

Dielectric study on the miscibility of binary polymer blends

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The α -relaxations of various polymer blends have been measured by broad-band dielectric relaxation spectroscopy (1 Hz to 1 MHz) over a wide temperature range (-50 to 220°C). In all blends under investigation the dipole moment of one polymer was negligible compared with that of its counterpart, which simplified the evaluation of blending effects on the α -relaxation. In mixtures of poly(vinyl methyl ether) (PVME) with polystyrene, which are well known to exhibit lower critical solution temperature behaviour, the α -relaxation of PVME could be measured in the one- and two-phase region. The results are compared with differential scanning calorimetric measurements of this system. The dielectric miscibility criterion ensured for the blend PVME/polystyrene was then used to study miscibility of other polymer blends. In the temperature range under investigation, mixtures of PVME/poly(*p*-methylstyrene) and PVME/poly(styrene-*block-p*-methylstyrene) are incompatible, whereas poly(*o*-chlorostyrene) blended with poly(methylphenylsiloxane) is either compatible or semicompatible.

(Keywords: polymer blends; compatibility; dielectric spectroscopy; phase behaviour; miscibility criterion)

INTRODUCTION

It is well known¹⁻³ that the miscibility of amorphous polymer blends with widely separated glass transition temperatures (T_g) of the two components can be studied by differential scanning calorimetry (d.s.c.), as the blends exhibit one single T_g if the polymers are compatible and two T_g if they are phase-separated. As the d.s.c.-measured glass transitions in polymer blends are very broad, for evaluation steepening has to be achieved, which requires relatively fast heating rates on the sample (10 to 20 K min^{-1}). Under these circumstances a compatible polymer blend (at room temperature) is never in thermal equilibrium and might not phase-separate or remix even if it had a binodal within the investigated temperature range.

Dielectric relaxation is a more sensitive tool for studying miscibility of polymer blends. The dielectric α -relaxation of polymers is related to T_g ⁴. Within the frequency range from 1 Hz to 1 MHz it may be observed in the temperature region of $T_g + 20\text{ K}$ to $T_g + 80\text{ K}$, depending on the activation energy of the process. Taking advantage of the effect that a homogeneous blend exhibits one single T_g whereas two T_g exist in a phase-separated sample, measurements of the dielectric α -relaxation over a wide frequency range provide a miscibility criterion within a temperature range of about 80 K above T_g , whereas d.s.c. simply covers the glass transition itself. Furthermore, dielectric experiments can be performed on polymer blends in thermal equilibrium, as the sample is kept at a constant temperature for a reasonable time (usually less than 30 min) before the frequency dependence of the complex dielectric constant is

measured. Thus the investigation of semicompatible polymer blends, which are homogeneous in a certain temperature range above T_g , but phase-separate at a critical temperature T_c below the decomposition temperature, is an interesting field for these measurements, especially if the critical temperature occurs near T_g .

EXPERIMENTAL

Sample preparation

Pure samples were obtained from different companies. Their origin and specifications are given in *Table 1*. For the dielectric measurements, sample preparation was performed by dissolving both polymers in a good solvent⁵, evaporating the solvent for about two days, keeping the sample under vacuum at 50°C for another three days and finally—still under vacuum—heating it to a temperature $T_g + 20\text{ K}$ until all bubbles disappear, which usually took about 24 h . For d.s.c. on polymer blends the polymers were dissolved as well in a good solvent but then a small amount was filled into an aluminium pan and dried under vacuum. This procedure was repeated several times until the pan contained about $20\text{--}30\text{ mg}$ of the polymer blend. The pure poly(vinyl methyl ether) (PVME) sample was prepared in the same way, whereas the other pure samples were used as they were purchased, namely powder for polystyrene (PS), poly(*p*-methylstyrene) (PpMS), poly(styrene-*block-p*-methylstyrene) (P(S-*b*-pMS)) and liquid for poly(methylphenylsiloxane) (PMPS). In *Table 2* the blends under investigation and the solvents used for sample preparation are listed. In *Table 3* chemical structures and dipole moments of the essentially pure polymers are given.

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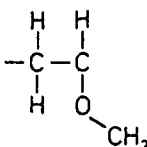
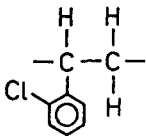
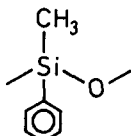
Table 1 Origin and specifications of sample materials. Molecular weights by g.p.c. with PS standards; glass transitions by d.s.c. (heating rate 20 K min⁻¹)

Material	Origin	T _g (°C)	M _n	M _w	M _w /M _n
Poly(vinyl methyl ether) PVME	Polysciences Ltd, St Goar	-18	6 600	30 500	4.62
Polystyrene PS	Polymer Standards Service (PSS), Mainz	107	65 000	66 000	1.02
Poly(<i>p</i> -methylstyrene) PpMS	PSS, Mainz	117	125 000	131 000	1.05
Poly(styrene- <i>block-p</i> -methylstyrene) P(S- <i>b</i> -pMS) ^a	PSS, Mainz	118	104 000	109 000	1.05
Poly(<i>o</i> -chlorostyrene) PoClS	Bayer AG, Leverkusen	128	35 700	133 000	3.73
Poly(methylphenylsiloxane) PMPS	Petrarch	-45	1 850	2 840	1.54

^a PS weight fraction: 0.615**Table 2** Polymer blends and their solvents

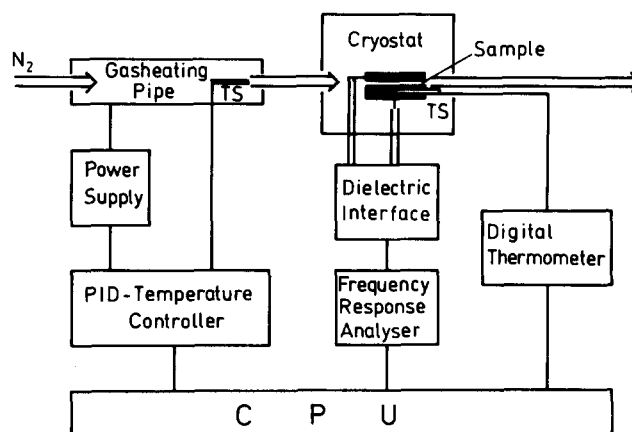
Blend	Solvent
PVME/PS	Toluene
PVME/PpMS	Tetrahydrofuran, dichloromethane, toluene
PVME/P(S- <i>b</i> -pMS)	Toluene
PMPS/PoClS	Dichloromethane

Table 3 Chemical structures and dipole moments. The dipole moments and bonding angles are all given in ref. 6 except for the PMPS values, which were taken from ref. 7. The *m_M* are the monomer molecular weights

Polymer	<i>m_M</i>	Chemical structure	Angle α (deg)	Dipole moments (D)	
				μ	μ _⊥
PVME	58		55	1.23	0.71
PoClS	138		60	1.69	0.85
PMPS	136		55	1.2	0.69

Dielectric instrumentation

For dielectric measurements within the range from 1 to 10⁴ Hz, a frequency response analyser (Solartron Schlumberger FRA 1254) combined with a high-impedance preamplifier of variable gain (Chelsea Dielectric Interface⁸) was used. At higher frequencies, 10² to 10⁷ Hz, an impedance analyser (Hewlett Packard 4192A) could be employed. In both cases the sample was kept within two gold-plated stainless-steel plates of 40 mm diameter at a distance of 200 μm maintained by four small fused silica spacers (~2 mm² each). The overall capacitance of the sample cell then measured 120–190 pF, which is the optimal region for the electronic measuring equipment described above. This assembly was mounted in a temperature-controlled nitrogen gas stream. The complete set-up is shown schematically in Figure 1. The apparatus allows for sample temperatures

**Figure 1** Schematic diagram of the dielectric equipment: temperature control system and frequency response analysis. For higher frequencies an impedance analyser is mounted in place of dielectric interface and frequency response analyser. TS: temperature sensor (Pt100)

between -180°C (liquid N₂: -196°C) and +250°C, with a stability of 0.05 K, during one frequency sweep of at most 30 min.

Calorimetric equipment

Differential scanning calorimetry was performed with a Mettler DSC 30 (temperature range -700 to 650°C) at heating rates of 10 and 20 K min⁻¹. Evaluation of the relatively broad glass transition of polymer blends was impossible unless at least 20 mg of sample material were deposited in the aluminium measuring pan. Owing to the broad transition and high sample mass, the accuracy of the T_g values given for blends in the one-phase region is limited^{1,2} (see Figure 7).

RESULTS AND DISCUSSION

PVME/PS

Polymer blends of PVME and PS have been studied extensively by various methods, especially by fluorescence emission analysis⁹, light scattering¹⁰, electron microscopy¹¹ and neutron scattering¹². It is well known that the blends are semicompatible, exhibiting lower critical solution temperature (LCST) behaviour.

The dielectric loss curves of the PVMA α-relaxation are strongly affected by blending with PS, as Figure 2 demonstrates. Their broadening is due to the heterogeneous local environment of each relaxing PVME segment^{13,14}, whereas the shift in temperature is due to T_g. The dielectric loss curves were fitted by the Havriliak-Negami equation¹⁵ (Figure 3), which provides

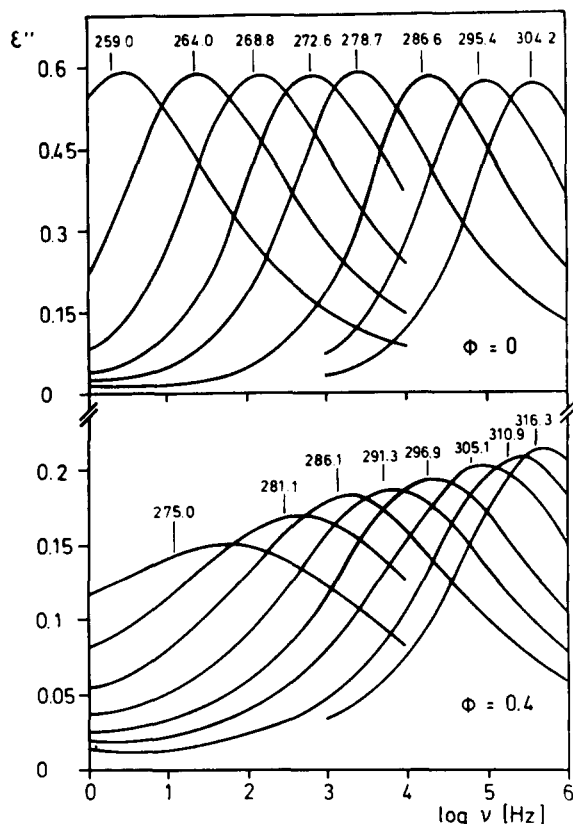


Figure 2 Dielectric loss curves $\varepsilon''(\nu)$ of pure and blended PVME at different temperatures (K); ϕ is the polystyrene weight fraction

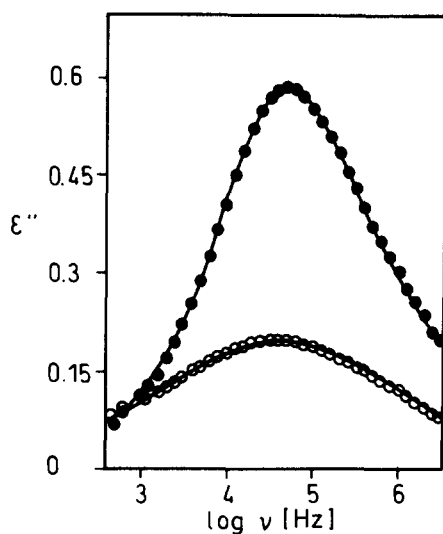


Figure 3 Dielectric α -relaxation in pure PVME at $T = 291.53 \text{ K} = 18.38^\circ\text{C}$ (●) with a least-squares fit by equation (1); Havriliak-Negami parameters, $\alpha = 0.65$, $\beta = 0.68$, $\tau = 5.8 \times 10^{-6} \text{ s}$. Dielectric α -relaxation for the blend PVME/PS at $T = 299.55 \text{ K} = 26.4^\circ\text{C}$ (○) with PS weight fraction $\phi = 0.4$; Havriliak-Negami parameters, $\alpha = 0.44$, $\beta = 1$, $\tau = 4 \times 10^{-6} \text{ s}$

the mean relaxation time τ of the process. For an α -relaxation the temperature dependence of τ can be described by the Williams-Landel-Ferry equation¹⁶ (Figure 4).

The complex Havriliak-Negami equation reads¹⁵:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\Delta\varepsilon} = \frac{1}{[1 + (i\omega\tau)^\alpha]^\beta} \quad (1)$$

which gives the dielectric loss ε'' in its imaginary part ($\Delta\varepsilon$ is the relaxation strength, α and β are fitting parameters):

$$\varepsilon'' = \frac{\Delta\varepsilon \sin(\beta\psi)}{[1 + 2(\omega\tau)^\alpha \sin(\frac{1}{2}\pi\alpha) + (\omega\tau)^{2\alpha}]^{\beta/2}} \quad (1a)$$

where

$$\psi = \arctan \frac{(\omega\tau)^\alpha \cos(\frac{1}{2}\pi\alpha)}{1 + (\omega\tau)^\alpha \sin(\frac{1}{2}\pi\alpha)} \quad (1b)$$

The Williams-Landel-Ferry equation¹⁶ for $\tau(T)$ reads (Figure 4):

$$\log \tau = \log \tau_g - \frac{c_1(T - T_g)}{c_2 + T - T_g} \quad (2)$$

As the dielectric α -relaxation is a segmental movement perpendicular to the polymer axis⁴, the dipole moments μ of both polymers in this direction are relevant (see Table 3). Compared with PS the PVME dipole moment contributes much more to the entire dielectric loss ε'' of the blend. At a given temperature the relaxation strength according to the Onsager equation¹⁷ is:

$$\Delta\varepsilon \sim n\mu^2 \quad (3)$$

where n is the number of dipoles in the sample.

For a polymer mixture this leads to (4) in a first-order approximation:

$$\Delta\varepsilon = C_1 \frac{\phi_1}{m_1} \mu_1^2 + C_2 \frac{\phi_2}{m_2} \mu_2^2 \quad (4)$$

with material constants $C_{1,2}$, weight fractions $\phi_{1,2}$ and monomer molecular weights $m_{1,2}$. For the blend PVME/PS the systematic error due to neglecting the dielectric loss of PS (PS = polymer 1 and PVME = polymer 2):

$$\frac{\Delta(\Delta\varepsilon)}{\Delta\varepsilon} = \frac{m_2 C_1 \phi_1 \mu_1^2}{m_1 C_2 \phi_2 \mu_2^2} < \frac{\phi \mu_1^2}{(1 - \phi) \mu_2^2} \leq 0.5\% \quad (5)$$

with $\phi = \phi_1 = 1 - \phi_2 \geq 0.1$.

For high PVME concentrations the errors are even much less. Thus it is sufficient to focus on the molecular dynamics of PVME in the blend.

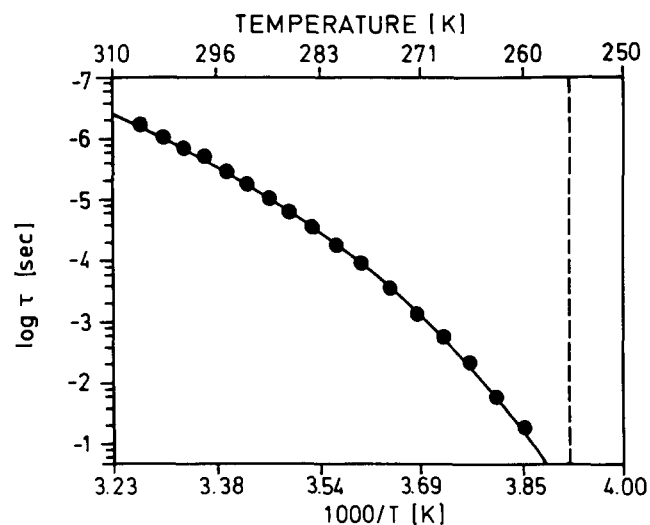


Figure 4 WLF diagram and least-squares fit by equation (2) for the PVME α -relaxation. The broken line marks the d.s.c.-determined T_g : $T_g(\text{PVME}) = 291.1 \text{ K} = -17.9^\circ\text{C}$ (heating rate: 20 K min^{-1})

Quantitative analysis of the dielectric loss data of pure and blended polymer over a broad temperature and frequency range (Figures 2 and 3) yields differences in Havriliak–Negami parameters, i.e. different relaxation time distributions¹⁸. A simple comparison of the temperature-dependent dielectric loss curves $\epsilon''(T)$ of pure and blended polymers provides information about polymer–polymer miscibility (Figure 5). For miscible polymers (e.g. PVME/PS) the maxima of $\epsilon''(T)$ are shifted due to T_g and broadened compared with pure PVME. In phase-separated samples two relaxation processes occur (Figure 6). This can be observed by d.s.c. measurements as well. The homogeneous sample exhibits one T_g , and its value lies between the T_g values of the two pure polymers. The phase-separated sample, which has been obtained by annealing the blend at 205°C (in

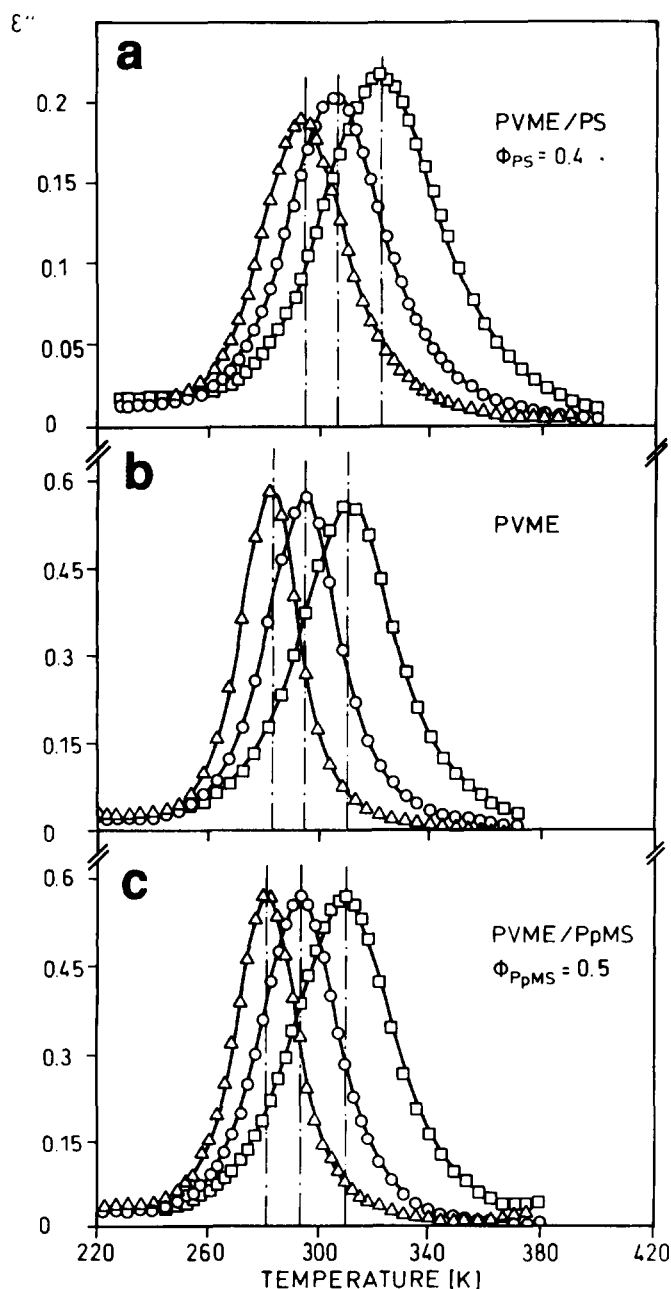


Figure 5 Temperature shift of the dielectric loss function in polymer blends at (Δ) 10 kHz, (\circ) 100 kHz, (\square) 1 MHz (ϕ indicates weight fractions). (a) A compatible mixture: PVME/PS. (b) Pure PVME. (c) An incompatible mixture: PVME/PpMS. Dielectric loss of one component is unaffected by blending

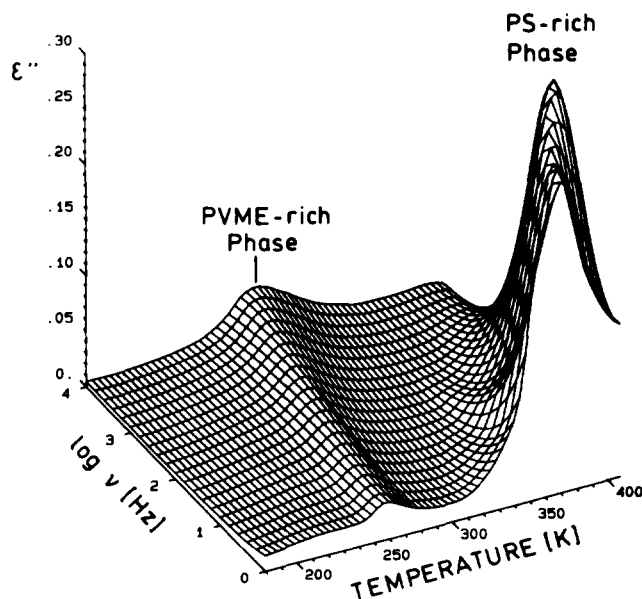


Figure 6 Dielectric loss of a phase-separated PVME/PS blend; PS weight fraction $\phi=0.8$

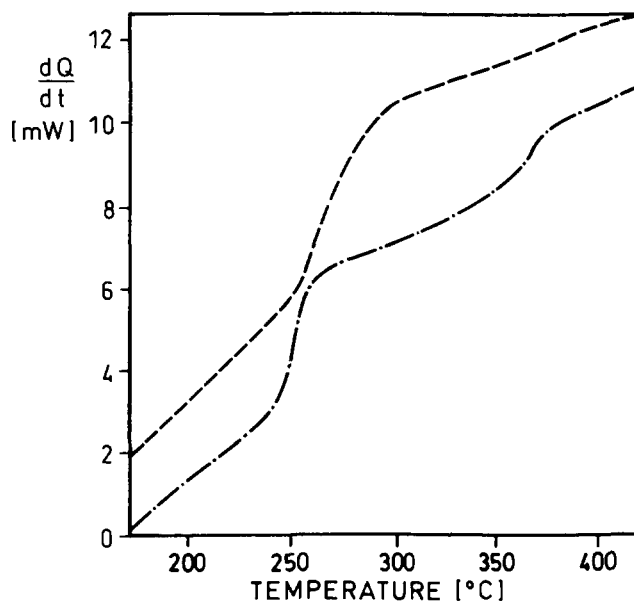


Figure 7 D.s.c. measurements on a blend of PVME/PS (PS weight fraction $\phi=0.4$, heating rate 20 K min⁻¹), in the one- and two-phase region (the sample phase-separates while kept at 205°C for 30 min): (—) homogeneous mixture; (---) phase separated sample

the two-phase region of PVME/PS) for 30 min and then quenching it below -18°C (T_g of pure PVME), shows two T_g as expected (Figure 7). It might be worth noticing that the isothermal measurement of broadened dielectric loss curves requires a wide frequency range (Figure 2). Furthermore the α -relaxations of the two separated phases (Figure 6) cannot be measured in the high-frequency range above 1 kHz, where one would have to heat up the sample above the PVME degradation temperature to measure the relaxation of the PS-rich phase.

Polymer–polymer miscibility

Havriliak–Negami analysis and corresponding relaxation time distributions of dielectric loss curves can be

employed for detailed studies on polymer mixtures. Furthermore the temperature-dependent diagram of dielectric loss curves provides quick information about the status of a blend under investigation. We used this method to test miscibility of some other polymer blends.

The blend PVME/PpMS as well as PVME/PS consists of two polymers that differ extremely in T_g and dipole moments (Table 1, $\mu_{\perp}(\text{PpMS})=0.1 \text{ D}^6$). As comparison of the dielectric loss curves shows, the PVME α -relaxation is unaffected by blending with PpMS (Figure 5), i.e. these polymers are incompatible. This was confirmed by well defined separated regions found under the light microscope. We also blended PVME with a block copolymer of PS and PpMS, but at the given block lengths (61.5% of PS) the dielectric loss curves again were identical with pure PVME; thus PVME/P(S-b-pMS) is immiscible within the investigated temperature region.

Another completely different polymer blend was analysed by the dielectric miscibility criterion and by d.s.c.: the system poly(*o*-chlorostyrene)/poly(methylphenylsiloxane) (PoCIS/PMPS). Again the T_g values of the two polymers are widely separated (Table 1), but this time there is only a small difference in dipole moments (Table 3). This might make a detailed analysis difficult, but it does not affect the miscibility criterion. As the system is almost uninvestigated, miscibility evaluation via d.s.c. is impossible. The dielectric loss curves provide the following information: (i) The blend PoCIS/PMPS

does not pass a phase transition within the temperature range from 380 to 460 K (Figure 8). If there was a phase transition within this region at least one of the dielectric loss curves $\epsilon''(T)$ would be asymmetric, as the broadening of the curves is due to mixing and phase separation causes narrowing¹³. (ii) As the loss curves of the blend are significantly shifted compared with pure PoCIS, the blend must be at least semicompatible. Further experiments (dielectric spectroscopy at different weight fractions, light microscopy, etc.) should investigate the exact phase behaviour.

CONCLUSIONS

Measurements of the dielectric α -relaxation in polymer blends provide two criteria for miscibility studies. First of all the dielectric loss curves of one polymer are broadened compared to the pure sample. This indicates a broadened relaxation time distribution, which is due to the inhomogeneous environment of the relaxing dipole in the blend. The second feature is a shift in temperature of the polymer dielectric loss curves. This shift depends on T_g and, as demixing causes two T_g , phase-separated samples exhibit two α -relaxations.

Both criteria were observed in the blend PVME/PS, which was shown to be compatible below 150°C, whereas phase-separated samples exhibit two dielectric α -relaxations. Furthermore the miscibility criteria were applied on the systems PVME/PpMS, PVME/P(S-b-pMS) and PoCIS/PMPS. For PVME/PpMS and PVME/P(S-b-pMS) we find immiscibility, whereas the blend PoCIS/PMPS is either compatible or semicompatible within the investigated temperature range (70–200°C).

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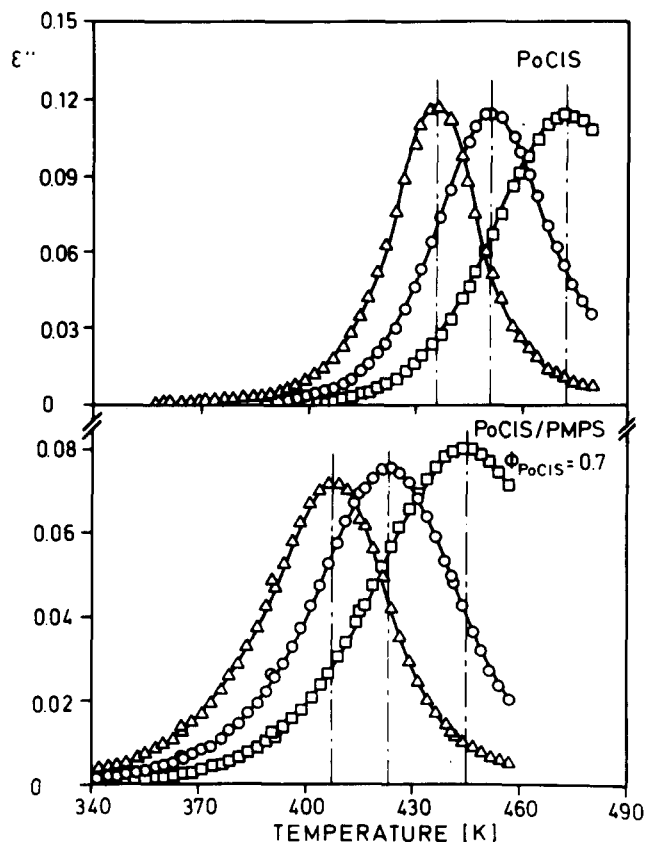


Figure 8 Dielectric loss of PMPS/PoCIS compared to pure PoCIS (weight fraction of PoCIS in the blend $\phi=0.7$) at (Δ) 10 kHz, (\circ) 100 kHz, (\square) 1 MHz