

Molecular Mobility in Styrene-co-methacrylic Acid Random Copolymers from 100 to 450 K

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SYNOPSIS

Molecular mobility of both the polystyrene homopolymer and a series of styrene-co-methacrylic acid copolymers with various amounts of methacrylic acid is analyzed in the temperature range from 100 to 450 K, by high-resolution dynamic mechanical spectrometry, IR, and differential scanning calorimetry. Isochronal spectrometry exhibits for polystyrene homopolymer two relaxations, the β and α relaxations, with increasing temperature. Styrene-co-methacrylic acid copolymers exhibit three mechanical relaxations, the γ , β , and α relaxations, from 100 to 450 K. These relaxations could be related to the progressive occurring of motions of the side groups and of the backbone chains when increasing the temperature. This could be due to the progressive breakdown of hydrogen bonds, which could show a somewhat wide range of magnitude. Furthermore, the decreasing of the magnitude of the α relaxation with increasing methacrylic acid content could suggest the presence of a stable network of chemical cross-links induced by the presence of anhydride so that molecular mobility could be partially inhibited above T_g . The remaining of a fluctuation network of hydrogen bonds (labile contacts) above T_g could also emphasize the decrease in molecular mobility. © 1993 John Wiley & Sons, Inc.

I. INTRODUCTION

Many investigations by dynamic mechanical spectrometry, dielectric loss, and NMR have been carried out on polystyrene and its derivatives such as modified polystyrene by ring or chain substituents, copolymers, or blends to give some contributions about molecular motions occurring at various temperatures. Let us recall the reported observations on polystyrene. Polystyrene homopolymer displays at least three transitions designated as γ , β , and α with increasing temperature.¹⁻⁶

The α relaxation related to the glass transition is exhibited by dynamic mechanical spectrometry, dielectric loss, and NMR experiments.^{5,7,8} This transition located at about 373 K at 1 Hz¹⁻⁶ is shifted toward higher temperatures when chemical modifications such as α -CH₃, orthomethyl substituent, or copolymerization with acrylic acid are performed.

These substituents or comonomers induced an increase in the barrier for rotation around the backbone chain.¹⁻¹¹ This relaxation obeys, in a first approximation, the time-temperature principle and its apparent activation energy is about 400 kJ/mol.^{5,9} Chemical modification or copolymerization with acid induced an increase in the apparent activation energy.

The β relaxation is located at about 300 K at 1 Hz.^{1,5,7,12,13} This wide relaxation appears in both dielectric loss and dynamic mechanical spectrometry.⁵ The β relaxation related to local motions, i.e., rotational motions of the backbone chains inducing 4-8 monomers,^{1,5} is regarded by some authors⁷ as the primary transition inducing the main transition, i.e., rotational motions over large segments of the backbone chain. This β relaxation is a thermorheologically simple process and its temperature dependence can be expressed by the Arrhenius equation.¹ There are some discrepancies about the activation energy that is estimated between 70 and 120 kJ/mol.^{1,5} These discrepancies could be due to the weak magnitude of the β relaxation extended over a wide

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range of temperature and that can merge into the main relaxation. The magnitude of the β relaxation is higher in anionic polystyrene than in quenched isotactic polystyrene. Alternating copolymers of styrene and acrylonitrile induce an enhancement of the β peak, whereas this relaxation is not observed in copolymers of styrene and butadiene.¹ Chemical substitution by an *ortho*-methyl substituent suppresses this relaxation, whereas *meta*-methyl enhances it.¹ Stress increases the β relaxation magnitude, whereas densification leads to a suppression of the β peak maximum.¹⁴

Some authors^{1,5,15} have reported the presence of a γ transition in some polystyrene homopolymer relaxation spectrum located at about 160 K at 1 Hz.^{15,16} But there are discrepancies about the presence of such a relaxation. This relaxation occurs in both dynamic mechanical spectrometry and NMR experiments but not in dielectric loss experiments.⁵ According to Yano and Wada,⁵ this could suggest that the γ peak could be related to the rotation of phenyl groups around the bond of the backbone chain. Moreover, the γ peak height and the area under the γ peak decreased as molecular weight increased from 1.2 to 4.6 10^5 g/mol. According to Tonelli,¹⁶ the γ relaxation could not result from free phenyl group rotations because of the low probability of a conformation allowing it. But a value of about 30–40 kJ/mol for the activation energy of the γ process agrees with such phenyl group rotation.¹⁷ Moreover, the very weak magnitude of the γ relaxation could result from the low probability of favorable conformation. But, some controversies about the presence and the origin of the γ relaxation remain. Thus, according to Illers and Jenckel,¹⁵ the γ relaxation results from torsional motions of methylene units in the main chain due to head-to-head enchainments, but these units are in a restricted number in atactic polystyrene. Moreover, the increase in the γ peak magnitude in the series *para* H, F, Cl, and Br and the shift of the γ maximum

toward higher temperatures in these series could be indicative of a mass effect on an end group.^{15,18}

Other relaxations displayed by polystyrene have been reported. Thus, a γ' peak located at about 100 K at 10 kHz is observed only by dielectric loss spectrometry.⁵ Its activation energy is about 12 kJ/mol. This γ' peak is assigned to weak polar bonds such as oxygen bonds in the chain. The δ peak located at about 55 K at 10 kHz appears in dynamic mechanical spectrometry and NMR experiments. Its activation energy is about 16 kJ/mol. The δ transition has been related to defects in tacticity by Yano and Wada.⁵ According to Boyer and Turley,¹ this transition is attributed to combined phenyl group oscillation and wagging.

The present work attempts to make some contributions about molecular mobility occurring in polystyrene homopolymer and in styrene-*co*-methacrylic acid random copolymers over the temperature range 100–450 K. The investigations are carried out by high-resolution dynamic mechanical spectrometry. Furthermore, calorimetry experiments and FTIR investigations have been performed to study the microstructure of the analyzed materials.

II. EXPERIMENTAL

1. Materials

Polystyrene homopolymer and styrene-*co*-methacrylic acid (SMAA) random copolymers with various weight fractions of methacrylic acid have been provided by Orkem Co. Characteristics of such materials are reported in Table I. The copolymer compositions were determined by chemical titration and the molecular weight size distribution by chromatography analysis (GPC) in carbon tetrachloride (CCl₄) solution.

The polymers were extruded at 470 K by using a twin-screw extruder from Leistritz (LSM 30-34).

Table I Mean Molecular Weights of PS Homopolymer and SMAA Copolymers (*I*: Polydispersity Ratio)

Polymer	% Wt Methacrylic Acid	% mol Methacrylic Acid	\bar{M}_n	\bar{M}_w	<i>I</i>
PS	0.0	0	99,500	306,800	3.1
SMAA1	8.4	10	125,500	325,500	2.6
SMAA2	10.0	12	204,000	581,700	2.9
SMAA3	12.8	15	168,300	459,200	2.7
SMAA4	19.2	22	103,200	243,700	2.4

Then, the polymers were molded at 470 K under high pressure (200 bars) and cooled at room temperature. To give the same thermal history at each sample, specimens were heated at a temperature higher than their glass temperature and then cooled to room temperature at the same cooling rate (10 K/min). For experimental works, all samples were cut to the following dimensions: $20 \times 6 \times 1$ mm for dynamic mechanical analysis and $2 \times 2 \times 1$ mm for calorimetry experiments and density measurements. FTIR spectra were recorded on the polymer powder (before extrusion) and on the extruded and molded specimens.

2. Density Measurements

Density was measured with a CCl_4 /ethanol gradient density column at 296 K. For each sample, five measurements are carried out and the reported density is the average value.

3. Differential Scanning Calorimetry

Thermograms were recorded using a Perkin-Elmer DSC7 apparatus over the temperature range from 320 to 470 K at a heating rate of 10 K/min. The glass temperature for this heating rate was determined for each polymer.

4. FTIR

Infrared spectra were recorded at room temperature on a Nicolet 20SX Fourier transform infrared (FTIR) spectrometer. The purpose of this IR analysis was to determine if chemical modifications could occur in the analyzed polymers during the extrusion and molding processes. Thus, spectra were performed both on the nonextruded polymer and on the extruded polymer. Therefore, the polymers are intimately mixed with 2 wt % dry powdered potassium bromide (KBr). Mixing was effected by thorough grinding in an agate mortar, then with a small vibrating ball mill. The mixture was pressed under pressure *in vacuo* to form transparent disks.

5. Dynamic Mechanical Spectrometry

Dynamic mechanical spectrometry was carried out by a high-resolution automated low-frequency inverted torsion pendulum (Micromechanalyser, Metravib Co., France). This setup provides the real (G') and imaginary (G'') parts of the shear modulus and the internal friction $\tan \phi (= G''/G')$ as a function either of the temperature (for one or several

frequencies) or of the frequency (under isothermal conditions). In this work, runs were performed by increasing the temperature from 100 to 450 K at 15 K/h and at three frequencies: 1, 0.1, and 0.01 Hz.

III. RESULTS AND DISCUSSION

1. Density and DSC Measurements

With increasing the weight fraction of methacrylic acid, density increases and glass temperature is shifted toward higher temperatures (Table II). The increase in density could be due to a decrease in free volume induced by addition of methacrylic acid.⁹ The shift of the glass temperature toward higher temperatures with increasing the weight fraction of methacrylic acid could be related to a decrease in molecular mobility.⁹ This kind of variation is in agreement with Brannock et al.'s data¹⁹ determined for a series of styrene-acrylic acid copolymers containing from 0 to 9 mol % acrylic acid.

2. FTIR Spectra

This part attempts to determine the influence of hydrogen bonds on the polymer properties. In more reactions, the first step consists of the formation of molecular and ionic complexes with a hydrogen bond:



Equilibrium (1) describes the formation in the molecule of a hydrogen-bond complex between the free proton-donor molecule A—H and the acceptor B. In our case, it could be related to the formation of associated acid groups without transfer of a proton (the two acid groups are in two different planes). These hydrogen bonds are weak or moderately

Table II Glass Temperatures (Heating Rate = 10 K/Min) and Density Measurements of PS Homopolymer and SMAA Copolymers

Polymer	T_g (K)	Density at 296 K (g/cm ³)
PS	274	1.0535
SMAA1	290	1.0797
SMAA2	294	1.0824
SMAA3	297	1.0851
SMAA4	316	—

strong and could constitute a physical fluctuation network with contacts between macromolecular units. The lifetimes of these labile contacts are in the same order of magnitude as are characteristic periods of molecular mobility.²⁰ Furthermore, equilibrium (2) could agree with the formation of acid dimers with transfer of a proton by means of the hydrogen bond (the two acid groups are in the same plane), as illustrated in Figure 1. The H bonds in acid dimers are semicovalent because of the electron delocalization. Thus, it can be concluded that hydrogen bonds do range from weak to strong in polymers.

Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) of the PS homopolymer and the SMAA4 copolymer (before extrusion) are compared in Figure 2. All SMAA copolymers show some differences when compared to polystyrene (PS) homopolymer, in particular,

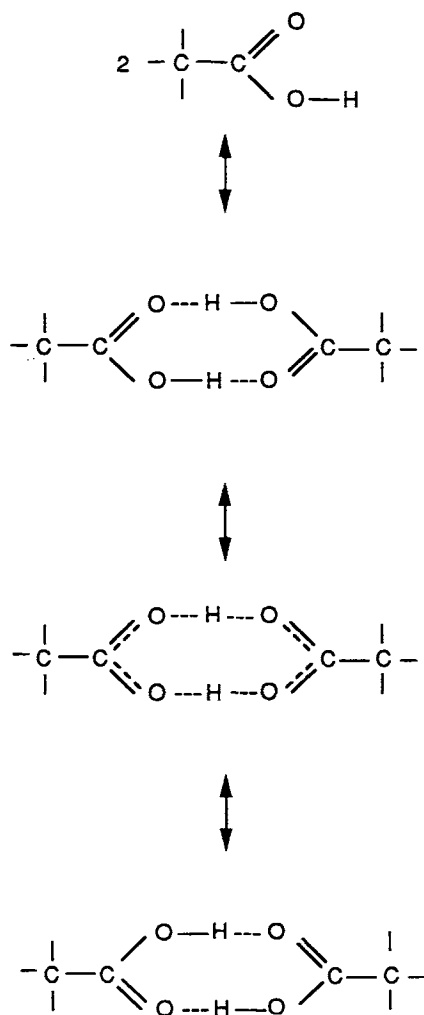


Figure 1 Formation of acid dimers.

- (i) a large band centered near 3440 cm^{-1} , which could be related to the free O—H stretching²¹;
- (ii) a broad band extended from 3300 to 2500 cm^{-1} , which could be due to the combined O—H stretching²¹; and
- (iii) a doublet located at about 1740 and 1696 cm^{-1} , which could be indicative of the C=O stretching of free acid groups (monomer) and the C=O stretching of the combined acid groups (dimer), respectively.

From these data, it can be concluded that the presence of methacrylic acid could lead to additional specific interactions (dimers) because of the carboxylic acid H-bond formation. This conclusion is in agreement with the decrease in specific volume induced by the copolymerization of styrene with methacrylic acid as described above.

The FTIR spectra on extruded and molded specimens were performed to determine if the copolymers undergo chemical modification during the extrusion process resulting in the formation of anhydride. As, for example, extruded SMAA3 and SMAA4 copolymers spectra are compared in Figure 3. This figure shows the effect of heating the polymers at 470 K (extrusion process) upon the carbonyl stretching region from 1840 to 1600 cm^{-1} of the infrared spectrum. A band as a shoulder at 1760 cm^{-1} is observed and its magnitude increases with increasing the methacrylic content. According to Lee et al.,²² cyclic anhydrides (characteristic bands at 1802 and 1764 cm^{-1}) can be formed in acid-containing polymers by raising the temperature to 310 K . Moreover, this figure exhibits a band at 1733 cm^{-1} that could be related to the formation of linear anhydrides²² during sample elaboration. The schematic diagram showing the carboxylic acid monomer and dimer together with the formation of anhydride is given in Figure 4.

3. Dynamic Mechanical Spectrometry

Plots of $\log G'$ and $\log(\tan \phi)$ vs. temperature of the PS homopolymer at three frequencies, 1, 0.1, and 0.01 Hz, are exhibited in Figure 5.

The $\log(\tan \phi)$ spectrum shows a well-defined peak located at about 381 K at 0.1 Hz. This relaxation, related to the glass transition, is designated as the α relaxation or main relaxation. The frequencies of $\log(\tan \phi)$ maxima from isochronal plots are plotted against the reciprocal temperature in Figure 6. It can be observed that the time-temperature dependence follows in a first approximation

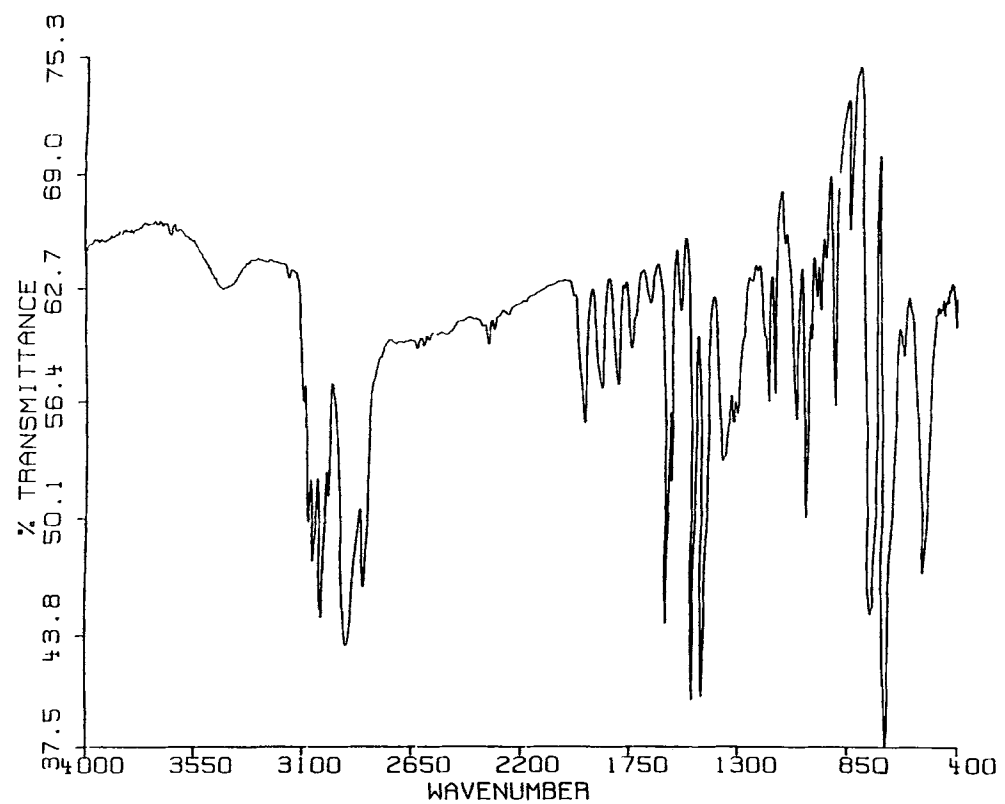
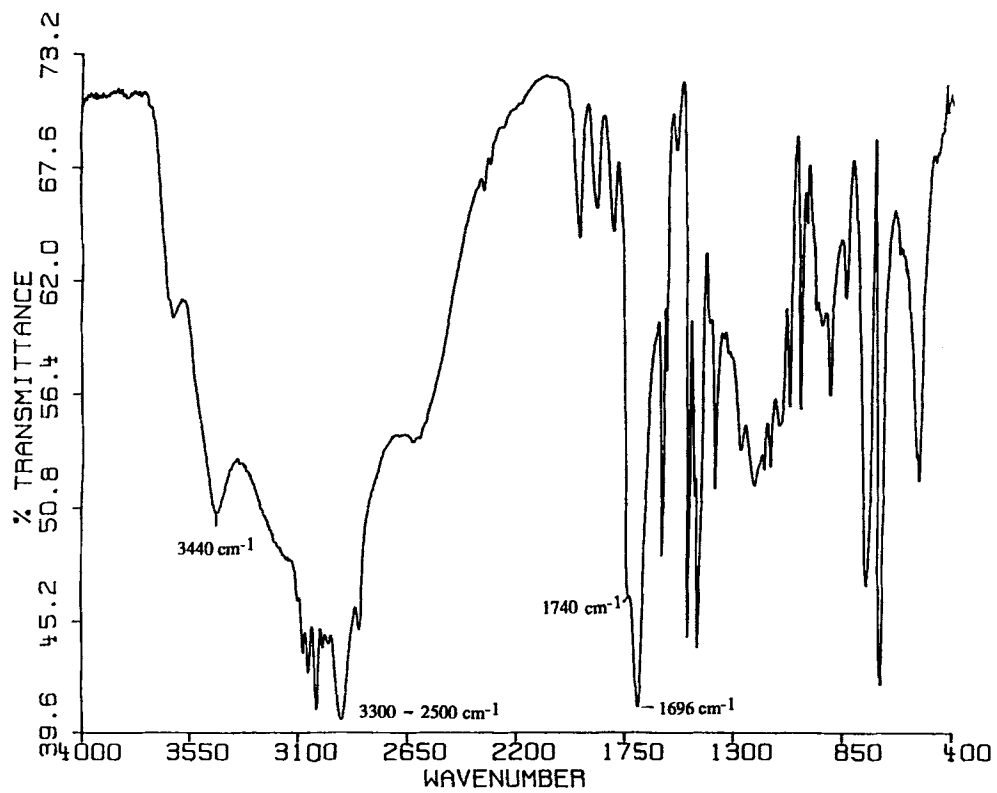


Figure 2 FTIR spectra of (a) nonextruded SMAA4 copolymer and (b) nonextruded PS homopolymer.

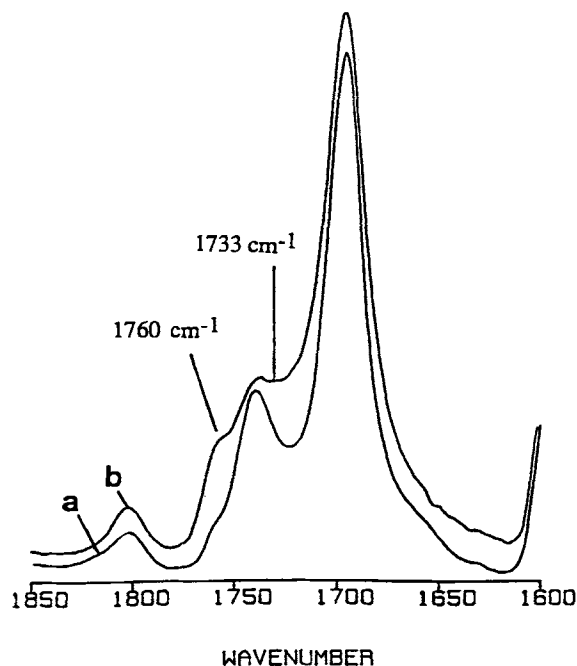


Figure 3 FTIR spectra of (a) extruded SMAA3 copolymer and (b) extruded SMAA4 copolymer.

an Arrhenian law over the temperature range. But, it is well known that the main relaxation is not a thermorheologically simple process and that the time-temperature dependence of the α relaxation is of the WLF type.^{1,5,7} Such an Arrhenian representation allows one to determine the apparent activation energy evaluated to 562 kJ/mol at 381 K.

At about 273 K, the $\log(\tan \phi)$ spectrum at 0.01 Hz shows a weak peak that could be related to the β relaxation.^{1,5,7} The activation energy of this relaxation cannot be determined from these data because β relaxation displayed at 0.1 and 1 Hz merged into the main relaxation at these frequencies.

At lower temperatures, in disagreement with some authors, the analyzed PS homopolymer does not exhibit any relaxation, in particular, near 160 K. According to these authors, the PS homopolymer exhibits a relaxation related to the phenyl rotations^{5,16} or to termination by coupling of two growing PS chains.¹⁵ This result adds to the controversy about the existence/origin of such a relaxation.

To show the main differences between dynamic mechanical spectra of the PS homopolymer and styrene-*co*-methacrylic acid copolymers, Figure 7 reports plots of $\log G'$ and $\log(\tan \phi)$ vs. temperature at the three frequencies 1, 0.1 Hz and 0.01 Hz displayed by the SMAA4 copolymer.

The main relaxation related to the glass transition is greatly shifted toward higher temperatures. Thus,

the α relaxation for the SMAA4 copolymer is located at about 420 K at 0.1 Hz, whereas it was centered around 381 K for PS. Moreover, the height of the $\tan \phi$ maximum is decreased (1.97) compared to the $\tan \phi$ peak shown by the PS homopolymer (3.74).

This copolymer shows a weak but well-defined peak at the three frequencies located at about 350 K at 1 Hz. In the temperature range of the β relaxation shown by the PS homopolymer (at about 273 K), no relaxation is observed. Thus, the subvitreous relaxation displayed by the copolymer could be assigned to the β relaxation that is shifted toward higher temperatures compared to the β relaxation exhibited by the PS homopolymer.

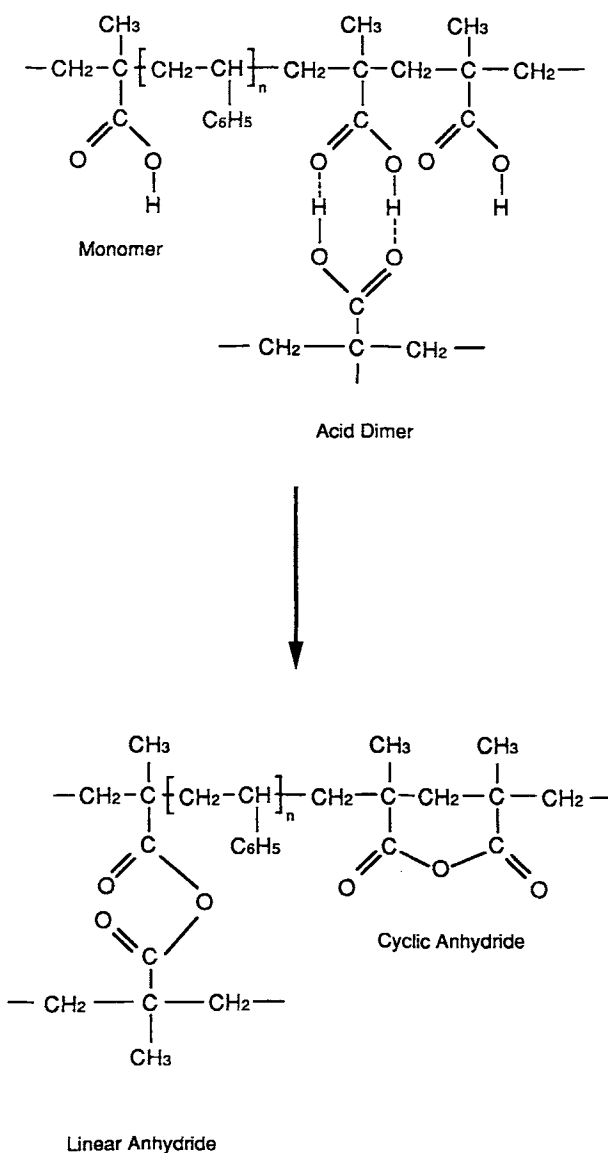


Figure 4 Schematic diagram showing anhydride formation.

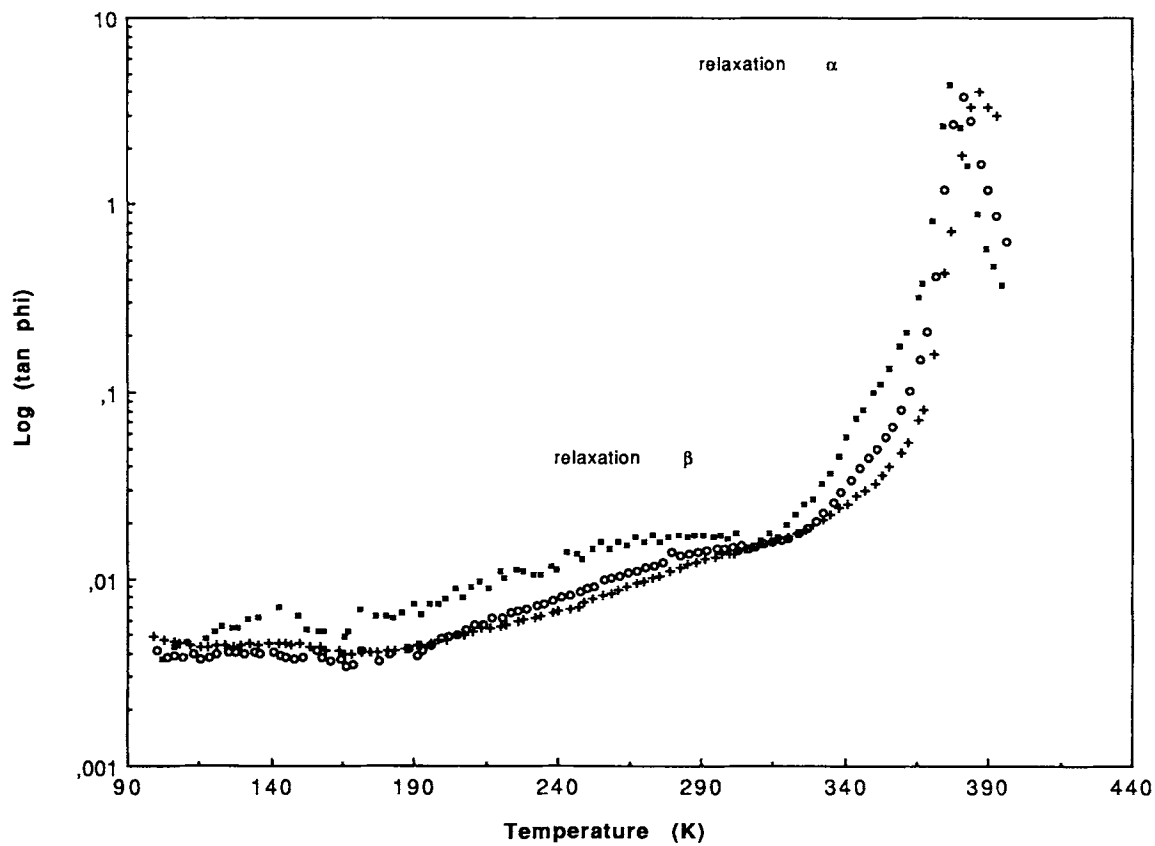
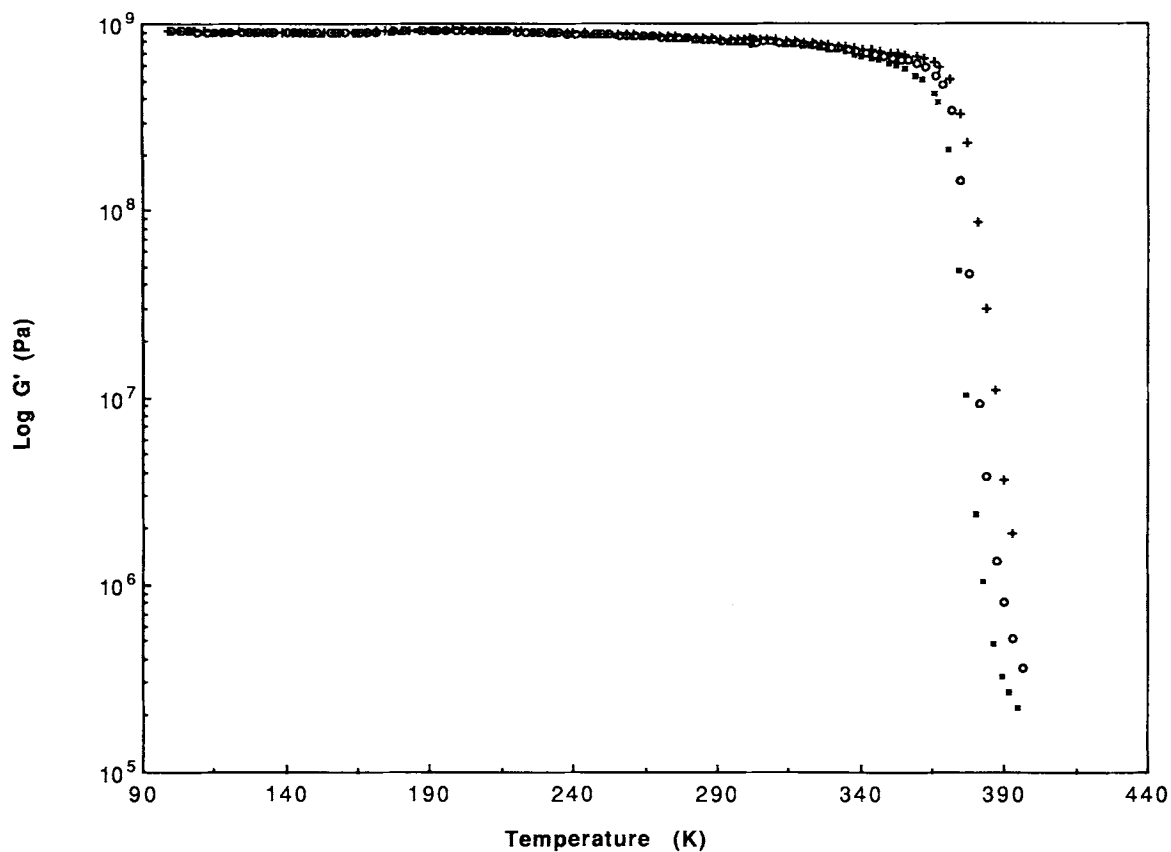


Figure 5 Plots of (a) $\log G'$ and (b) $\log(\tan \phi)$ vs. temperature for PS homopolymer for various frequencies: (■) 0.01 Hz; (○) 0.1 Hz, (+) 1 Hz.

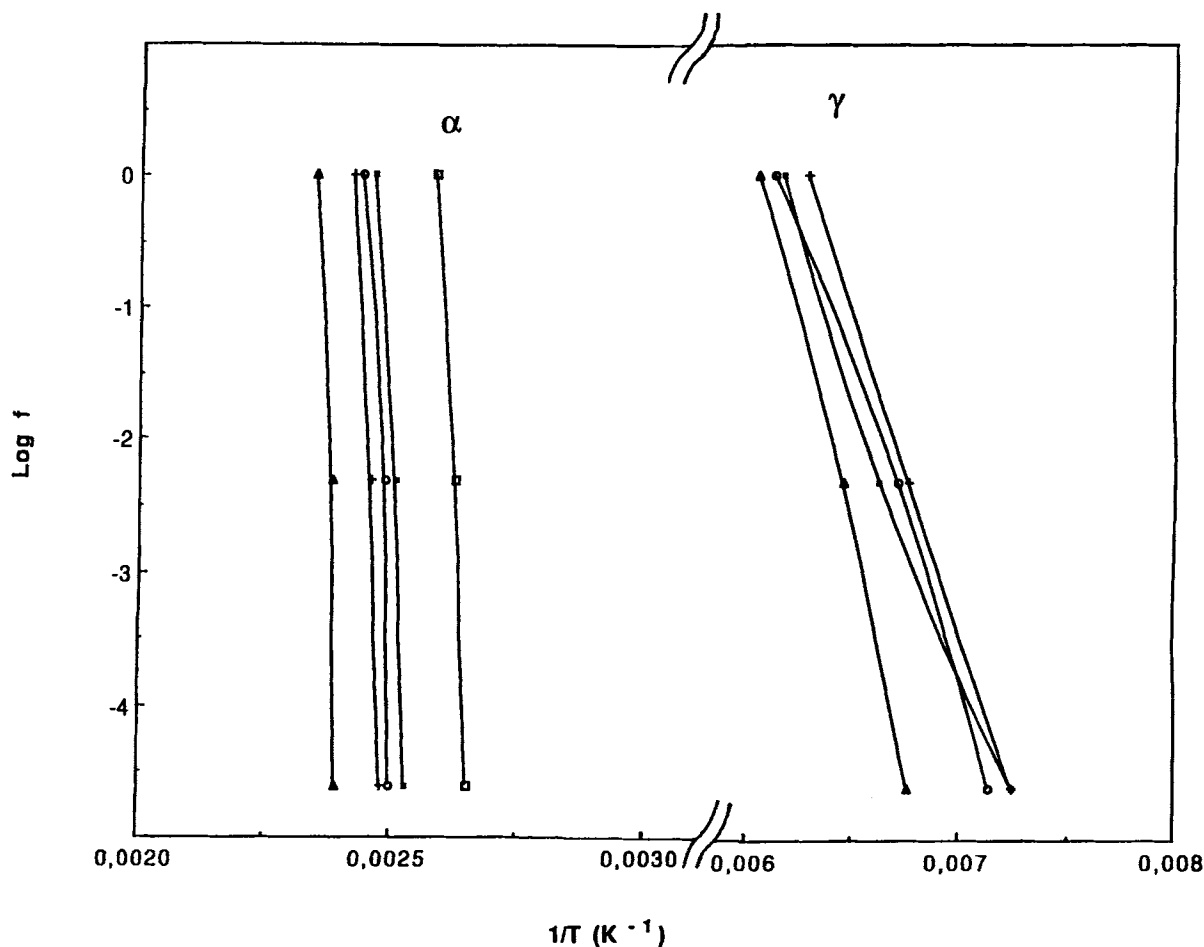


Figure 6 Plots of $\log f$ [frequency of $\log(\tan \phi)$ maxima of the α and γ relaxations] against reciprocal temperature for the PS homopolymer (\square) and the copolymers: (\blacksquare) SMAA1; (\circ) SMAA2; ($+$) SMAA3; (\blacktriangle) SMAA4.

At lower temperatures, the copolymer shows well-defined peaks at the three frequencies. This γ relaxation is located at about 168 K at 1 Hz. Let us recall that for the PS homopolymer no particular mobility occurs over this temperature range.

After describing the main features characterizing the dynamic mechanical spectrum, it is valuable to analyze each copolymer relaxation vs. the weight fraction of methacrylic acid.

The γ Relaxation

Figure 8 displays $\tan \phi$ spectra recorded at 1 Hz for the set of SMAA copolymers. There is no change in the location of the $\tan \phi$ maxima with increasing the weight fraction of methacrylic acid except for the SMAA4 copolymer. This copolymer, showing the higher acid ratio, exhibits a γ relaxation at 1 Hz located at about 168 K against 163 K for the other copolymers. Another important feature is the mag-

nitude of the γ relaxation that increases with increasing the weight fraction of methacrylic acid.

To quantify the intensity of the relaxation, the area under the γ peak is approximately evaluated through

(half-width of the $\tan \phi$ maximum)

\times (height of the $\tan \phi$ peak)

after subtracting the background profile. Figure 9 shows the variations of the area under the γ peak recorded at 1 Hz with the weight fraction of methacrylic acid. The area under of the γ peak increases with increasing the methacrylic content.

The time-temperature dependence of the γ relaxation is of the Arrhenius type as shown in Figure 6. The activation energy of the γ relaxation of all copolymers is about 40 kJ/mol and the value of the frequency at infinite temperature in the Arrhenius equation is about the Debye frequency (10^{13} Hz).

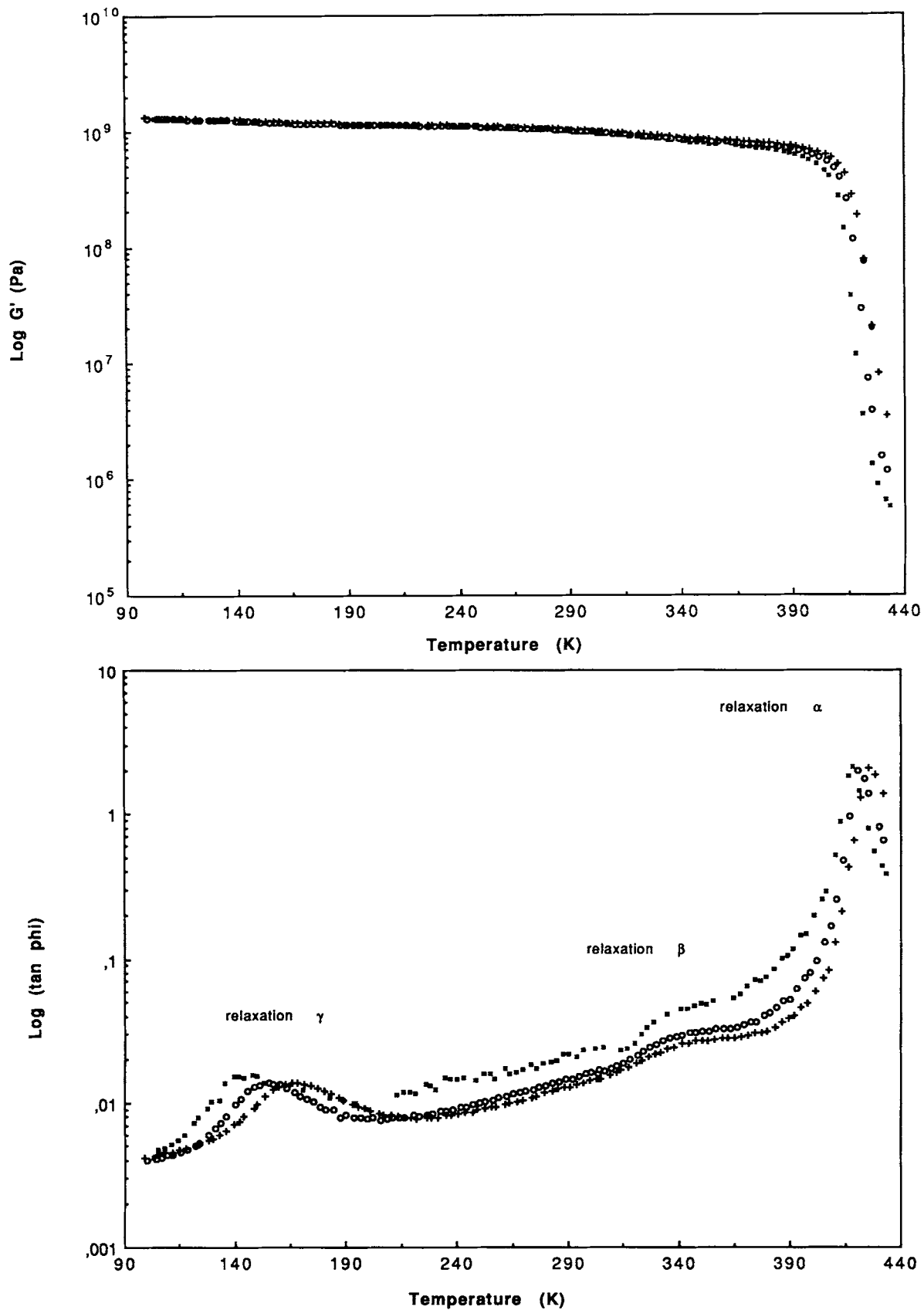


Figure 7 Plots of (a) $\log G'$ and (b) $\log(\tan \phi)$ vs. temperature for SMAA4 copolymer for various frequencies: (■) 0.01 Hz, (○) 0.1 Hz; (+) 1 Hz.

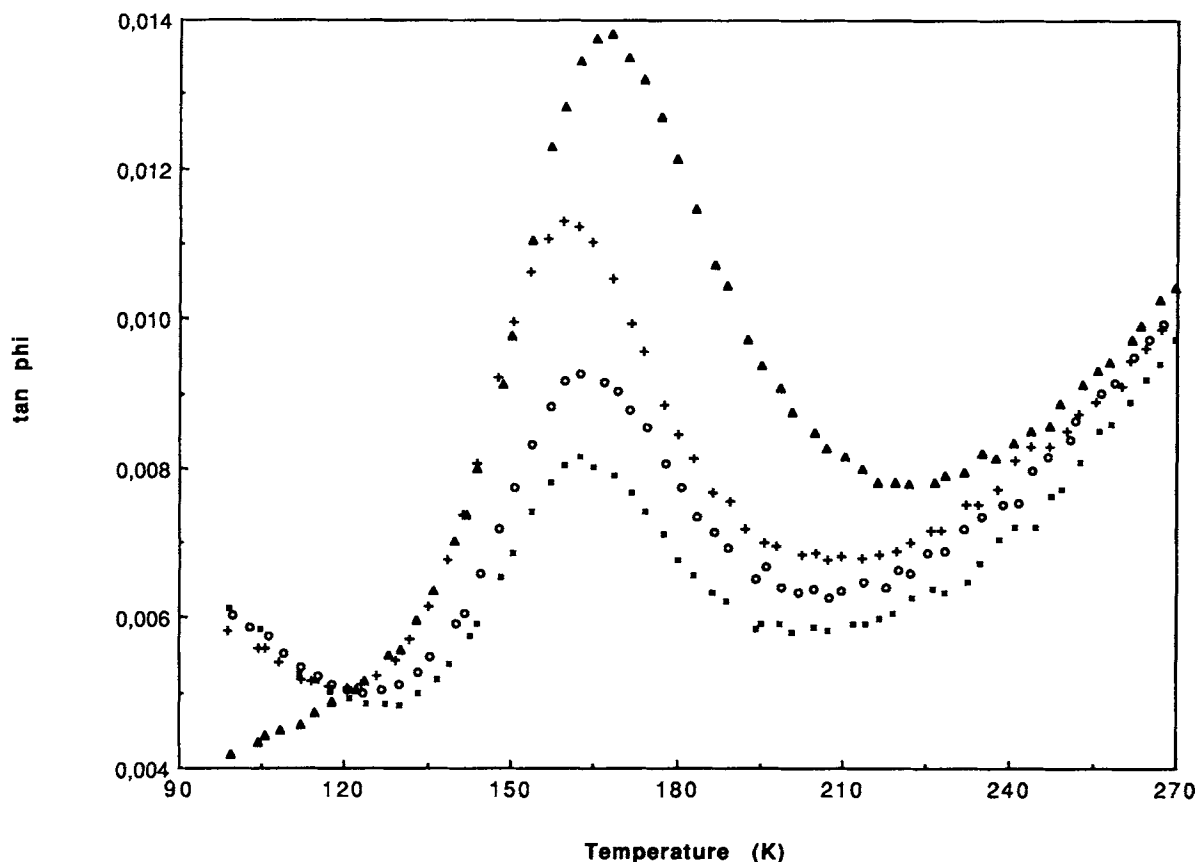


Figure 8 Plots of $\tan \phi$ vs. temperature at 1 Hz in the γ relaxation range for the copolymers: (■) SMAA1; (○) SMAA2; (+) SMAA3; (▲) SMAA4.

From these results and from the FTIR analysis, it can be concluded that the γ relaxation could be related to the occurrence of local motions induced by the breakdown of the weakest hydrogen bonds (no proton transfer). Furthermore, the increase in the magnitude of the γ relaxation with increasing the weight fraction of methacrylic acid could be due to an increase in the relative number of these weak hydrogen bonds.

The β and α Relaxations

Figure 10 shows $\log G'$ and $\log(\tan \phi)$ spectra recorded at 1 Hz for the series of SMAA copolymers. Furthermore, the β relaxation that appears as a shoulder of the main relaxation for the copolymer SMAA1 is progressively separated from the α relaxation with increasing the weight fraction of methacrylic acid (Fig. 10). Thus, because of the merging of the β and α relaxations at each frequency for all copolymers except for the SMAA4 copolymer, it cannot be concluded about the influence of increasing weight level of methacrylic acid on the β

location. But the comparison between the PS homopolymer and the SMAA4 copolymer shows that the β relaxation is shifted toward higher temperatures when methacrylic acid is added. Unfortunately, because of the vicinity of the α relaxation, the activation energy of the β relaxation in such copolymer cannot be accurately determined. However, this β relaxation shown by SMAA copolymers could be related as it is for the PS homopolymer to local motions, i.e., rotational motions of backbone chains.^{1,5} The shift of this subvitreous relaxation toward higher temperatures induced by addition of methacrylic acid could be due to intermolecular hydrogen bonds. The magnitude of such hydrogen bonds are intermediate between the intensity of those invoked for the occurring of γ relaxation and those related to the main relaxation.

With increasing the weight fraction of methacrylic acid, the main relaxation related to T_g is greatly shifted toward higher temperatures, from 399 K for the lower acid level to 420 K for the higher one. Then, for a given frequency, this shift could be related to a decrease in motion ability of the mac-

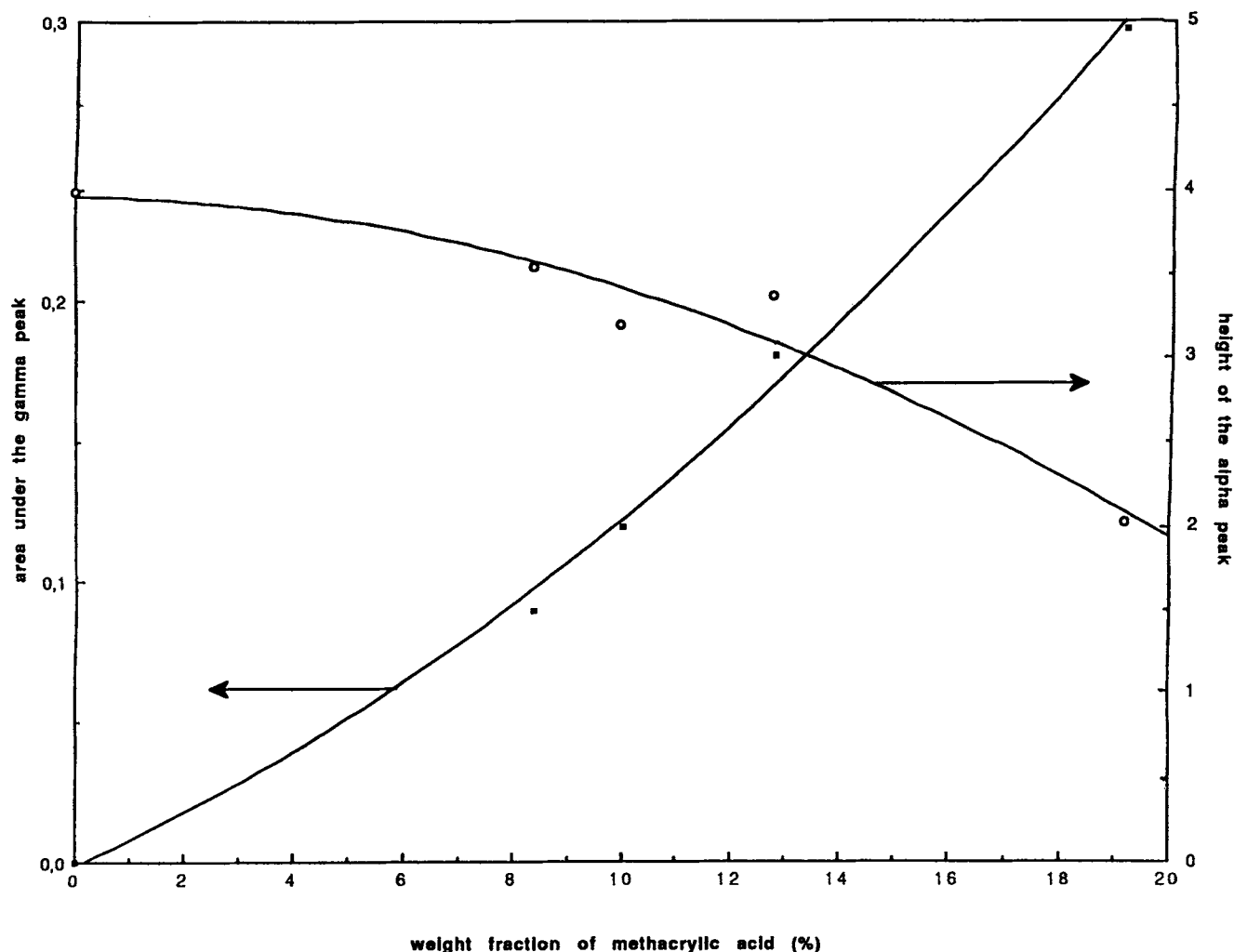


Figure 9 Plots of the height of the α peak and of the area under the γ peak vs. methacrylic acid weight fraction.

romolecular chains. This result agrees with the T_g determination data reported above. The apparent activation energy, determined through the Arrhenius equation at the temperatures corresponding to the $\tan \phi$ maxima at 1 Hz, increases with increasing the weight fraction of methacrylic acid. Thus, the apparent activation energy determined at about 400 K for the SMAA1 copolymer is about 530 kJ/mol, whereas that evaluated close to 420 K for the SMAA4 copolymer is near 910 kJ/mol. Moreover, the magnitude of the α relaxation evaluated through the height of the $\tan \phi$ peak (the area under the α peak cannot be determined through the method used for the γ relaxation) decreases (Fig. 9) with increasing the methacrylic acid content. All these changes in the α relaxation characteristics with increasing the methacrylic acid content could be related to an increase in the number of specific inter-

actions. As a matter of fact, H bonds and anhydride formations could lead, respectively, to the development of dynamic and stable networks in the polymer. Such networks could reduce cooperative segmental motion of macromolecules. The decrease in the magnitude of the α relaxation with increasing the weight ratio of methacrylic acid could confirm the presence of a stable network of chemical cross-links induced by the presence of anhydride (cf. FTIR analysis) above T_g . Furthermore, the fluctuation network of hydrogen bonds could partially remain above T_g , emphasizing the decrease in molecular mobility above T_g .

IV. CONCLUSION

Molecular mobility of a PS homopolymer and a series of styrene-*co*-methacrylic acid copolymers with

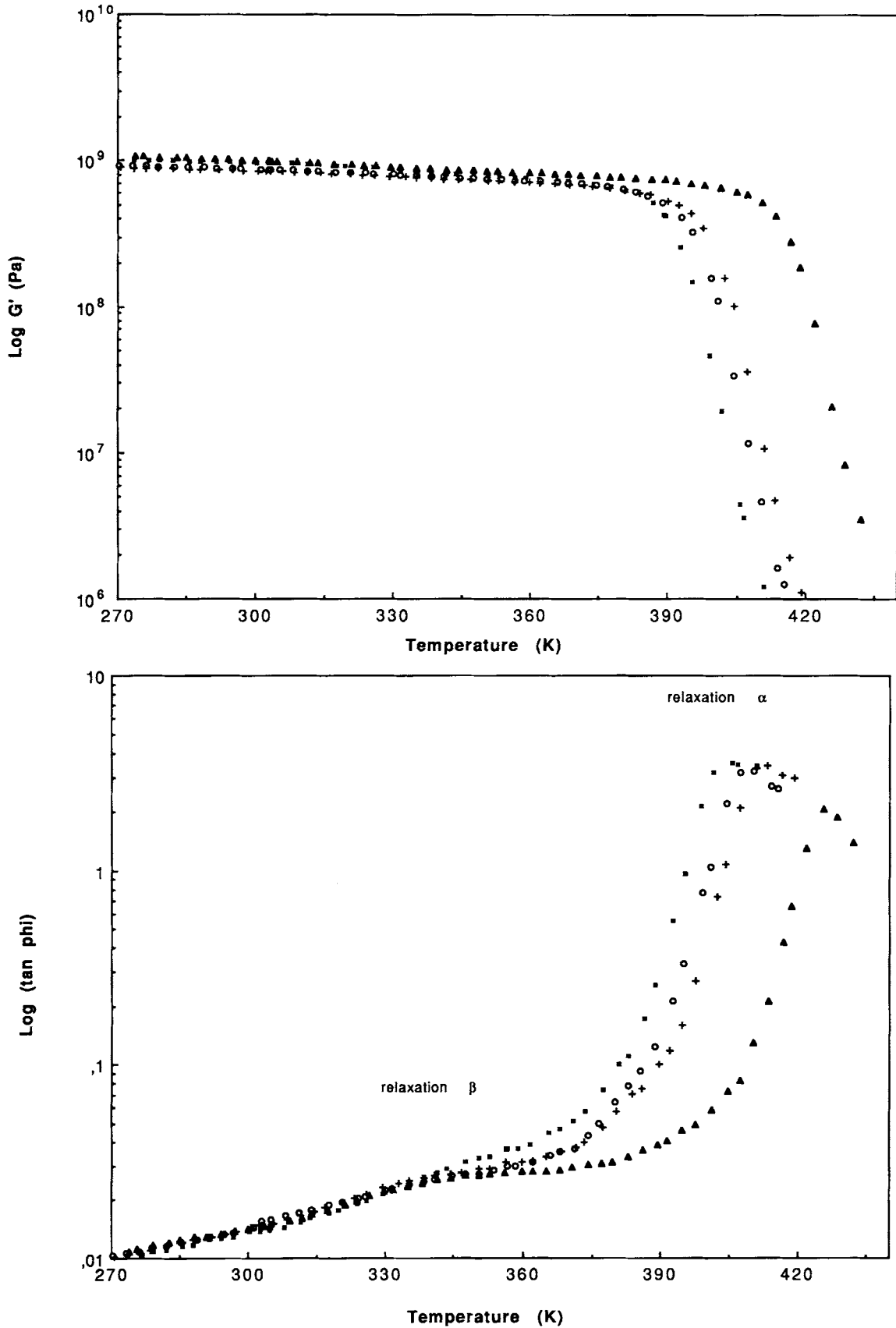


Figure 10 Plots of (a) $\log G'$ and (b) $\log(\tan \phi)$ vs. temperature at 1 Hz in β and α relaxations range for the copolymers: (■) SMAA1; (○) SMAA2; (+) SMAA3; (▲) SMAA4.

various contents of methacrylic acid have been analyzed by high-resolution dynamic mechanical spectrometry. The PS homopolymer shows two mechanical relaxations, the β and α relaxations, related, respectively, to local motions and the large-scale mobility of the backbone chains. Styrene-co-methacrylic acid copolymers present an additional relaxation (γ) so that they exhibit three mechanical relaxations: the γ , β , and α relaxations. The γ relaxation located at about 163 K could be related to local motions of methacrylic acid due to the breakdown of the weakest hydrogen bonds. The β relaxation is located at higher temperature than this shown by the PS homopolymer. This subvitreous relaxation could be attributed to local motions of the backbone chains induced by the breakdown of stronger hydrogen bonds than those invoked for the γ relaxation. Finally, the α relaxation displayed by the SMAA copolymers is located at a higher temperature than the one displayed by the PS homopolymer. With increasing the weight fraction of methacrylic acid, the α peak related to the glass transition is shifted toward higher temperatures and its magnitude decreases. These changes in the α relaxation characteristics with increasing the methacrylic acid content could suggest the presence of a stable network of chemical cross-links induced by the presence of anhydride so that molecular mobility could be partially inhibited above T_g . The remaining of a fluctuation network of hydrogen bonds (labile contacts) above T_g could also emphasize the decrease in molecular mobility.

This work has been supported by Composi'tec (Savoie Technolac, BP 234, 73374 Le Bourget du Lac, France), by the Rhône Alpes Region, and by the Research and Technology Ministry (M.R.T.) and we would like to gratefully thank J. L. Favre for his help. The contributions of Dr. P. Cassagnau and Dr. A. Michel (Laboratoire Matériaux Organiques, CNRS) for the sample extrusion were also greatly appreciated. The authors are also indebted to T. Sarraf (Groupement Recherches Lacq, Elf/Atochem, BP 34, 64170 Lacq, France) who provides us with the analyzed polymers.

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Received June 16, 1992

Accepted September 29, 1992