflect the bimodal character of the relaxation spectra obtained for the different samples (including the D1 diblock) at all the temperatures studied. As an example, Fig. 7 shows that, even at the highest temperatures for the R1, the $\phi(t)$ curves could not be fitted with

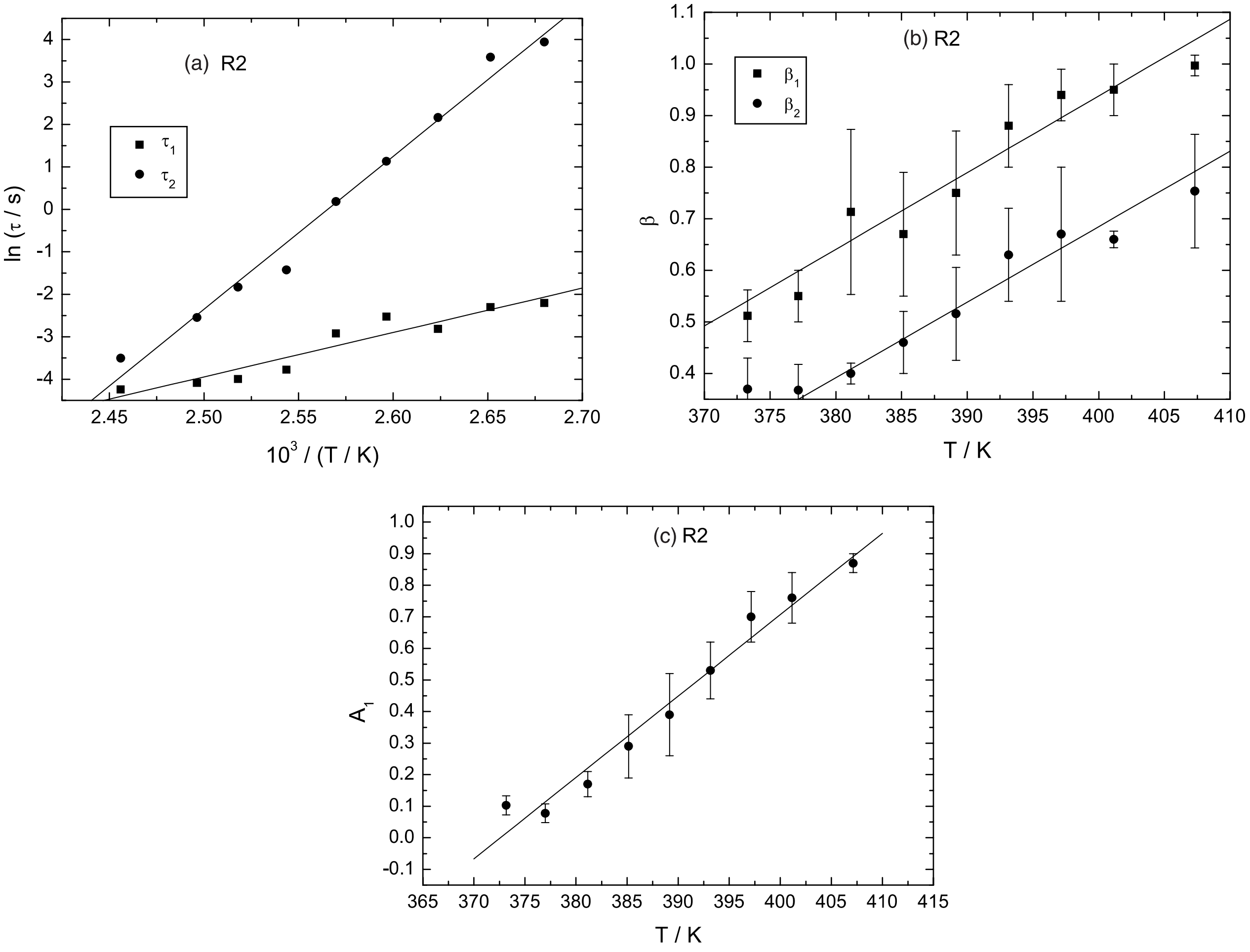

Fig. 8. Temperature dependence of the parameters of Eq. (5) for the R2 copolymer. The size of the errors bars in the ln τ_1 and ln τ_2 parameters are smaller than the size of the points. Notice that within the scattering of the points, the relaxation times can be described by an Arrhenius curve. Similar fits were found for the other samples.

Table 3
Temperature dependence of the parameters of Eq. (5)

	A1	R1	R2	D1	D2	D3
	$\beta_1=a_1+b_1\,(T\,(\mathrm{K}))$					
a_1	−4.01	−6.76	−5.01	−3.79	−2.85	−3.45
10^2b_1 (K^{-1})	1.28	1.98	1.49	1.20	0.93	1.09
	$A_1=a_2+b_2\,(T\,(\mathrm{K}))$					
A_2	−14.95	−6.68	−10.56	−12.15	−0.42	−2.40
10^2b_2 (K^{-1})	4.07	1.88	2.82	3.27	0.21	7.47
	$\ln\tau_{\mathrm{KWW},1}=a_3+(E_{\mathrm{A},1}/R)/(T\,(\mathrm{K}))$					
a_3	−41.77	−42.71	−29.94	−36.84	−10.24	−19.69
$10^{-3}(E_{\mathrm{A},1}/R)$ (K)	14.59	15.11	10.40	12.95	2.65	6.42
	$\beta_2=a_4+b_3\,(T\,(\mathrm{K}))$					
a_4	0.59	0.62	−0.14	−0.95	−1.37	2.56
10^3b_3 (K^{-1})	0.0	0.0	1.80	3.90	4.54	5.40
	$\ln\tau_{\mathrm{KWW},2}=a_5+(E_{\mathrm{A},2}/R)/(T\,(\mathrm{K}))$					
A_5	−43.10	−97.87	−99.60	−107.06	−67.17	−37.20
$10^{-3}(E_{\mathrm{A},2}/R)$ (K)	16.15	37.33	38.78	41.04	27.38	15.03

a single KWW function. The same was found for the other samples at all the temperatures, thus we have described our results using the sum of two KWW functions to describe $\phi(t)$

$$\phi(t) = A_1\exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW},1}}\right)^{\beta_1}\right] + A_2\exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW},2}}\right)^{\beta_2}\right] \qquad (5)$$

Eq. (5) leads to fits which agree with the experimental data within their experimental uncertainty. Fig. 8 shows the parameters characteristic of each of the two KWW, and their relative intensities for the R2 sample. Within their uncertainties, the temperature dependence of the parameters can be described by straight lines for all the copolymers studied. Table 3 gives the parameters of the linear fits. Due to the uncertainty inherent to the determination of the relaxation spectra, and to the limited temperature range for which the $E^*(\omega)$ curves are within the experimental window, we have described the temperature dependence of the relaxation times by an Arrhenius function; Table 3 gives the corresponding activation energy. It can be observed that the values corresponding to the D2 and D3 samples (the two block copolymers with large block sizes) have values of E_A/R smaller than those of the random copolymers and of the D1 (the block copolymer with a small PMMA block). Except for the alternate copolymer (A1 sample), the temperature dependence of τ_2 is much larger than that of τ_1 (Fig. 8(a)), and both relaxation times get closer as T is increased. Simultaneously, the intensity of the first dynamic contribution (A_1 in Eq. (5)) increases with T, (A_2 decreases because $A_1+A_2=1$, Table 3, and Fig. 8(c)). The stretching parameters increase with temperature, as it usually happens for homopolymers, which indicates that the two dynamic components broaden as the temperature is decreased. It is important to note that β_1 and β_2 significantly differ from unity through the whole temperature range for all the samples studied. This means that the bimodal character of the dynamics cannot be described as the simple sum of two exponentials. This stresses the physical significance of Eq. (5) to take into account the dynamic heterogeneity of the copolymers studied. These results also point out the relevance of the analysis of the DMTA data in the time domain. The change of the β's, and thus of the shape of the relaxation function, with T explains the thermorheological complexity found for all the copolymers studied. However, the DMTA data do not allow us to discuss the molecular origin of the two dynamic processes; a more local probe, e.g. NMR relaxation, would be necessary.

5. Conclusions

The calorimetric and mechanical behaviour of six copolymers with different architecture (random, alternate, and diblock) have been studied. The DSC experiments show a single broad glass transition for the random, alternate and the diblock with a short PMMA block. There is no correlation between the value of T_g and the content of MMA of the copolymer, the architecture playing a major role on this variable. Two well differentiated glass transitions are seen in the other two block copolymers with large PS and PMMA blocks.

The DMTA technique shows a single broad transition for all the copolymers, and that they behave as thermorheologically complex materials. It has been found that the E'' vs. ω curves cannot be fitted to a single KWW or to a single Havriliak–Negami function. The analysis of the $E'(\omega)$ and $E''(\omega)$ curves in terms of the relaxation spectra has allowed us to obtain relaxation functions that are clearly bimodal, thus showing the existence of two dynamic processes that overlap in the original $E'(\omega)$ and $E''(\omega)$ curves at all the temperatures studied. The relaxation times of the two processes show a simple Arrhenius behaviour, which is probably due to the small temperature range for which the relaxation can be studied with the frequency range experimentally available.

Acknowledgements

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