A comparison of the micromechanical properties of various poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene (PPO–PS) polymer blends

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The real and imaginary parts of the dynamic shear modulus (G' and G'' respectively) of 10%, 20% and 30% poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene (PPO–PS) blends were measured near T_g (metastable equilibrium, i.e. supercooled liquid state) and at lower temperatures (isoconfigurational state) in the frequency range from 5×10^{-5} to 5 Hz. The results were compared with others obtained on pure PS. In a first approximation, two types of behaviour were observed: (i) a WLF law is observed in the former case; and (ii) an Arrhenius law is verified at least in part of the frequency range in the latter case. But a closer analysis shows that near T_g the time–temperature superposition principle is not well verified and a method to test its adequacy is proposed. In addition results on the secondary, or β, relaxation are given and discussed.

(Keywords: blends; polystyrene; poly(dimethyl phenylene oxide); d.t.a.)

INTRODUCTION

It is well known that glassy materials including glassy polymers present two types of behaviour depending on temperature: at high temperature (i.e. near or above the glass transition temperature T_g) the material is in the supercooled liquid state, i.e. in metastable equilibrium; in contrast, with decreasing temperature, because the structural unit mobility becomes lower, experiments can be done in an isoconfigurational state depending on the thermal history[1,2]. Generally, it is assumed that the former behaviour can be described by a WLF equation, and the latter by an Arrhenius law (depending on the relaxation process that is studied, e.g. β process, γ process, etc., each of which has a particular activation energy).

A lot of work has been done over several years[3,4] in an attempt to connect each process to a microstructural movement; in order to perform even more accurate experiments on the mechanical properties, a new apparatus has been built in our laboratory, allowing dynamic shear modulus measurements *versus* temperature and/or frequency (from 10^{-5} to 5 Hz) for very low relative strain (near 10^{-5})[5–7]. Because the behaviour of glassy homopolymers seems well known, and because of increasing interest in polymer blends, the same types of experiments have been done on poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene (PPO–PS) mixtures. For the compositions studied here, PPO and PS are known to be compatible polymers[8,9].

EXPERIMENTAL

The polymer samples had an average molecular weight of 254 200 for polystyrene and 50 000 for poly(phenylene oxide), except in the case of pure PS where the molecular weight was 100 000. The polymer blends were prepared by D. Lefebvre[9], and were used as prepared. The samples were cut to the dimensions of 2 mm × 8 mm × 40 mm for measurements of the real and imaginary parts of the modulus with an inverted forced oscillation pendulum as described before[7]. Several measurements were repeated for both the frequency and the temperature variation in order to verify that the material is in equilibrium (metastable, $T \geqslant T_g$) or in an isoconfigurational state ($T \ll T_g$); the results were reproducible within a few per cent in each case. The temperature of the sample remained constant to within 0.2 K, thus ensuring that the errors arising from the temperature variations were minimal.

The viscoelastic behaviour observed above T_g and the relaxation behaviour below T_g were independent of the

Table 1 Glass transition temperatures of the blends (percentage is that of PPO in PPO–PS samples)

Blend	T_g (K)
0%	378
10%	383
20%	390
30%	403

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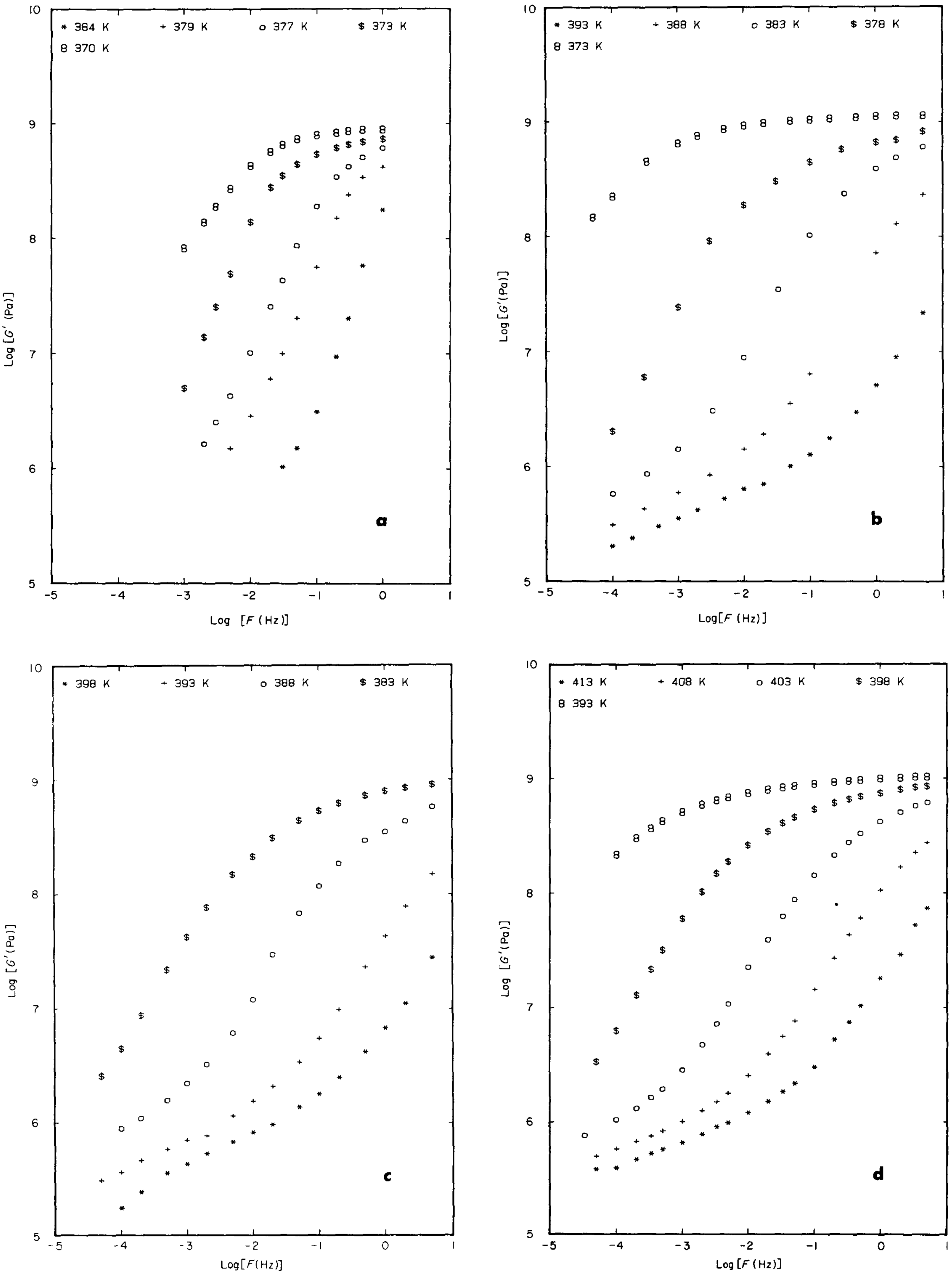

Figure 1 Real part of the shear modulus, G', plotted against frequency for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS (supercooled liquid)

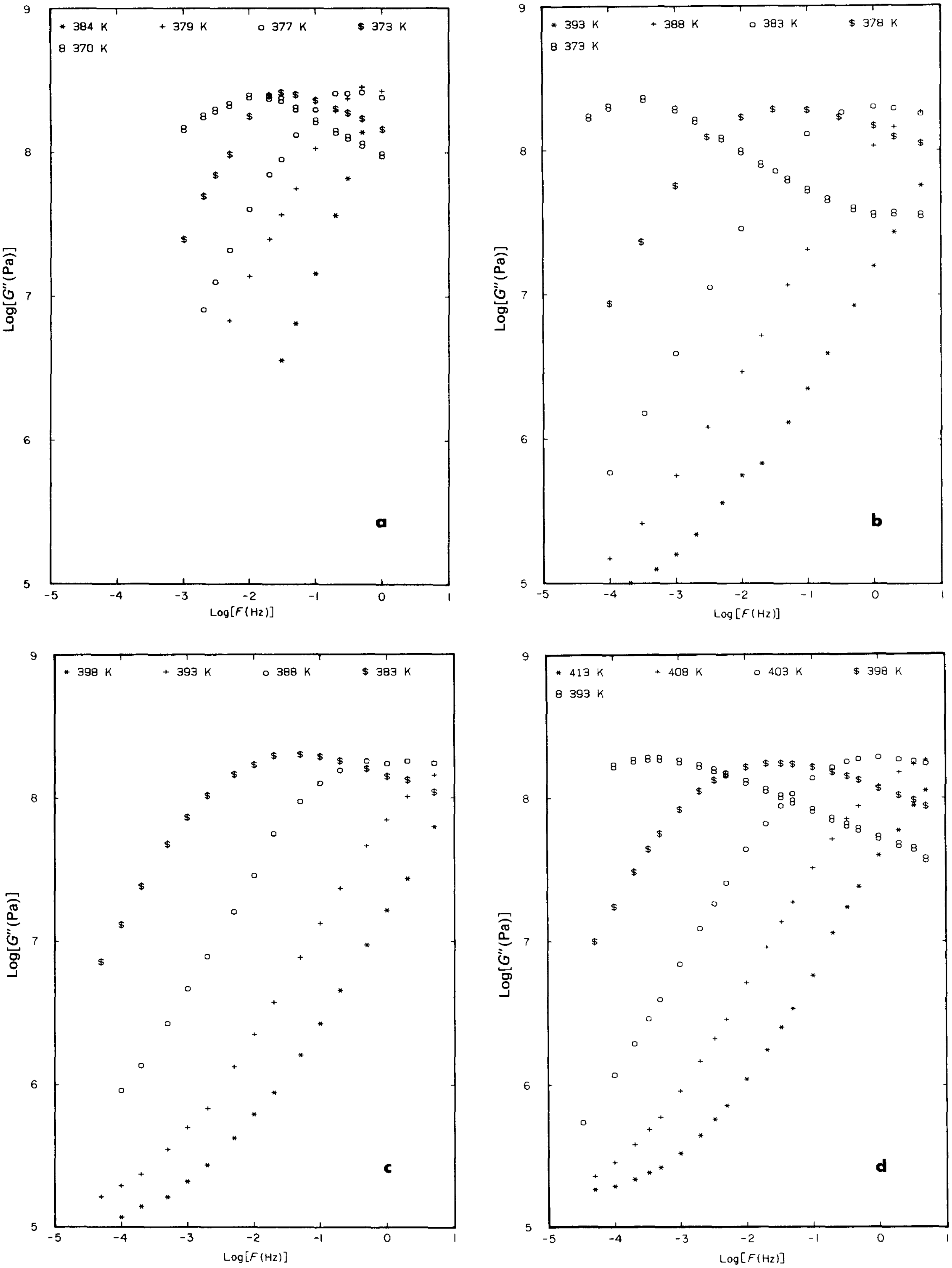

Figure 2 Imaginary part of the shear modulus, G'', plotted against frequency for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS

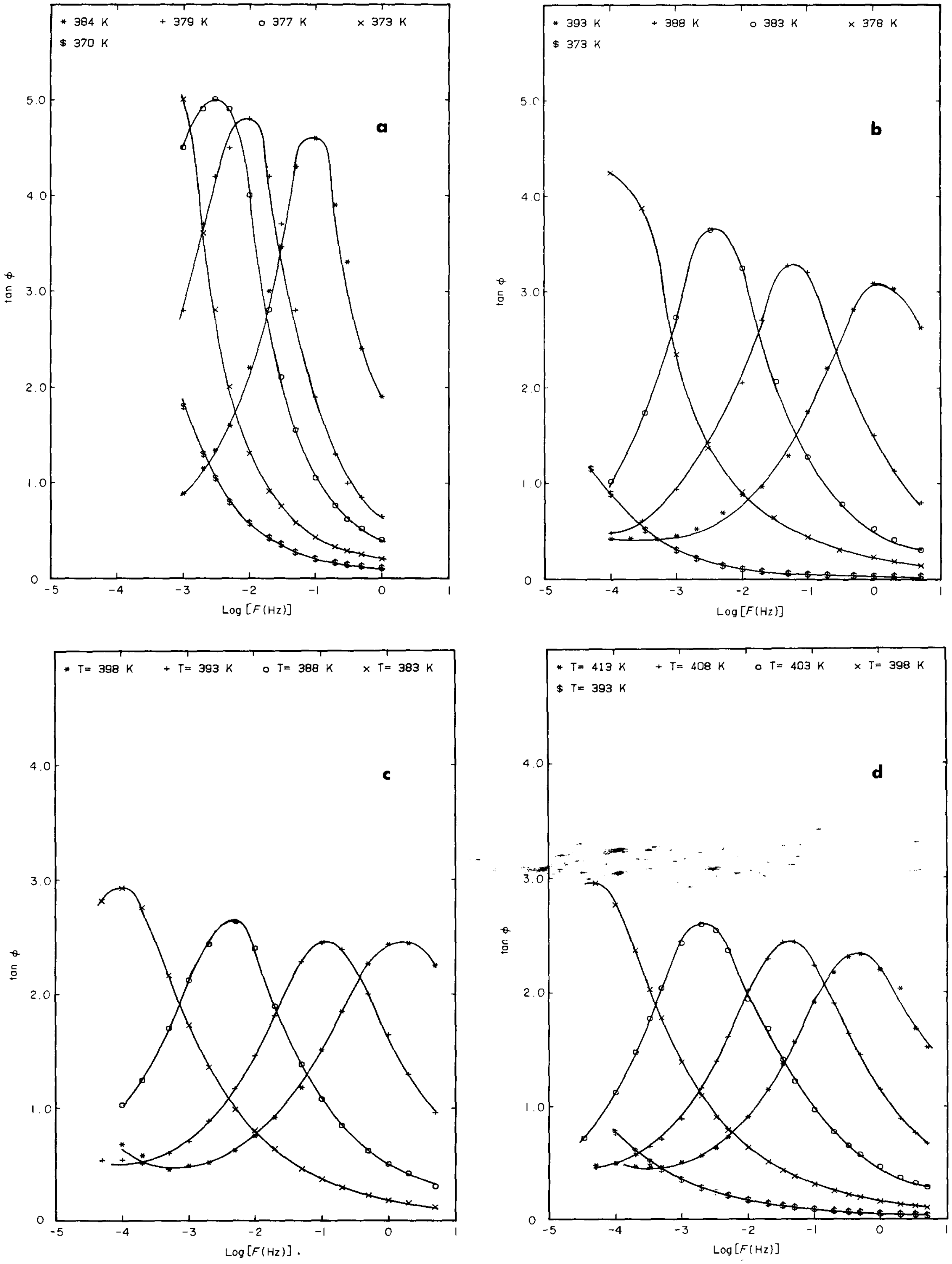

Figure 3 Tan φ on a linear scale plotted against frequency for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS. The time and temperature ranges correspond to the α relaxation in the supercooled liquid state for *Figures 1, 2* and *3*

applied stress over the strain amplitudes (of the order of 10^{-5}) of our measurements, thus confirming a linear viscoelastic and relaxation response characteristic of compatible polymer blends. The calorimetric glass transition temperature of the blends is given in *Table 1*[9].

RESULTS

The real and imaginary parts of the dynamic shear modulus (G' and G'' respectively) and the internal friction $\tan\phi$ ($=G''/G'$) of pure polystyrene and 10%, 20% and 30% mixtures of PPO with PS (blends) were measured at frequencies of 5×10^{-5} to 5 Hz at their respective transition temperatures (supercooled liquid). The measured values of G', G'' and $\tan\phi$ are plotted against frequency at different temperatures in *Figures 1*, *2* and *3*. The halfwidth of the G'' plot for the blends is reported in *Table 2*. The halfwidth increases with the quantity of PPO in the blend. The plots of $\tan\phi$ against frequency in *Figure 3* show that, when the temperature decreases, $\tan\phi_{max}$ increases and the halfwidth of the peak decreases. The values given in *Table 2* also show that, as the quantity of PPO in the blend is increased, the magnitude of its internal friction for the same value of T/T_g decreases.

The values of G' and G'' at several temperatures far below T_g are plotted against frequency in *Figures 4* and *5* for each material except pure polystyrene. They show a minimum in G'' whose position shifts to higher frequencies as the temperature is increased; this suggests that the contribution to G'' at lower frequencies is predominantly from the main, or α, relaxation and at higher frequencies from the secondary, or β, relaxation. The effect of β relaxation is shown in *Figure 6*. The value of G'' plotted against frequency exhibits a maximum in a temperature range where the effect of α relaxation is very low.

To clarify this point further, G' and G'' were measured as a function of temperature for three frequencies, 0.01, 0.1 and 1 Hz, for each composition after the materials were annealed for several months at room temperature. The results are given in *Figures 7* and *8*. The same experiment has been done on a quenched sample (30%) and the results show a very large increase in the α relaxation and a slight increase in the β relaxation.

Table 2 The logarithmic halfwidths of G'' and $\tan\phi$ and $\tan\phi_{max}$ of polystyrene and PPO–PS blends as a function of temperature

Blend	T (K)	T/T_g	$\Delta w_{1/2}$ (G'')	$\Delta w_{1/2}$ ($\tan\phi$)	$\tan\phi_{max}$
0%	384	1.02	–	1.70	4.6
	379	1.00	–	–	4.8
	370	0.98	2.7	–	5.0
10%	393	1.03	–	2.5	3.2
	388	1.01	–	2.3	3.3
	383	1.00	–	2.15	3.6
	378	0.98	3.0	–	4.2
20%	398	1.02	–	–	2.4
	393	1.01	–	2.55	2.40
	388	0.99	–	2.36	2.60
	383	0.98	3.46	–	3.00
30%	413	1.02	–	2.85	2.35
	408	1.01	–	2.55	2.50
	403	1.00	–	2.47	2.60
	398	0.99	3.65	2.40	3.00

DISCUSSION AND CONCLUSIONS

Time–temperature superposition

As is usually done[10] in the temperature range of the supercooled liquid state, we attempted to superpose the G' and G'' curves in *Figures 1* and *2* by shifting the timescale of each measurement by a factor α_T. *Figure 9* shows that, when the plots are made on a logarithmic scale, approximate and satisfactory superposition is possible. In addition *Figure 10* shows, for the 10% blend, the same treatment taking into account results obtained with other experimental methods[9]. This figure shows good agreement (although less good for G' than for G''). This was done for each composition. In *Figure 11*, the variation of $\log\alpha_T$ against inverse temperature ($1/T$) for 0%, 10%, 20% and 30% blends using the experimental results are shown. In *Figure 12*, as in *Figure 10*, data of Lefebvre and Monnerie[9,11] have been included. In *Table 3* the values of WLF coefficients calculated from the two methods are given and it is shown that a change in their values from the Prest equation[8] is necessary to take into account the whole results.

In the literature such superpositions of mechanical behaviour are often made in order to extrapolate the behaviour of a polymer material to longer times. But for dielectric properties the superposition of curves by merely shifting the time is inadequate. Therefore, we carefully examine whether an alternative procedure more sensitive to small deviations in G' and G'' can be used here.

If the time–temperature superposition is adequate, one obtains a master curve for each property G' and G''. Therefore, $\tan\phi$ ($=G''/G'$) should also have a master curve obtainable from a mere displacement along the frequency axis. But $\tan\phi_{max}$ and the halfwidth in *Table 2* and *Figure 3* show that a precise superposition is not possible even using two displacements, one along the $\tan\phi$ axis. This suggests a change in the modulus with temperature according to the theory of rubber elasticity, and this should correspond to a vertical shift factor of $T_g d_g/Td$, where d is the density at temperature T and d_g that at T_g. It is often assumed that the effect is small and a simple displacement along the time or frequency axis is made. Our analysis in terms of $\tan\phi$ clearly demonstrates the inadequacy of the superposition for both polystyrene and blends; similar results have been found for selenium and Se–As[12].

We suggest that time–temperature superposition in the viscoelastic behaviour of polymers at or near T_g should be used with caution. An analysis in terms of $\tan\phi$ is necessary before making conclusions about the reliability of the superposition principle. However, as observed by Chai and McCrum[13] in two cases, it is known that superposition cannot be satisfactorily applied to crystalline polymers and perhaps more generally to multiphase materials. Our analysis shows its inadequacy over a large range of frequencies and suggests a method by which the adequacy can be tested. The measurement of $\tan\phi$ is more sensitive than that of G' and G'' because $\tan\phi$ is independent of the sample size, which may vary slightly during the experiments.

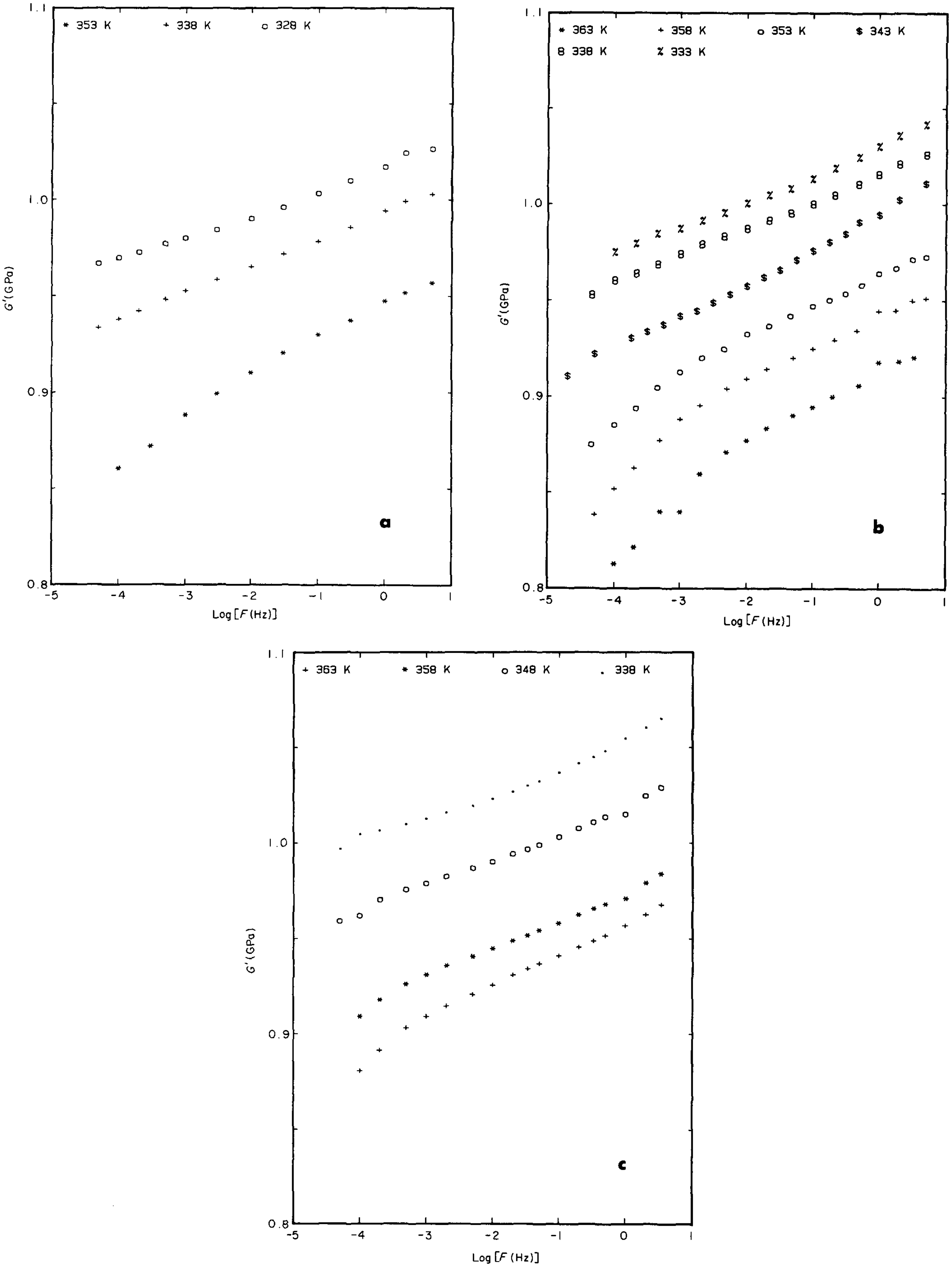

Figure 4 G′ on a linear scale plotted against frequency in the isoconfigurational state for (a) 10%, (b) 20% and (c) 30% PPO–PS. The temperature range corresponds to the α relaxation

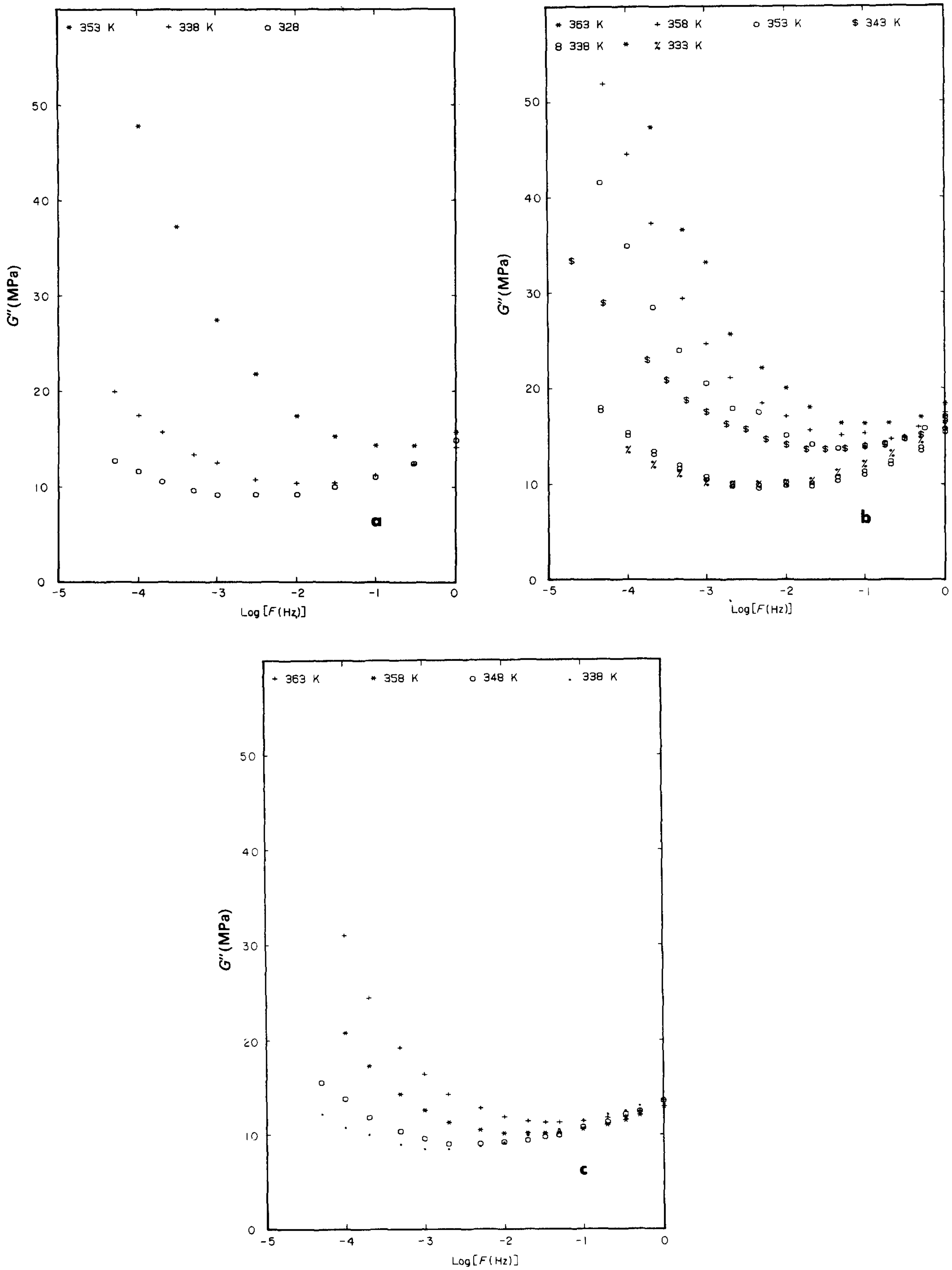

Figure 5 As *Figure 4*, but for G''

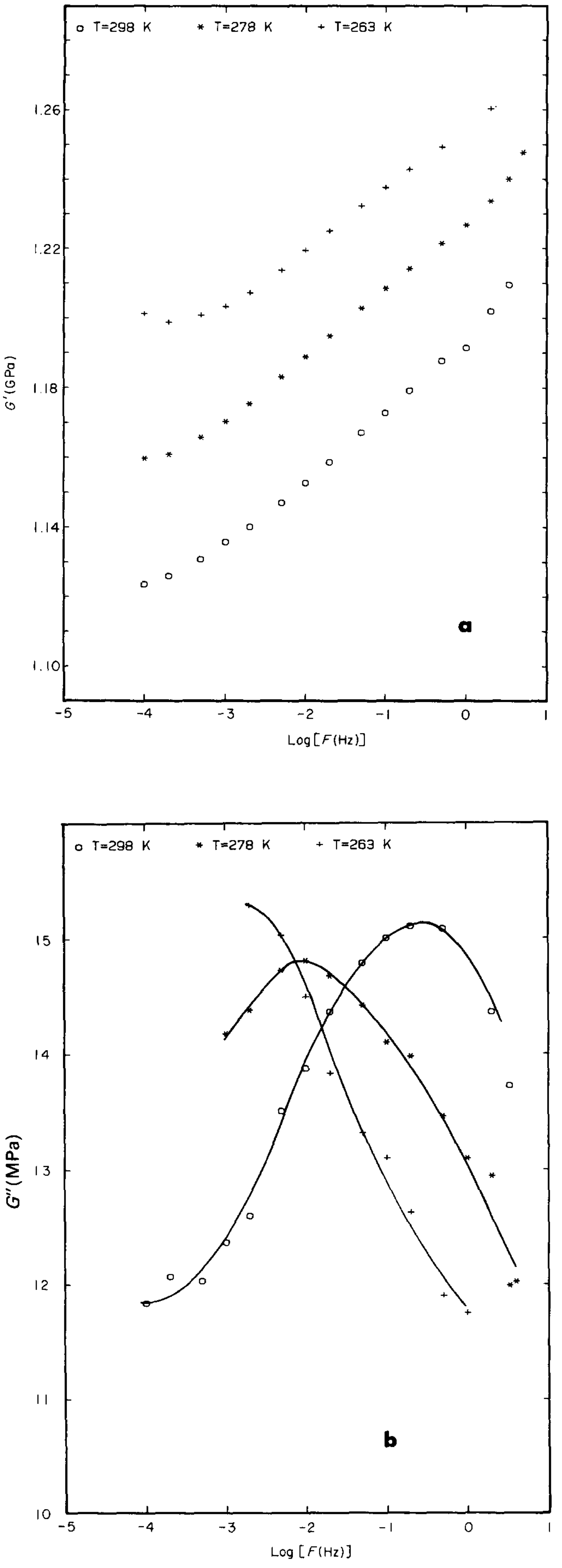

Figure 6 (a) G' and (b) G'' plotted against frequency in the isoconfigurational state for 30% PPO–PS. The temperature range corresponds to the β relaxation

Cole–Cole representation

In *Figures 13* and *14*, G'' is given *versus* G' for different temperatures in a so-called 'complex plane plot' or 'Cole–Cole diagram'; *Figure 14* is drawn for the low values of G' and G''. From these curves, and for each blend and pure PS, three parameters can be determined: The first one, k (ref. 16), is obtained from the slope of the G''/G' curve corresponding to lower temperatures (*Figure 13*) but neglecting the β relaxation effect. The second one, h, is obtained from the slope of the tangent to the G''/G' curve corresponding to the temperature and frequency range between rubber plateau and α process. The last one, G_0, is obtained by extending this tangent onto the G' axis. These values are given in *Table 4*. The way to determine each of these parameters is indicated in *Figure 14*: $k = 2\Theta/\pi$ and $h = 2\Omega/\pi$.

Behaviour of the materials in the isoconfigurational state

Main, or α, relaxation process. As shown in *Figure 5*, at lower frequencies the contribution to G'' (and $\tan\phi$) is predominantly from the main, or α, relaxation. If it is assumed that β relaxation can be neglected at lower frequencies, it is possible to shift these parts of the curves in order to determine if the α process follows a simple frequency–temperature law. *Figure 15* shows that the α process behaviour can be described by an Arrhenius law and activation energies for every blend are given in *Table 5*. The values seem to decrease as the quantity of PPO in the blend increases. Though these values seem to be unusually high, let us note that they are of the same order as those for an inorganic polymer, selenium[12].

Secondary, or β, relaxation process. From the curves in *Figure 8*, the maximum of G'', corresponding to the β relaxation, is determined for each blend and pure PS. At 0.01 Hz, the value is about 250 K and does not vary with composition. In contrast, as the quantity of PPO in the blend increases, the glass transition temperature increases and the contribution from the α process decreases in the β relaxation range; so it seems that β relaxation in the blends is not changed on changing the composition. In addition, the frequencies corresponding to the peaks have been plotted in *Figure 16* on a logarithmic scale against $1/T$: (i) from the results reported in *Figure 6*, and (ii) from the results reported in *Figure 8*. The mean enthalpy value is $\Delta H = 0.8$ eV or 77 kJ mol^{-1}.

In conclusion, the study of the micromechanical properties of PS compared with those of its blends with PPO have shown several features of interest. Our work confirms more accurately the earlier finding of the increase in rubber modulus[11]. It is well known that the PPO and PS polymers are compatible from a rheological point of view[9,11]. This is also confirmed by the fact that there is only one glass transition zone at temperatures that increase with the quantity of PPO.

This point has to be examined more precisely. Our results show that, in a first approximation, it is possible to draw master curves for each composition, but these curves cannot be derived from each other by changing the composition or by a simple temperature shift. This is also shown from (i) Cole–Cole diagrams and (ii) $\tan\phi$ peaks in the glass transition zone. This observation, pointing out the interest in very low-frequency measurements, shows the sensitivity of $\tan\phi$ for micromechanical properties of polymeric materials.

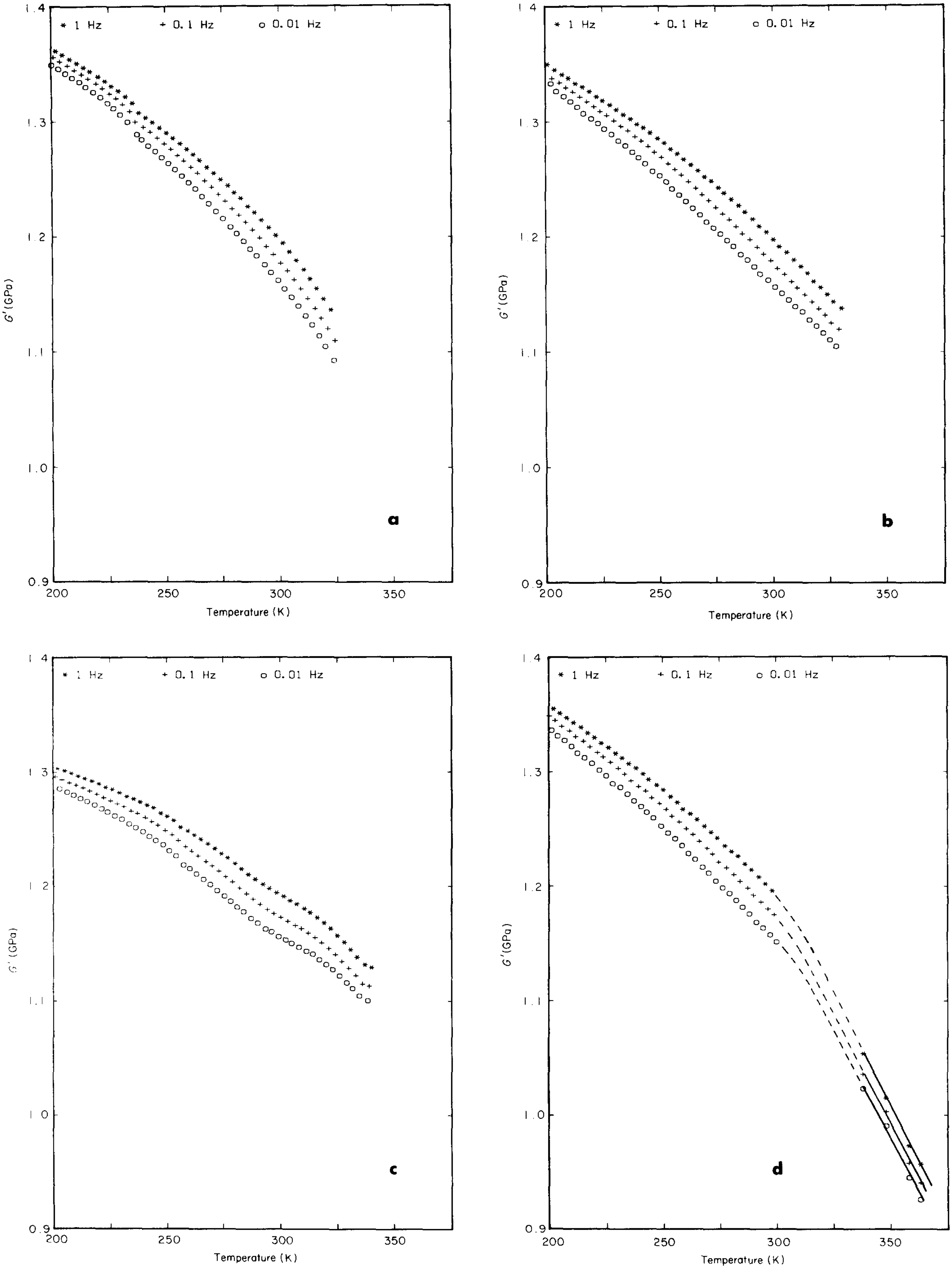

Figure 7 *G′* on a linear scale plotted against temperature for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS. For the 30% blend, the values from *Figure 6* are added

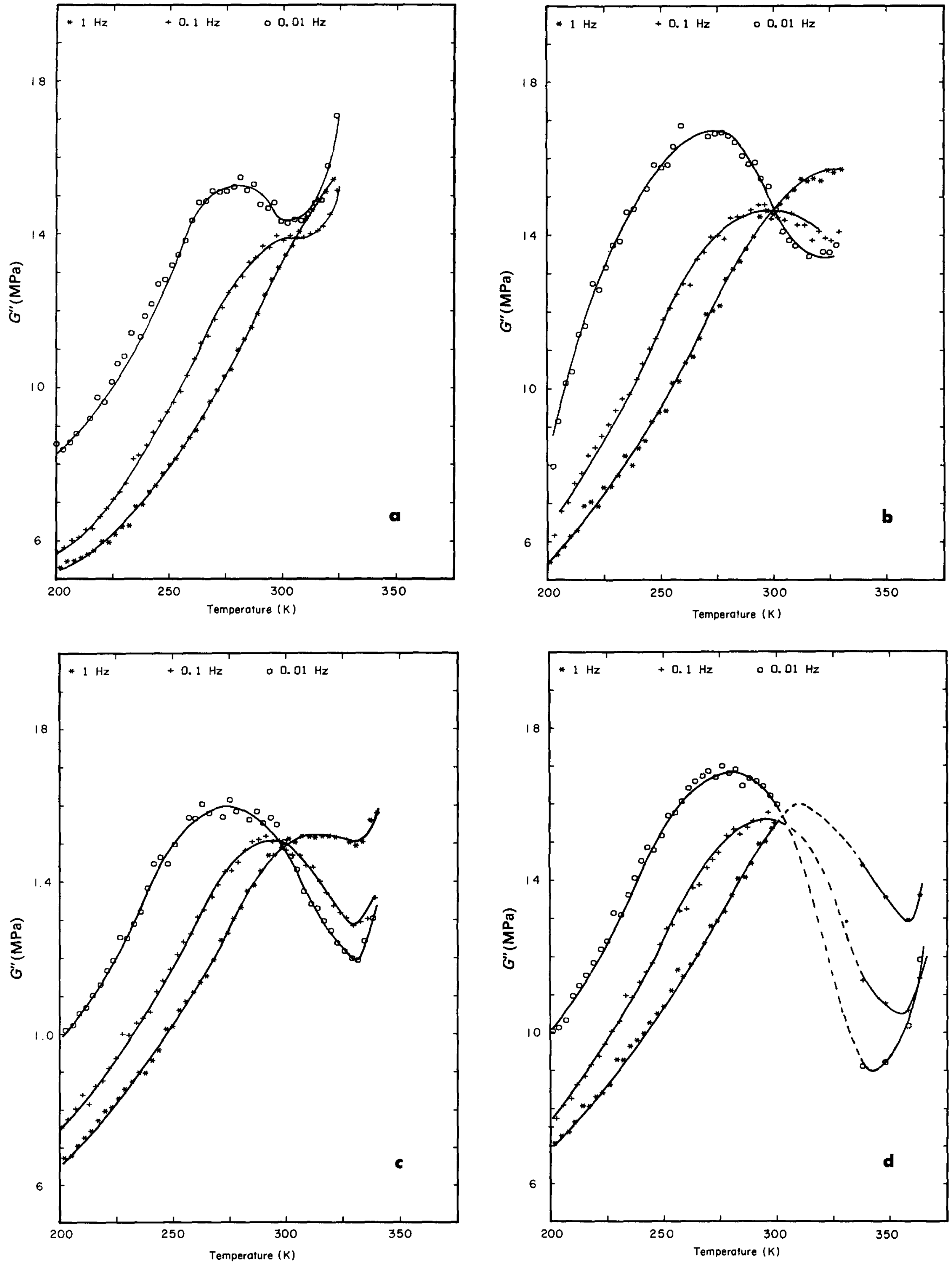

Figure 8 As *Figure 7*, but for G″

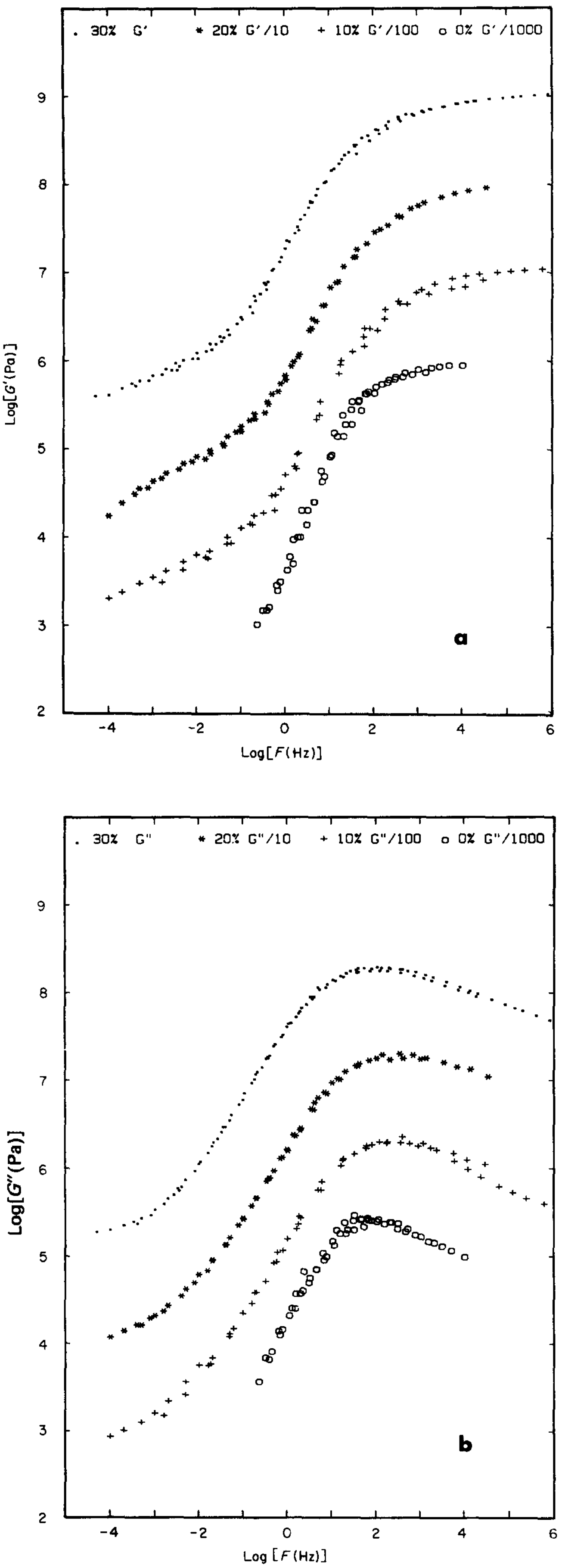

Figure 9 Master curves from microtorsional experiments: (a) real part of the shear modulus; (b) imaginary part of the shear modulus

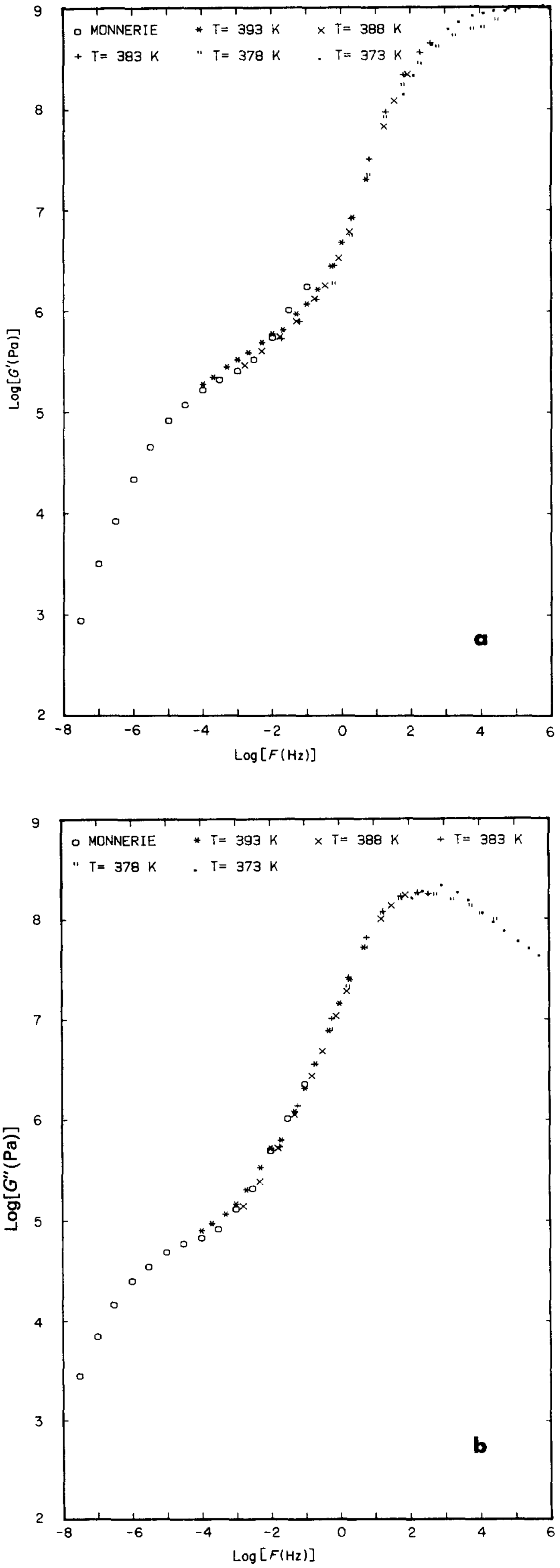

Figure 10 Master curves from both microtorsional experiments and Rheometrix experiments, for 10% PPO–PS: (a) real part of the shear modulus; (b) imaginary part of the shear modulus

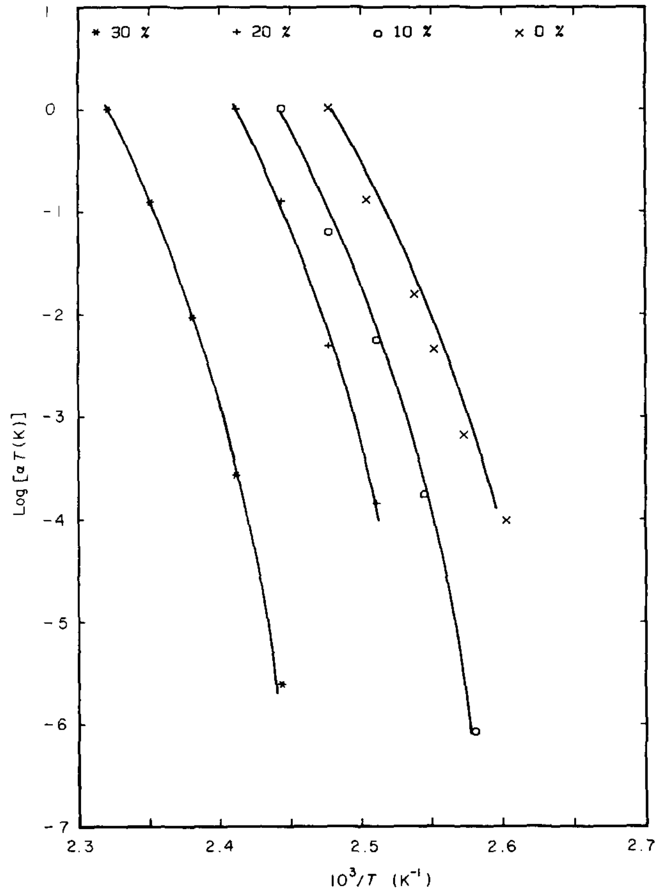

Figure 11 Shift coefficient plotted against $1/T$ (supercooled liquid state) corresponding to *Figure 9*

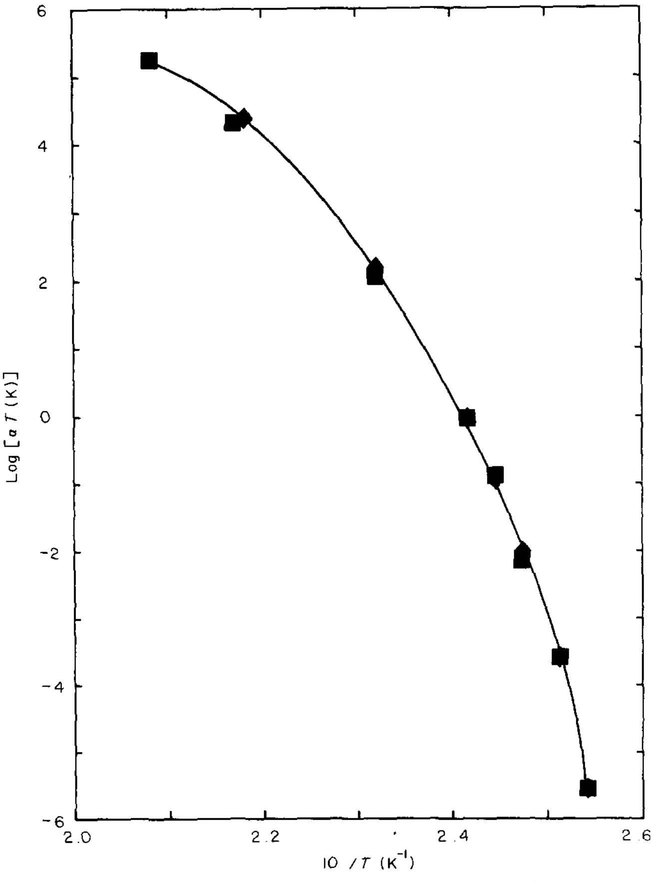

Figure 12 Shift coefficient plotted against $1/T$ corresponding to *Figure 10*: ◆, from calculations; ■, from experiments

Table 3 WLF coefficients obtained (1) by Lefebvre and Monnerie experiments[9,11] and Prest equations[8], and (2) considering all the results of Lefebvre *et al.* and this work

0%		10%		20%		30%	
1	2	1	2	1	2	1	2
10.04	–	10.01	8.0	10.20	7.6	10.27	7.8
62.6	–	64.1	46.4	65.7	44.6	67.4	47.8
388 K		393 K		400 K		413 K	

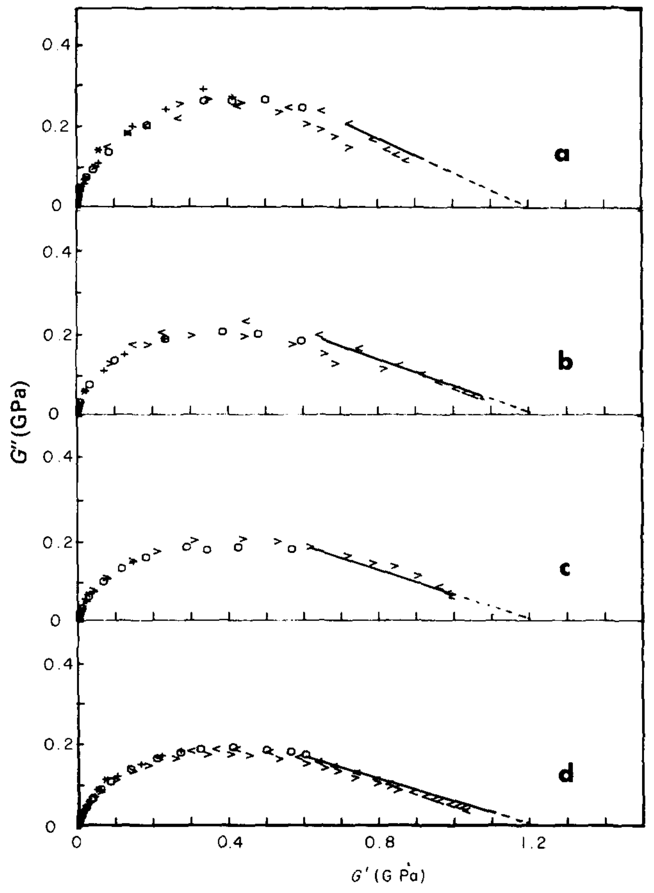

Figure 13 Cole–Cole diagrams for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS

Thus, the two types of diagrams (Cole–Cole and tan ϕ) lead us to the following further conclusions. The slope k (Cole–Cole diagram) decreases with increasing PPO content. This suggests a broadening of the time distribution for the high-frequency phenomena. The slope h decreases. The halfwidth of the glass transition peak (tan ϕ) increases and its height decreases. All these observations lead us to conclude that increasing the PPO ratio disorders the monomer segment arrangement in the blends.

However, even at constant composition, the superposition principle is only true in a first approximation; in fact the non-conservation of the glass transition peak (tan ϕ) characteristics, when the temperature varies, is associated with a slight variation in Cole–Cole diagram, in particular for the h parameter. It seems that the microstructural state (disorder in monomer segment arrangements) varies such that the

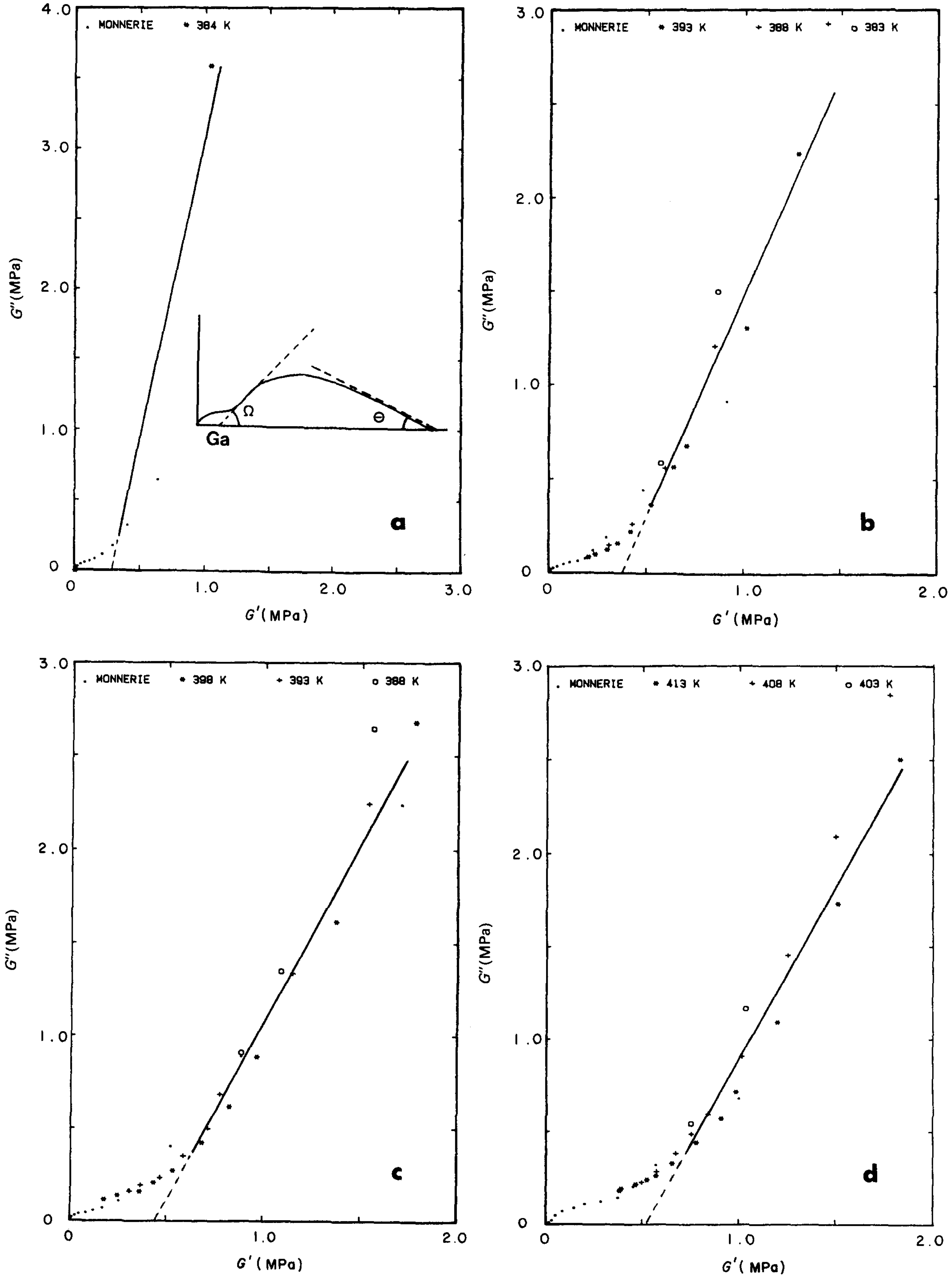

Figure 14 Cole–Cole diagrams (at low values of G' and G'') for (a) pure PS; and for (b) 10%, (c) 20% and (d) 30% PPO–PS

Table 4 The three parameters of the Cole–Cole representation

Blend	k	h	G_c (MPa)
0%	0.26	0.95	0.30
10%	0.23	0.90	0.32
20%	0.23	0.88	0.44
30%	0.23	0.85	0.53

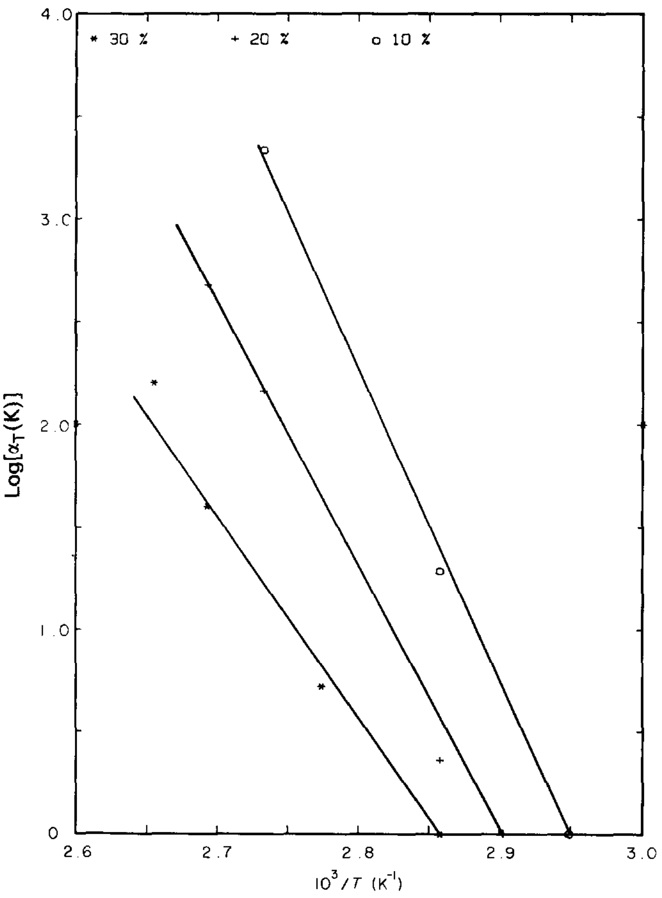

Figure 15 Shift coefficient plotted against $1/T$ in the isoconfigurational state corresponding to the α process

Table 5 Activation energies corresponding to the α process in the isoconfigurational state temperature range

				ΔH	
Blend	T (K)	log F	$10^3/T$	(eV)	(kJ mol^{-1})
10%	353	3.33	2.833	3.1	300
	338	1.28	2.958		
	328	0	3.049		
20%	358	2.68	2.793	2.6	250
	353	2.16	2.833		
	343	1.64	2.916		
	338	0.36	2.958		
	333	0	3.003		
30%	363	2.20	2.755	2.1	200
	358	1.60	2.793		
	348	0.72	2.874		
	338	0	2.958		

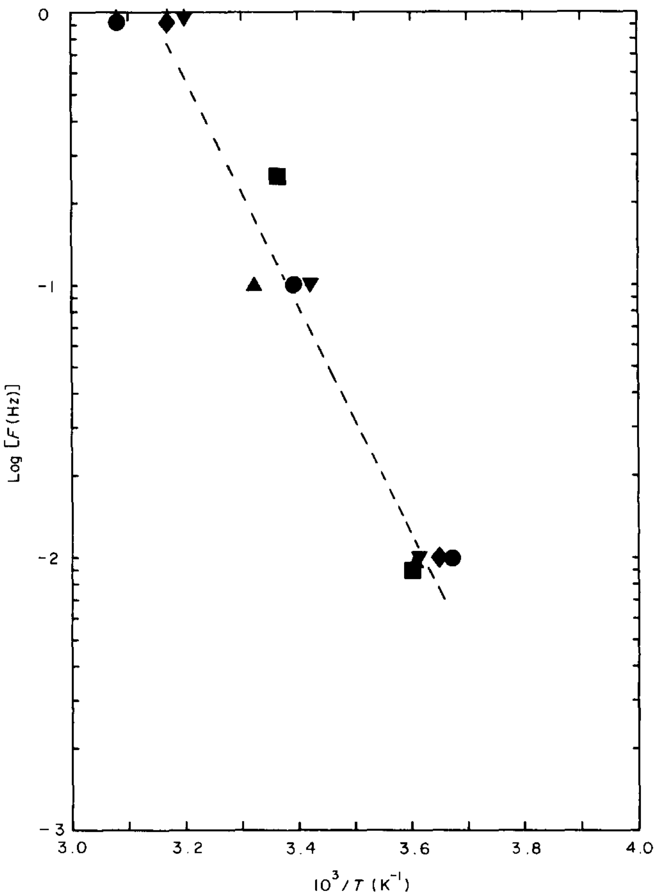

Figure 16 Frequency of the β relaxation peak, from *Figure 6*: ■, 30% PPO–PS; and from *Figures 7* and *8*: ▼, 30% PPO–PS; ◆, 20% PPO–PS; ●, 10% PPO–PS; ▲, pure PS

shape of the relaxation time distribution is modified when the temperature is changed.

All these observations would be confirmed by modelling the micromechanical properties of such materials. This modelling would point out the importance of physical parameters, especially those concerning local arrangements of monomer segments, and the intra- and intermolecular interactive forces. We plan to do such work in our laboratory[14–17].

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