Polymer 43 (2002) 2803–2810

polymer

www.elsevier.com/locate/polymer

Preparation of poly(*tert*-butyl acrylate-*g*-styrene) as precursors of amphiphilic graft copolymers: 2. Relaxation processes and mechanical behavior

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Received 19 October 2001; accepted 19 December 2001

Abstract

Viscoelastic relaxations of four poly(*tert*-butyl acrylate-*g*-styrene) copolymers are studied over a wide range of temperatures. The temperature location and apparent activation energy of the distinct relaxations observed under tension mode are discussed. As grafted polystyrene content increases in the copolymer, microdomains of both components occur and, consequently, two relaxations associated with cooperative motions of either the acrylate backbone or the graft are observed. A bending deformation mode is also analyzed in the region of the glass transition of the two components to study the phase separation. Moreover, the glass transition temperature of the acrylic backbone is estimated by microhardness measurements. The relationship between microhardness and storage modulus is established either below or above the glass transition of the *tert*-butyl acrylate backbone. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Activation energy; Storage modulus; Graft copolymers

1. Introduction

One of the purposes of researches during the years has been to create polymers where the final behavior can be fine-tuned based on the applications. The control of macroscopic properties, such as glass transition temperature, melting temperature, solubility, particle size, and viscoelasticity, can be attained by regulating the degree of branching. Graft and block copolymers have found numerous practical applications because of the interaction between segments belonging to the same or different polymer chains. They represent a class of macromolecular architecture with unique features, which include as structural variables for instance, the composition, backbone length, branch length, and branch spacing. Accordingly, such graft copolymers possess a great potential to provide new properties and, consequently, spread out their application in fields which include, at the present time, polymer alloys, surface modification, membranes, and coating [1]. On the other hand, graft copolymers present distinct physical properties to those exhibited by their linear counterparts in either solution or in solid state. The rheological and mechanical behavior is strongly influenced by the existence of microdomains. These structures are in turn determined by the segment composition and architecture, temperature (or segregation power), and concentration and solvent quality (for the cases of copolymer solution).

Dynamic mechanical thermal analysis (DMTA) allows to elucidate the different motions taking place in the macromolecular chains and, in addition, to learn about the mechanical behavior because of the relationship of the storage modulus, E', with the stiffness. The study of viscoelastic relaxations of poly(*tert*-butyl acrylate-*g*-styrene), P*t*BAS, copolymers can be performed by taking into account the different relaxation processes exhibited in both 'parent' homopolymers [2], poly(*tert*-butyl acrylate), P*t*BA, and polystyrene (PS). The comparison of viscoelastic spectra in these copolymers with those displayed by homopolymers seems to be an adequate route to assess the influence of composition on the viscoelastic behavior and mechanical properties of such copolymers. Moreover, DMTA provides valuable information about, on the one hand, the existence of the mentioned microdomains by the observation of the glass transition temperature, T_g, of both the pure components or, on the other hand, the assumption of a homogeneous graft copolymer if a unique T_g is empirically seen.

The Vickers microindentation hardness test measures the resistance of a given material to a plastic deformation

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PII: S0032-3861(02)00063-0

Table 1
Some characteristics of the polymer samples obtained in the free-radical polymerization of *tert*-butyl acrylate in the presence of polystyrene macromonomer in benzene solution and 8.0×10^{-3} mol l^{-1} of AIBN as initiator at 70 °C [8]

Sample	$\bar{M}_n$	$\bar{M}_w$	N_{graft}
P*t*BA	148 000	379 000	–
P*t*BAS1	175 000	465 000	7
P*t*BAS2	170 000	509 000	10
P*t*BAS3	178 000	569 000	15
P*t*BAS4	204 000	797 000	32

produced by the impact of an indenter. Therefore, amorphous and semicrystalline polymers provide a different response related to the rigidity of the system. Differences in microhardness can even exist within amorphous polymeric materials if they are composed by microdomains of distinct stiffness (for instance, block or graft copolymers). Microhardness (MH) tests allow a rapid evaluation of variations in mechanical properties that are affected by changes in chemical or processing conditions [3–5]. In addition, MH results can be related to other mechanical parameters such as the elastic modulus and yielding stress [6,7].

In a previous article [8] the preparation, kinetic study, and thermal properties of poly(*tert*-butyl acrylate-*graft*-polystyrene) copolymers have been reported. The simple desprotection of *tert*-butyl acrylate (*t*BA) group by hydrolysis allowed to obtain the amphiphilic graft copolymers. The aim of the current work is to study the relaxation processes of these graft copolymers by DMTA, either under a tensile deformation mode or a bending one, and to determine whether they exhibit or not the phase separation at the microscopic level. In addition, the T_g of the *tert*-butyl acrylate backbone is measured by microhardness measurements. Finally, the relationship between storage modulus and microhardness is established for the distinct graft copolymers at temperatures either below or above the glass transition of the backbone.

2. Experimental

2.1. Materials

Macromonomer SR-4500 (ARCO Chemical Company), a poly(styrene) carrying a methacryloyloxy group at the chain end with a number-average molecular weight of 13 000 g mol^{-1} and $M_w/M_n = 1.05$, was used as received. 2,2′-Azobis(isobutyronitrile), AIBN, (Fluka) was purified by successive crystallizations from methanol. Benzene (Merck) and *tert*-butyl acrylate, *t*BA, (Merck) were purified by conventional methods [9].

2.2. Graft copolymer

The copolymer reactions were conducted in benzene solution using 8.0×10^{-3} mol l^{-1} of AIBN as initiator at 70 °C. Feed compositions consisted of *tert*-butyl acrylate monomer concentration of 1.5 mol l^{-1} and variable amounts of macromonomer. The reactions were followed by conventional dilatometric technique to attain limit conversion. Conversions of *t*BA were calculated from dilatometric data, since the low molar concentration of macromonomer in the mixture compared with that of *t*BA has practically no influence on the volume shrinkage of the system. The resulting polymer solutions were precipitated into methanol/water 1/1. The polymers were dried under vacuum at 40 °C, until a constant weight was reached.

The molecular weight distributions were measured by size exclusion chromatography (SEC) using a chromatographic system (Waters Division Millipore) equipped with a Waters Model 410 refractive index detector. Tetrahydrofuran, THF, (Scharlau) was used as an eluent at a flow rate of 1 cm^3 min^{-1} operated at 35 °C. Styragel packed columns, HR1, HR3, HR4E, and HR5E were used. P*t*BAS graft copolymers were analyzed based on 14 narrow-distribution standards of poly(methyl methacrylate), pMMA, (Polymer Laboratories) in the range between 1.4×10^6 and 3.0×10^3 g mol^{-1}. The values of the apparent weight-average and number-average molecular weights and number of grafts per chain obtained are listed in Table 1.

2.3. Specimen preparation

Sheet specimens of the poly(*tert*-butyl acrylate), P*t*BA, and the different P*t*BAS copolymers were obtained as films by compression molding in a Collin press between hot plates, at a temperature of 90 and 110 °C, respectively, at a pressure of 2.5 MPa for 4 min and, subsequently, quenched to room temperature. However, sheets of polystyrene, PS, homopolymer could not be obtained because of the film fragility.

2.4. Techniques

Viscoelastic properties were measured, on the one hand, with a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in a tensile mode. The real (E') and imaginary (E'') components of the complex modulus and the loss tangent (tan δ) of each sample were determined at 1, 3, 10 and 30 Hz over a temperature range from −150 to 150 °C, at a heating rate of 1.5 °C min^{-1}. On the other hand, the glass transition regions of the two components were additionally analyzed under a bending deformation mode in a Rheometrics DMTA V dynamic mechanical thermal analyzer. The E' and E'' components of the bending complex modulus and its corresponding bending loss tangent (tan δ) of each specimen were determined at 0.1, 0.5, 1 and 3 Hz over a temperature range from 35 to 150 °C, at a heating rate of 1.5 °C min^{-1}. The apparent activation energy values were estimated according to an Arrhenius-type equation, having an accuracy of 1 °C in the temperature assignment of *loss modulus* maxima. The frequency dependence on temperature in the relaxation mechanism associated with the glass transition has also

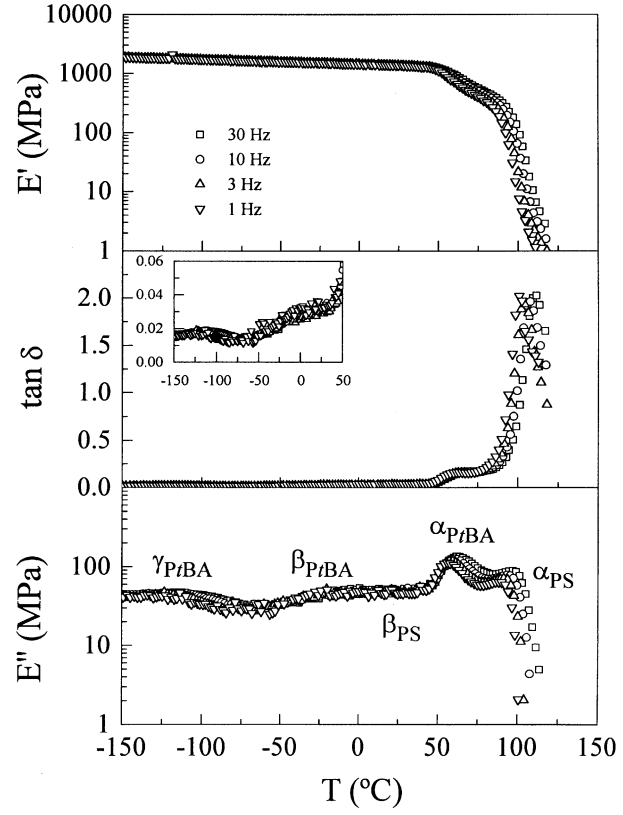

Fig. 1. Temperature dependence of the storage and loss modulus and loss tangent of P*t*BAS4 copolymer at the four different frequencies studied. In the insert, dependence on frequency of loss tangent in the secondary relaxation region.

been considered to follow an Arrhenius behavior though it is due to cooperative motions [2]. This approximation can be made without a significant error, since the analyzed frequencies are low enough to be fitted to such a linear behavior just mentioned. However, if measurements were carried out at a wider frequency range, the linear dependence would no longer be exhibited because of the non-Arrhenius inherent character of this process [2].

A Vickers indentor attached to a Leitz microhardness tester was used to carry out microindentation measurements. Measurements were performed over a temperature range from 30 to 90 °C. The heating control was performed with a hot stage Linkam TM S 92 and an aluminum adaptor. The temperature was increased in steps of about 2 °C. Specimens were held at the temperature of measurement before performing MH determination for a period of 3 min to reach equilibrium at a given temperature. All samples were initially heated above T_g to refresh. A contact load of 0.98 N and a contact time of 25 s were employed. MH values (in MPa) were calculated according to the relationship [10]:

$$\mathrm{MH} = 2 \sin 68° P/d^2$$

where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area.

3. Results and discussion

3.1. Viscoelastic behavior

The viscoelastic response of graft copolymers is primarily determined by the mutual solubility of the two homopolymers [11]. Fig. 1 shows the storage, E', and loss, E'', moduli and tan δ for one of the graft copolymers, P*t*BAS4, at different experimental frequencies used under tensile deformation. Temperature location and apparent activation energy of the distinct relaxation processes are listed in Table 2. E' values do not practically change with frequency up to approximately 50 °C since below this temperature the relaxation processes observed are secondary (γ_{PtBA}, β_{PtBA}, and β_{PS}) with a relative low activation energy associated compared with that related to a glass transition. Therefore, E' drops steadily, mostly because of thermal expansion [12]. However, a clear dependency with frequency is exhibited at temperatures higher than 50 °C in this graft copolymer due to the proximity of the α_{PtBA} relaxation related to the glass transition of the *tert*-butyl acrylate backbone and attributed to cooperative motions. In P*t*BAS4 at higher temperatures another relaxation mechanism is also observed that is associated with cooperative motions taking place within the PS grafted chains, the α_{PS} process. Consequently, a phase separation occurs in this copolymer as pointed out by its calorimetric characterization [8].

Fig. 2 shows the viscoelastic behavior under tension of the P*t*BA and the four P*t*BAS copolymers examined at 3 Hz. The relaxation processes empirically observed depend entirely on the graft content. In P*t*BAS3 the α_{PS} mechanism, associated with glass transition of PS grafted chains, is

Table 2
Relaxation temperatures and activation energies for the different relaxation processes in the P*t*BAS graft copolymers under tensile deformation

Sample	*T* (°C)					Δ*H* (kJ mol^{-1})				
	γ_{PtBA}	β_{PtBA}	β_{PS}	α_{PtBA}	α_{PS}	γ_{PtBA}	β_{PtBA}	β_{PS}	α_{PtBA}	α_{PS}
P*t*BA	−119	–	–	–	–	55	–	–	–	–
P*t*BAS1	−119	18	–	48	–	55	120	–	> 400	–
P*t*BAS2	−119	10	–	49	–	55	120	–	> 400	–
P*t*BAS3	−120	7	–	52	86	50	115	–	> 400	> 400
P*t*BAS4	−124	−25	18	59	91	45	115	220	> 400	> 400

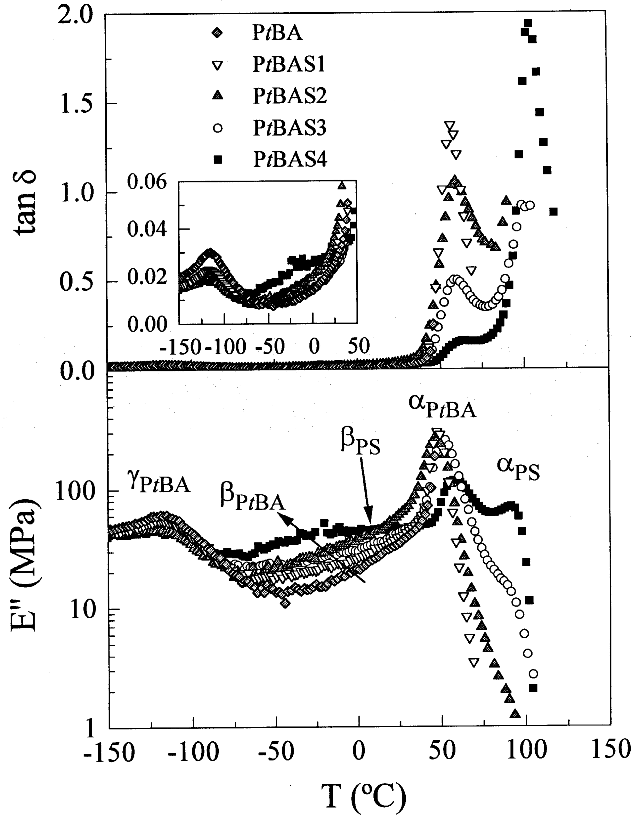

Fig. 2. Temperature dependence of the loss modulus and loss tangent of the different P*t*BAS copolymers analyzed at 3 Hz under tensile deformation.

hardly noticed in tan δ. P*t*BAS3 does not exhibit a tensile mechanical strength as large as P*t*BAS4 since the rigid comonomer content is lower in the former copolymer. Looking at the E'' plot, such a process appears as a shoulder overlapped with the $\alpha_{\mathrm{P}t\mathrm{BA}}$ relaxation at the highest temperature side. Accordingly, it seems that there are also microdomains within the microstructure of this graft copolymer. However, at lowest graft content, this relaxation process is no longer noted either in tan δ or in E''. Similarly, the β_{PS} mechanism is observed in P*t*BAS4 and gets completely merged into the $\beta_{\mathrm{P}t\mathrm{BA}}$ one as PS content diminishes in the copolymer. It seems that $\beta_{\mathrm{P}t\mathrm{BA}}$ relaxation is moved to higher temperatures with the decrease in graft content and this β_{PS} motion is no longer detected. On the other hand, in P*t*BA homopolymer the relaxation related to its glass transition temperature cannot be measured under tension since the material is extremely soft at that temperature and its tensile resistance is, therefore, very small being not able to bear the imposed deformation. The different observed relaxation processes are analyzed separately as follows in the order of increasing temperatures.

3.2. γ_{PtBA} *relaxation*

A γ mechanism has been observed since the mid 50's in acrylates and methacrylates due to relaxation exhibited by the alkyl group which is independent of that owed to the whole oxycarbonyl group and the main chain [2]. A rotation around the oxygen-alkyl bond has been considered as molecular mechanism. Moreover, a partial rotation within the alkyl group combined with a complete rotation has been taken into consideration, though exclusively when this alkyl group is long enough [13]. Therefore, a loss peak has been observed in the range of -200 and -100 °C (about 100 c s^{-1}) [2]. Location of such a process is strongly dependent on the length and nature of the mentioned alkyl group. This relaxation has also been observed in acrylates and methacrylates in which the side-chain joined to the oxycarbonyl group contained a dipolar unit. In the graft copolymers under study, this secondary relaxation is observed at temperatures around -120 °C (in E'' basis) due to the large volume of the *tert*-butyl group which has to rotate around the *O*-*tert*-butyl bond. Its intensity is dependent on the graft composition, as expected. It diminishes as the graft content increases in the copolymer since the number of groups participating in such a motion decreases, as shown in Fig. 2. On the other hand, its location is also affected by the graft content (see Table 2). This process is shifted to lower temperatures as the number of side chains grafted increases. This feature is probably due to the reduction of the intramolecular steric hindrance with the introduction of grafted chains. Such a steric hindrance is caused by the large size of the *tert*-butyl side group, which is involved in this $\gamma_{\mathrm{P}t\mathrm{BA}}$ movement. Accordingly, as graft content increases in the copolymer, a slight diminishing in the value of the apparent activation energy associated with this relaxation process is also observed (Table 2).

3.3. β_{PtBA} *relaxation*

In some acrylate polymers, a β relaxation has been exhibited [2]. The mechanism of this process is not clearly understood, but it seems to involve some limited movement of the –COOR side chains. The activation energy associated with these motions is higher than that involved in the γ relaxation of the P*t*BA just explained. This $\beta_{\mathrm{P}t\mathrm{BA}}$ process is of considerably smaller magnitude and broader than the α relaxation associated with the glass transition of the *tert*-butyl acrylate backbone. In these P*t*BAS graft copolymers, this relaxation process is moved to significantly higher temperatures in comparison with its location in some other acrylates because of the large volume of the alkyl substituent (*tert*-butyl) bonded to the oxycarbonyl group. Because of the subsequent steric constraints, the apparent activation energy associated is also considerably higher than that previously reported [2].

In Fig. 2 and Table 2 it is also observed that an increase in the PS graft content causes the $\beta_{\mathrm{P}t\mathrm{BA}}$ process to shift to lower temperatures and a decrease in the activation energy, similar to that explained earlier for the $\gamma_{\mathrm{P}t\mathrm{BA}}$ relaxation. Accordingly, these results seem to be related to the reduction of steric hindrance in the local rotational motion of the

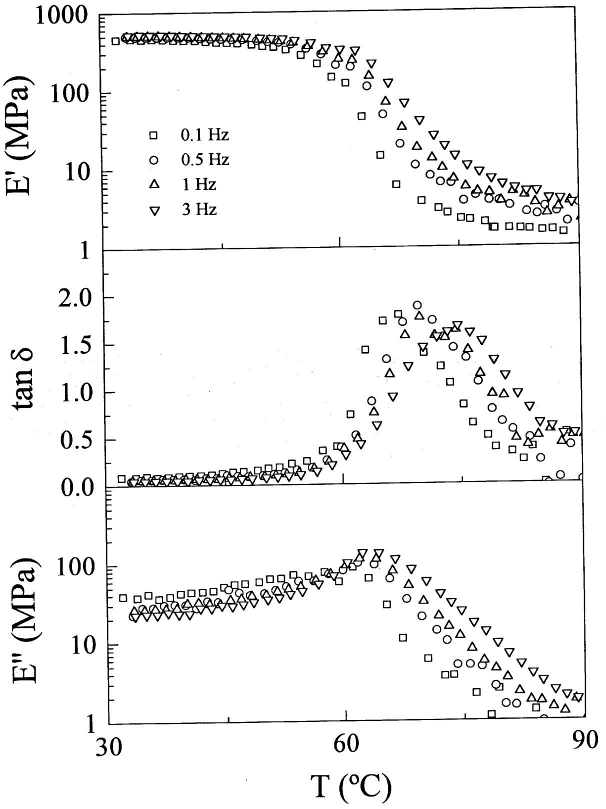

Fig. 3. Temperature dependence of the storage and loss modulus and loss tangent of P*t*BAS homopolymer at the four different frequencies studied under bending deformation mode in the glass transition region.

–COO*tert*-butyl groups as the incorporation of grafts is increased. In P*t*BA homopolymer this mechanism is quite overlapped with that owed to cooperative motions whereas in P*t*BAS4 it takes place at subambient temperatures.

3.4. β_{PS} relaxation

PS shows a β process in tan δ centered at about 27 °C [12]. By observing the intensity and temperatures of this process for PS and other poly(α-olefins) with ring structures in side chains [14], as well as in substituted PS [15], it can be shown that the β mechanism is most likely due to phenyl ring reorientation [12] and that the intensity of the relaxation is sensitive to conformational changes in the polymer chain backbone. For many polymers the strength of the β relaxation has been related to toughness [16], as long as the molecular motion responsible for the relaxation involves backbone motion and not just the reorientation of side groups. The lack of toughness of the unmodified PS can be interpreted as a consequence of the minimal backbone reorientation associated with this β_{PS} relaxation. In the current study, this relaxation is only clearly observed in the P*t*BAS4 with the highest graft content, as explained earlier. It appears to be completely merged with the β_{PtBA} relaxation. Accordingly, the summation of the contribution of these two secondary relaxations provokes the highest intensity in this region for that copolymer. Its location absolutely agrees with that previously reported [2]. On the other hand, its apparent activation energy, estimated by the separation of the overall viscoelastic response into different peaks, also correlates well with the values found in the literature [12] by mainly taking into consideration the high rigidity of the *tert*-butyl group. As graft content is lowered, the DMTA is not able to distinguish this relaxation process.

3.5. α_{PtBA} relaxation

The α_{PtBA} relaxation is considered as the glass transition in P*t*BA homopolymer. Under tension, P*t*BA does not present enough mechanical resistance at that temperature and, consequently, only the side of low temperature in that relaxation is observed without reaching the maximum of this relaxation process either in the tan δ or the E'' plots, as shown in Fig. 2. This feature is common in amorphous polymers since the large change in mechanical strength occurring along the glass transition, becomes even more critical when the deformation mode imposed is a tensile one. For that reason, DMTA measurements under bending were performed for the homopolymer from room temperature. Fig. 3 shows that this cooperative relaxation is perfectly observed for P*t*BA using this other deformation mode at different frequencies analyzed for both loss magnitudes, tan δ or the E''. Its location correlates with that already found by calorimetric measurements [8].

The different P*t*BAS copolymers also exhibit this cooperative mechanism, as shown in Figs. 2 and 4, related to the glass transition of the *tert*-butyl acrylate backbone. The intensity and location are dependent on the graft content in the copolymer, the former magnitude being much more sensitive. Accordingly, P*t*BAS1 presents a considerable lower intensity than the homopolymer though the graft content is very less, as shown in Fig. 4. The introduction of rigid PS segments in the *tert*-butyl acrylate structure modified the mobility of its amorphous phase hindering such a generalized motion. When higher content of grafts is included, the larger flexibility reduction is imposed on chains and, therefore, the α_{PtBA} process lowers significantly its intensity and shifts to slightly higher temperatures. Moreover, the relaxation time distribution is broadened as graft content increases in the copolymer also because of the mobility constraints. This feature is observed for the two deformation modes analyzed here.

3.6. α_{PS} relaxation

The α_{PS} relaxation is related to the glass transition of PS grafted chains. This relaxation process is only undoubtedly observed in P*t*BAS4 under a tensile deformation mode, as explained earlier. Such a feature means the existence of a phase segregation between the two components of this graft copolymer corroborating the two glass transition temperatures formerly found in the calorimetric study [8]. In P*t*BAS3, the α_{PS} mechanism appears as a shoulder in the

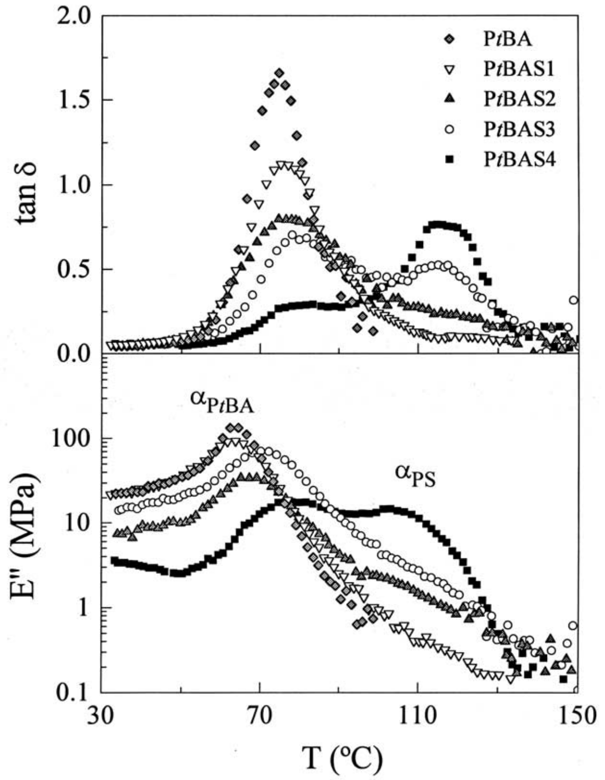

Fig. 4. Temperature dependence of the loss modulus and loss tangent of the different P*t*BAS copolymers analyzed at 3 Hz under bending deformation.

E'' plot overlapped with the α_{PtBA} relaxation and, then, microdomains would also remain within the microstructure of this graft copolymer though a unique T_g was attained by calorimetry. At the lowest graft content, this relaxation process is no longer noted either in tan δ or in E''. However, if bending deformation mode is applied, the cooperative motion in the amorphous phase of PS is clearly observed in P*t*BAS3 and slightly detected for the P*t*BAS2. Consequently, microdomains of the two components are exhibited for number of grafts of 10 or higher. The intensity diminishes as the PS graft content does in the copolymer because of the larger restriction imposed by comparatively higher amount of the *tert*-butyl acrylate. The location in tan δ basis seems to be quite independent of the graft content in the copolymers under analysis, as shown in Fig. 4. Its value of 104 °C under tension agrees with that reported by early studies [2,12] correlating well with that achieved in the styrene macromonomer by calorimetry [8]. However, in E'' basis, it is slightly changed because of the variation of E' with the graft content. The apparent activation energy associated with this process is really high (>400 kJ mol^{-1}) as it corresponds to the glass–rubber relaxation in an amorphous rigid polymer.

3.7. Mechanical behavior

Fig. 5 shows the effect on the elastic component in the complex modulus of the incorporation of rigid graft into the *tert*-butyl acrylate backbone. E' values increase as graft content does because of the stiffness enlargement. Therefore, the rigidity of the copolymer is raised with the introduction of PS branches. Accordingly, the lowest modulus values are observed in P*t*BA over the whole temperature range analyzed. At 45 °C when the glass–rubber transition is initiating, P*t*BA do not exhibit enough mechanical strength under tension due to its softness and the measurement cannot be continued. The introduction of few grafts confers a higher mechanical resistance to the *tert*-butyl acrylate rubbery state and, then, measurements can be performed up to 70 °C for the P*t*BAS1 and around 90 °C for the P*t*BAS2. Moreover, in those copolymers with the highest graft contents, P*t*BAS3 and P*t*BAS4, the glass transition of the PS segment can be observed looking at this mechanical magnitude.

MH measurements also provide an idea about the stiffness of these graft copolymers because its relationship with other mechanical parameters, such as the elastic modulus, provided in the current case by storage modulus. To correlate values of MH and E' over a temperature range, an analysis of the former parameter was performed with temperature as a variable, as shown in the upper plot of Fig. 6. From these results, a T_g determination of the *tert*-butyl acrylate backbone can be unambiguously done mainly in the copolymers with the highest number of grafts, P*t*BAS4 and P*t*BAS3, since at those compositions the resistance provided to the rubbery-like state of the backbone by the graft is high enough to be measured by the MH technique. As occurred in calorimetric measurements, the T_g

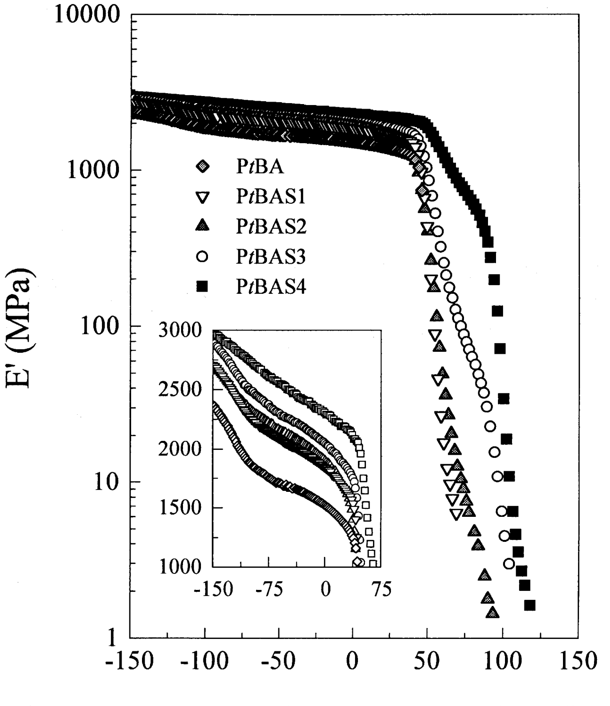

Fig. 5. Temperature dependence of the storage modulus of the different P*t*BAS copolymers analyzed at 3 Hz under tensile deformation.

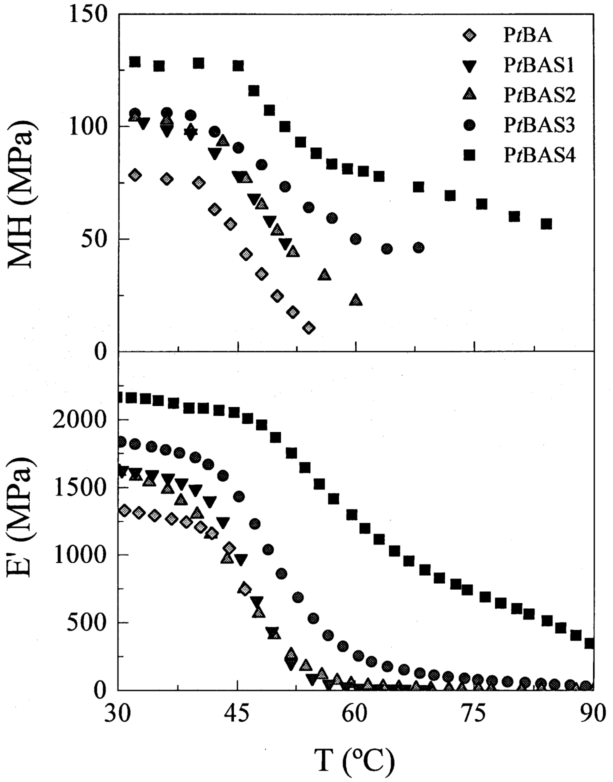

Fig. 6. Microhardness as a function of temperature for the different P*t*BAS copolymers and its comparison with the temperature dependence of the storage modulus at the same temperature interval.

estimation can be accomplished under three different criteria: (a) $\mathrm{MH}_{T_g}^{\mathrm{middle}}$: the temperature where MH diminishing is half of the total value at the transition; (b) $\mathrm{MH}_{T_g}^{\mathrm{onset}}$: the temperature of MH departure from the line obtained before the glass transition and (c) $\mathrm{MH}_{T_g}^{\mathrm{last}}$: the last temperature of the transition or, on the other hand, for P*t*BA and P*t*BAS1 where that temperature cannot be reached, the last temperature at which MH can be determined. It has been found for some ethylene–norbornene copolymers that the T_g measured by MH showing a better agreement with that obtained through other techniques is $\mathrm{MH}_{T_g}^{\mathrm{last}}$ [17].

Moreover, E' values have been plotted in the same temperature range indicating a similar behavior for both the mechanical magnitudes (lower plot in Fig. 6). The T_g estimation has also been performed to compare the dependence on the graft content for the T_g obtained by the different methods. Fig. 7 shows a similar variation with the composition for the calorimetric and microhardness T_g calculations being different to that found by taking into account E', E'' under tension or even E'' under bending. It seems that the effect of PS grafts on the *tert*-butyl acrylate amorphous phase is more significant when a deformation has to be held up along the amorphous-rubber transition, pointing out the enhancement in stiffness and the mechanical strength provided by the rigid PS microdomains.

Fig. 8 shows the similar dependence on the graft content of MH and E' either below or above the backbone T_g

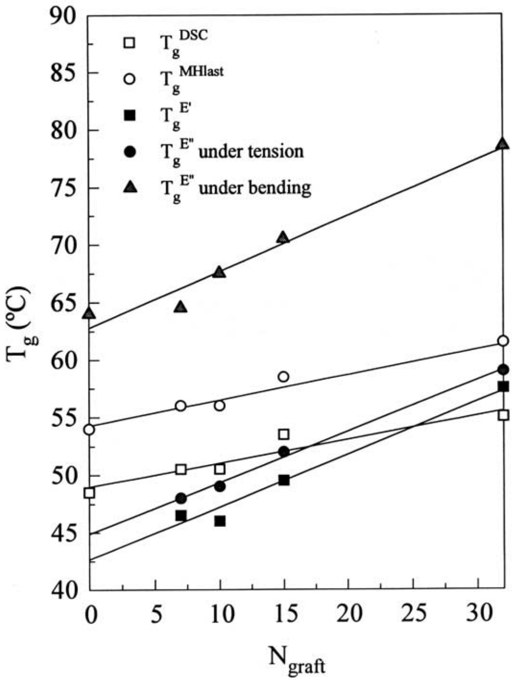

Fig. 7. Influence of the graft content on the *tert*-butyl acrylate T_g estimated from different types of measurements: calorimetric [8] (T_g^{DSC}), microhardness (T_g^{MHlast}), dynamic mechanical E' and E'' under tension ($T_g^{E'}$ and $T_g^{E''}$) and dynamic mechanical E'' under bending ($T_g^{E''}$).

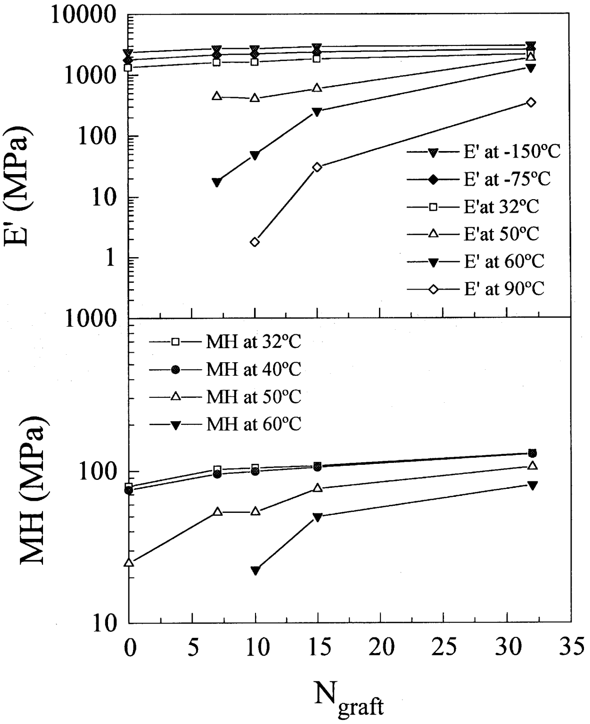

Fig. 8. Dependence of the storage modulus and microhardness values on the graft content for different P*t*BAS copolymers at different temperatures either below or above *tert*-butyl acrylate glass transition.

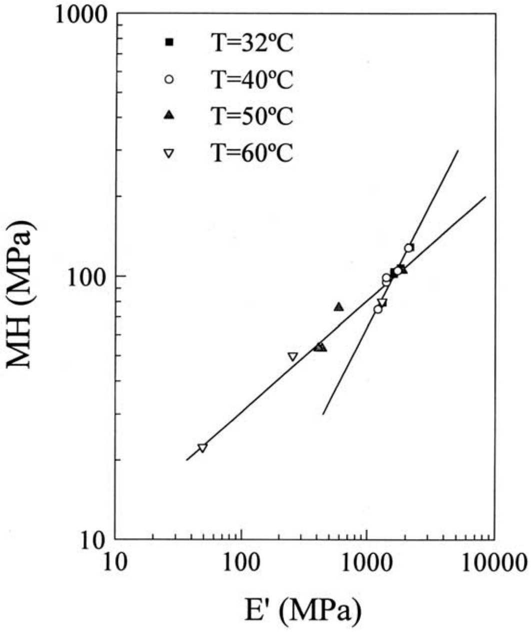

Fig. 9. Relationship of storage modulus and microhardness for the different P*t*BAS specimens.

increasing both the magnitudes as stiff graft content does in the copolymer at a given temperature. The variation is almost linear at temperatures well below T_g displaying the considerable deviation from linearity as the empirical temperature gets closer or even over the glass transition. This feature indicates the importance of the existence of the rigid microdomains in the mechanical behavior of these graft copolymers.

An empirical equation has been proposed for correlating E' and MH [10]:

$$\mathrm{MH} = aE^b$$

where a and b are constants. A good linear relationship has been obtained, as shown in Fig. 9, though two different slopes have been observed in the P*t*BAS copolymers analyzed depending on temperature: one for measurements performed below the T_g of the *tert*-butyl acrylate, which is related to the relationship of both magnitudes in the glassy state of the backbone, and the other slope as the temperatures are above that T_g being associated to the existing relationship between E and MH, but in this case, in the backbone rubbery state. This second slope can be attained because the mechanical resistance given by the PS grafts allows the copolymers to be measured at high temperatures.

Summing up, two relaxation processes associated with cooperative motions have been observed for a number of polystyrene grafts of 10 or higher measured under a bending deformation mode. From these two just mentioned mechanisms, the relaxation appearing at the lowest temperature is related to generalized motions within the *tert*-butyl acrylate backbone, whereas that at the highest temperature is associated with the cooperative motion within the PS graft chains. Consequently, microdomains of the two components are observed to depend on graft composition in these copolymers analyzed. Moreover, E' and MH values increase as graft content is raised because of their correlation with the stiffness. Therefore, a relationship between MH and E' has been established at temperatures either below or above the *tert*-butyl acrylate T_g. Such a T_g has been estimated by different techniques and its dependence on the graft content has been determined.

Acknowledgements

This research has been supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT), (MAT2000-1008). M. Fernández-García and M.L. Cerrada are grateful to the Comunidad Autónoma de Madrid and Ministerio de Educación y Cultura, respectively, for their financial support.

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