

Dielectric relaxation spectroscopy of a styrene/*n*-butyl methacrylate copolymer series

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A series of styrene–*n*-butyl methacrylate copolymers is investigated by dielectric relaxation spectroscopy over a wide frequency range (10^{-1} to 10^5 Hz). The relaxation observed is primarily due to the polar carbonyl side group of the *n*-butyl methacrylate units and behaves in the manner of an α -relaxation with the frequency–temperature locus showing non-Arrhenius behaviour. The relaxation peaks observed are analysed to determine the degree of intermolecular coupling as a function of composition and the broadness of the relaxation spectrum. Coupling is determined by measuring the slope of the log of the frequency maxima as a function of a reduced temperature, T_g/T , as is usual in coupling theory analysis. Intermolecular coupling is found to vary linearly with composition, the greater coupling occurring with increased styrene content. This is explained in terms of the interaction of the styrene units with adjacent chains. The broadness of the relaxation is quantified by the β parameter from the semi-empirical Havriliak–Negami relaxation function fitted to frequency scans. Increased styrene leads to narrower relaxations, the opposite effect to that expected from greater coupling. An explanation is proposed in terms of the range of secondary-bonded, molecular environments that polar units such as *n*-butyl methacrylate encourage. Increased content of the nonpolar styrene units would diminish this possibility. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Copolymers represent a relatively simple way in which a polymer series with a range of properties can be readily generated. Copolymer properties may vary quite markedly from those of the corresponding homopolymers and this allows manipulation of the softening point of the material, with the glass transition usually varying monotonically between those of the two homopolymers. In addition to altering the composition of the material by varying the comonomer feed, the nature of the polymerisation reaction can influence the chemical structure of the copolymer, leading to random, block, graft or alternating copolymers. Even in the conceptually simple case of copolymerisation of vinyl monomers by radical polymerisation, different reactivities and solubilities of monomer and evolving polymer can lead to non-random structures¹.

Alternatively, many recent developments in polymer science have involved blends of thermoplastic materials. Blending allows materials with different properties to be readily produced during the processing stage without recall to new materials synthesis. The high molecular weight of most polymers results in a low entropy of mixing with a range of miscibilities². A surprisingly large number of polymer pairs are, however, partially miscible and in quite a number of cases, intimate molecular mixing (full miscibility) occurs due to specific interactions between polymer

chains. In technological terms, miscible polymer blends appear to be of less importance than two-phase materials, with the latter often having superior mechanical properties, such as fracture toughness. However, the nature of full miscibility between polymers and the process of phase separation at the lower critical solution temperature is of much scientific interest. One aspect of the study of miscible blends in recent years has involved studying the molecular relaxations of polymers in such blends by techniques such as dielectric relaxation spectroscopy (DRS). DRS is particularly useful in that it can cover a much wider range of frequencies than other relaxation techniques such as dynamic mechanical analysis. A particularly interesting situation arises if only one of the components is polar (such as poly(methyl vinyl ether) (PVME) in the well-known miscible blend with non-polar poly(styrene) (PS)), since the other component is ‘invisible’ to the relaxation. The first DRS studies of miscible glass-forming systems and polymer blends observed that the width of the dielectric relaxation (isochronal scans) was related to the range of compositional fluctuations that occurred on a microscopic level in a blend with a nominal macroscopic composition³. More recent work has sought to model such effects, leading to estimations of the size of micro-regions with the same component concentrations⁴. In this paper we plan to use DRS to investigate copolymers in a similar manner.

Much work has also been undertaken considering the cooperativity and intermolecular coupling of polymer chains in homopolymers and blends^{5,6}. This work has

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arisen from consideration that homopolymer relaxations are coupled between chains, as well as within the chain. That is, molecular kinetic movements occur with regard to the motion of their neighbours which is responsible for broadening the width of the relaxation. This leads to motions which are not simple Debye relaxations, but show stretched exponential decay such as described by the Kohlrausch–Williams–Watts (KWW) function⁷, $\phi(t)$, where

$$\Phi(t) = \exp \left[- \left(\frac{t}{\tau} \right)^{\beta_{\text{KWW}}} \right] \quad (1)$$

where β_{KWW} is the KWW exponent. β_{KWW} is between 1 and 0 and thus ‘stretches’ the time necessary for dipoles to relax compared to the Debye relaxation. Since most dielectric data is collected primarily in the frequency domain, semi-empirical functions such as the Havriliak–Negami function⁸ are used

$$\epsilon^*(\omega) = \frac{\Delta\epsilon}{(1 + (i\omega\tau_{\text{HN}})^{\beta_{\text{HN}}})^{\gamma_{\text{HN}}}} \quad (2)$$

where $\Delta\epsilon$ is the dielectric relaxation strength ($\Delta\epsilon = \epsilon_r - \epsilon_u$, where ϵ_r and ϵ_u are the relaxed and unrelaxed permittivities of the α relaxation), τ_{HN} is the relaxation time, and the indices β_{HN} and γ_{HN} relate to the broadness of the relaxation and the high frequency skew, respectively. If both parameters are equal to 1 this would be a simple Debye relaxation process. The values of β_{KWW} and β_{HN} are somewhat similar in comparative terms and trends, although not precisely the same⁹.

Coupling as measured by the β parameters has also been related to the concept the fragility plots proposed for glassy systems¹⁰ and are often known in polymer science as ‘cooperativity plots’^{5,6,11}. These involve plotting of the relaxation time, τ (or the frequency maxima, f_m) as a function of a scaled variable T_g/T , where T is the experimental temperature and T_g the glass transition temperature, both in units of absolute temperature. The greater the slope of this line through a common point (such as $T_g/T = 1$), the more ‘fragile’ the system and the greater the level of intermolecular coupling. These aspects and those of compositional heterogeneity have been combined in a coupling model for blends¹².

In this work we intend to look at coupling as a function of copolymer composition. Whilst dielectric characterisation of copolymer systems has been long reported in the literature, much of the early work, usually involved copolymers of styrene with polar monomers such as poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) and has been summarised¹³. Most of those studies concentrated on the variation of the temperature ranges of the α - and β -relaxation temperatures with composition and their activation energies as a function of comonomer composition. More recently^{14–16}, DRS measurements of copolymers have again come to the fore as a potent method of probing intermolecular coupling dynamics of polymer chains, molecular mobility in semicrystalline copolymers, free volume and the nature of secondary relaxations in copolymers.

Holzer and Strobl¹⁴ used DRS to correlate the motion of the polar vinyl acetate moiety in a statistical ethylene–vinyl acetate copolymer with the restrictions on motions of the amorphous region that crystallinity imposes. Sanchis *et al.*¹⁵ used DRS to follow the level of chlorination of polyolefinic copolymers. Whilst the temperature of the α -relaxation increased with increasing content of polar chlorine units, an anomalously low T_g and dielectric strength were found at about 50% chlorine and was attributed to interaction and

cancelling of the polar units. Alvarez *et al.*¹⁶ looked at density fluctuations in a 50% random copolymer of MMA and isobornyl methacrylate (IMA), the latter containing the bulky isobornyl side group which leads to hindered mobility and high glass transition temperature. Whereas the PMMA shows an α - and secondary, β -relaxation (due to motion of ester group on the side chain), PIMA does not. However, two relaxations are seen in the 50% copolymer, with the β -relaxation from the MMA visible and unchanged to that in PMMA homopolymer. This indicates that even though the free volume of the polymer is different with the bulky groups, the β -relaxation in this case is local in nature and its temperature/frequency location is unaltered. Comparison of relaxation times with a scaled temperature (similar to considerations of a cooperativity plot) indicated that the copolymer moved in a manner closer to that of PMMA homopolymer, than the PIMA homopolymer.

Fitzgerald *et al.*¹⁷ studied the complete composition range of styrene–butyl acrylate copolymers and determined the variation of fractional free volume (f_g) and expansion coefficient for free volume (α_f), as determined from the parameters of the Williams–Landel–Ferry equation with copolymer composition. It was found that the fractional free volume at T_g was independent of composition, whilst α_f showed a maxima at intermediate compositions, as did glass transition relaxation times. Whilst this maximum could be explained by the effect of sequence distribution in copolymers (which can lead to a relaxation time greater than either homopolymer) it is not understood whether the effect on motion of the diads is inter- or intramolecular or both. Glatz-Reichenbach *et al.*¹⁸ examined the effect of crosslinking on relaxation parameters to the KWW function (equation (1)) and the HN function (equation (2)) at a reduced temperature. It was found that only the HN function fully fitted the crosslinked equations and that β_{HN} decreased (α -relaxation spectrum broadened) with addition of crosslinker due to the range of environments in which the butyl acrylate exists on the main chain. The product of α_{HN} and β_{HN} was invariant to crosslinking and is related to the high frequency limit of motions (according to the schema of Schoenhals *et al.*¹⁹), and is indicative that the motion of the secondary β -relaxation is so limited as to not be significantly affected by crosslinking.

In this work we examine the detailed dielectric relaxation behaviour of a copolymer radically polymerised from *n*-butyl methacrylate (NBM) and styrene comonomers. As with a number of the other systems mentioned above, the NBM component is polar and it is the motion of these units which is being monitored. This same copolymer system has been studied previously in blends with PS to determine the level of styrene comonomer content required to result miscibility²⁰. That study used temperature-scanning DRS to show that miscibility depended both on the composition of the copolymer, as well as the concentration of the copolymer and PS homopolymer, and that the blend miscibility depended on the frequency of the dielectric probe. We intend here to examine the DRS properties of the copolymers with reference to the effects of copolymerisation on coupling behaviour, as has been done previously for miscible blends⁴.

EXPERIMENTAL

Materials

A wide range of compositions of copolymers of NBM and styrene were obtained from Scientific Polymer Products,

with the molecular weights shown in *Table 1* (molecular weights determined by gel permeation chromatography using THF as the solvent and compared with polystyrene standards). The molecular weight average, M_w , the number average, M_n , and the polydispersity $PD = M_w/M_n$ are shown. These materials will be abbreviated in the text with reference to the wt.% NMB content, i.e. NBM 90 denotes a copolymer with 90% NBM units and 10% styrene units. The homopolymers of poly(*n*-butyl methacrylate) and polystyrene will be simply denoted PNBM and PS, respectively.

Differential scanning calorimetry (d.s.c.)

Glass transition temperatures were determined using a Perkin-Elmer Differential Scanning Calorimeter DSC-7. Temperature calibration was obtained using indium and zinc. All samples were sealed in aluminium pans, measured under a high purity nitrogen atmosphere and scanned at a rate of 10°C/min. The results are shown in *Table 1* and either represent the onset T_g (where the heat capacity curve first deviates from a tangent to the baseline on the low-temperature side of the glass transition) or as the midpoint of the heat capacity step observed at T_g .

Dielectric relaxation spectroscopy (DRS)

DRS measurements were obtained on a Novocontrol dielectric spectrometer based on a Novocontrol dielectric spectrometer based on a Solatron 1260 Frequency Analyser in conjunction with a Chelsea Dielectric Interface device and controlled by a computer and WINDETA software capable of measurements between 10⁻¹ and 10⁵ Hz. Samples were obtained in the form of powder and pressed at 110°C for 2 min. They were dried in an oven prior to measurement and silver foil adhered to the sample with conducting vacuum grease to improve electrical contact with the electrodes. Three terminal guarded cells were used for all measurements. The main dielectric parameter reported in this work is the imaginary component of the dielectric permittivity, ϵ'' . This is determined under the assumption that the sample is equivalent to a capacitor and resistor in parallel and is calculated by the equation

$$\epsilon'' = \frac{G}{C_o \cdot \omega} \quad (3)$$

where G is conductance, ω is angular frequency ($=2\pi \cdot f$ where f is in Hz) and C_o is the empty capacitance of the sample.

RESULTS AND DISCUSSION

Table 1 shows the molecular weights and the glass transitions determined by d.s.c. for the range of copolymers examined. It can be seen that the commercial materials have quite a broad range of molecular weights with the polydispersity index varying from approximately 2 to 4. The weight average molecular weight also varies, being predominantly above 100 000 apart from some of the copolymers near the mid-composition range which were less than this value. The glass transition temperatures were determined by d.s.c. from both the onset of the step observed in the heat capacity step and the midpoint. The onset T_g was easier to determine and required less judgement than the midpoint value and the dependence of both with composition is shown in *Figure 1*. The bulky phenyl ring of the PS hinders main chain motion and leads to a glass transition of almost 100°C, whereas the butyl unit of PNBM acts as an internal plasticiser, leading to a T_g of PNBM of approximately 30°C, some 70°C less than that of PMMA which has a much smaller side chain¹³.

It can be seen that the gradation of the T_g values of the copolymers compared to the homopolymers is not monotonic, as would be expected with simple random copolymerisation where the Fox equation is often found to hold²¹

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

where T_g , T_{g1} and T_{g2} are the glass transitions of the copolymer, polystyrene and poly(*n*-butyl methacrylate), respectively, the copolymer having a weight fraction w_1 of styrene units and $w_2 = 1 - w_1$ of NBM moieties. For equation (4) to be applied and included on *Figure 1*, a glass transition of PS of a molecular weight the same as that of PNBM had to be determined. Using the data and equations of Ueberreiter and Kanig²² a value of 94°C for PS with a molecular weight of 177 000 was determined²³. The dotted line in *Figure 1* made use of this value for T_{g1} and the d.s.c. midpoint T_g data. Whilst the d.s.c. midpoint data oscillates around this line, it clearly does not closely follow it. A closer examination of the data from *Figure 1* and the average molecular weight data in *Table 1* shows that the change in glass transition temperature are not correlated. That is, lower molecular weight samples do not necessarily have lower glass transitions, as would be expected. This raises the possibility that the glass transition behaviour may be due, in part, to the sequence distribution of the repeat

Table 1 Molecular weight, thermal and dielectric data for the *n*-butyl methacrylate (NBM) and styrene copolymer series

NBM (wt.%)	M_n	M_w	PD	T_g d.s.c. (°C) (onset)	T_g d.s.c. (°C) (midpoint)	T_g DRS (°C) (10 Hz)
100	86 856	176 934	2.04	22	31	34
95	103 675	314 270	3.03	24	33	43
90	68 011	313 182	4.60	30	40	47
70	31 605	80 370	2.51	34	42	55
50	18 759	53 397	2.84	41	52	63
20	135 223	342 862	2.53	76	81	87
15	119 147	315 989	2.65	78	82	94
10	137 017	320 719	2.34	77	82	90
5	87 027	237 205	2.72	73	85	87
1	138 040	357 145	2.55	87	94	102

Data include: M_n , weight average molecular weight; M_w , weight average molecular weight; PD, polydispersity index; T_g d.s.c., onset method; T_g d.s.c., midpoint method; T_g , from dielectric relaxation measurements at 10 Hz

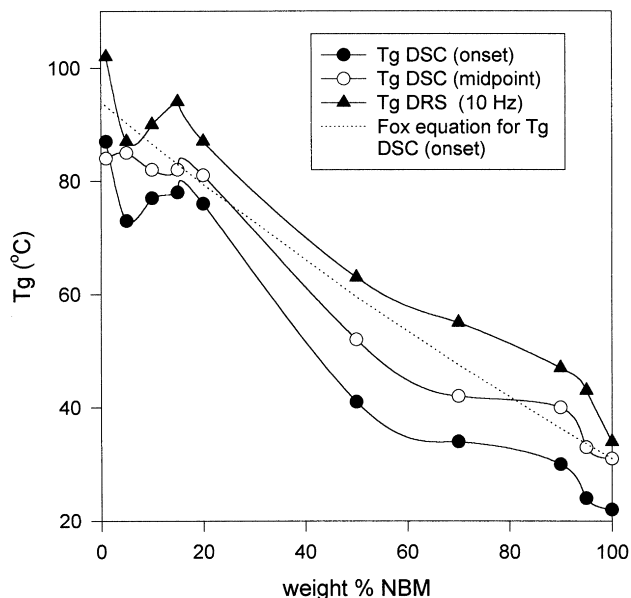


Figure 1 The glass transition temperature of the copolymer series determined from d.s.c. by various methods (onset and midpoint) and by dielectric relaxation spectroscopy (DRS) at 10 Hz. Results of the application of the Fox Equation (equation (4)) is shown for the T_g determined from d.s.c. by the midpoint method

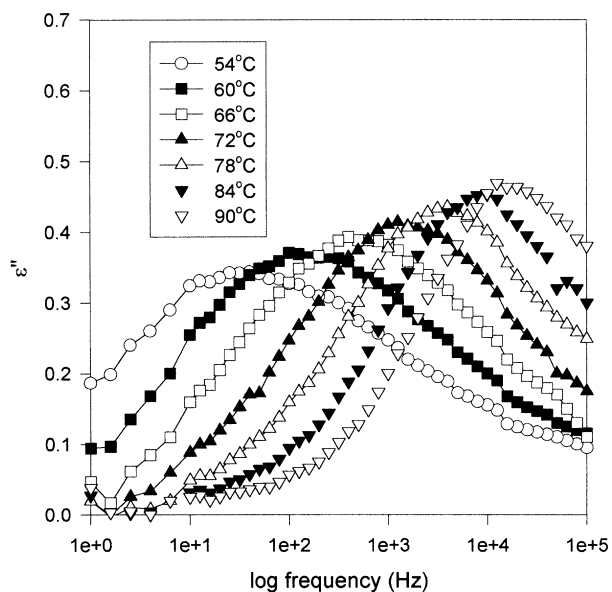


Figure 2 Isothermal dielectric relaxation loss curves (ϵ'') are shown for 90% *n*-butyl methacrylate/10% styrene units for a range of temperatures

units within the nominally random copolymer. Previous work has shown that the presence of diad units in copolymers can lead to a longer relaxation time of copolymers than the homopolymers¹⁷ due to formation of new interactions and thus it is possible that the precise sequence distribution of the copolymers could influence the T_g , although it is not clear whether such new interactions are inter- or intra-molecular in nature¹⁷, but in either case molecular motion of more than a few repeat units are most likely involved. The dielectric α -relaxation is thought to probe local segmental motions of between a few units to 10 backbone bonds, dependent on the placement of the dipole on the main chain and the degree of intercooperativity (known as

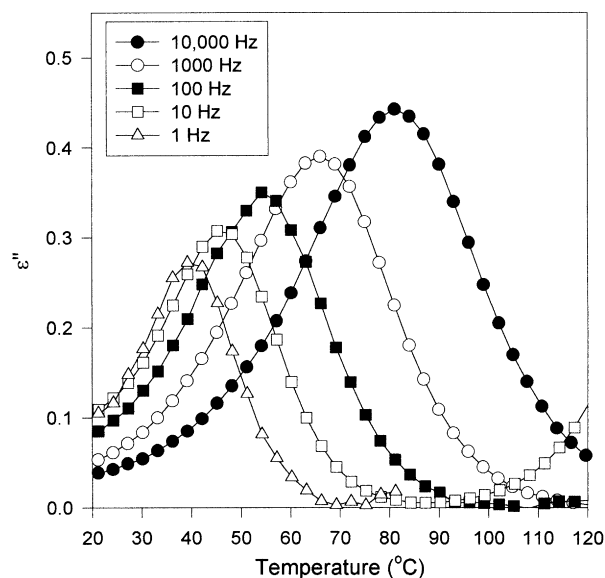


Figure 3 Isochronal dielectric relaxation loss curves (ϵ'') are shown for 90% *n*-butyl methacrylate/10% styrene units for a range of frequencies

the 'sub-Rouse' mode)²⁴. Dynamic mechanical relaxation, by comparison, is thought to measure cooperative motions involving up to 50 bonds or so ('Rouse-model')²⁴.

Dielectric relaxation measurements were made on all the samples. The full relaxation curves for the NBM 90 material are shown as an example in *Figures 2 and 3* as functions of temperature and frequency. As expected, in *Figure 3* the peak moves to higher frequency with temperature due to rapid motions of the dipolar units. Similarly higher measuring frequencies lead to a higher relaxation temperatures in *Figure 3*. Although the frequency scan data in *Figure 2* show a clear relaxation peak for this high NBM-content copolymer, its appearance for copolymers at the styrene-rich end is not as distinct and the curve maxima become very weak. However, data presented in the temperature range at a given frequency shows clear maxima across the whole composition range.

The data for the PNBM compare well to that measured previously^{25,26}, where it was shown that the α -relaxation occurred at 60.5°C at 1 kHz²⁵. It was shown that in PNBM polymer the relaxation observed is mainly that of the $\alpha\beta$ -relaxation²⁶ (a merging of the primary α -relaxation with the secondary, β -relaxation process which arises from local motion of the side chain). Higher pressures are able to separate out the $\alpha\beta$ -motion into the constituent relaxations, since the α -relaxation shows a more marked increase in relaxation time with pressure than the more local β -relaxation. In PNBM, the bulky, plasticising nature of the NBM side group results in the α -relaxation shifting to higher frequencies (compared to, say, the side group in PMMA) and thus is generally inseparable from the β -relaxation at normal measurement pressures (1-atmosphere)²⁶.

In order to make viewing of the data of the full series of copolymers more straightforward, the isochronal scans at 1 kHz are shown in two plots: for copolymers with an NBM content of 50 wt.% or greater (*Figure 4*) and for those with less than 50 wt.% NB (*Figure 5*). The dielectric properties of the high NBM content copolymers of *Figure 4* change as expected, with an increase in the bulky, non-polar styrene unit leading to an increase in the glass transition temperature and a decrease in the magnitude of the dielectric loss peak.

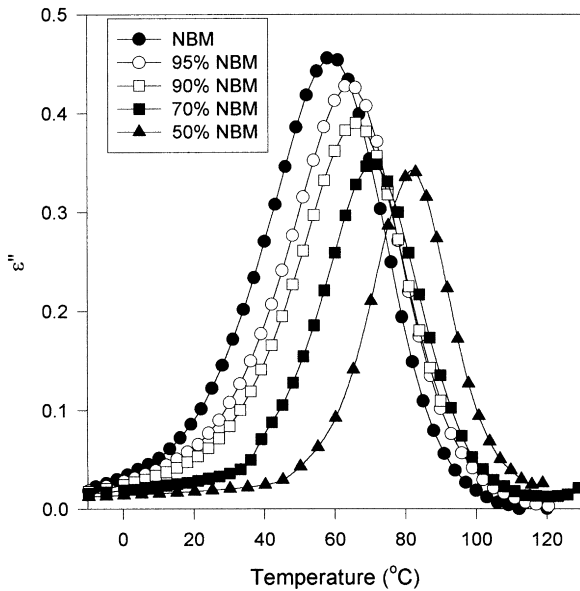


Figure 4 Isochronal dielectric relaxation loss curves (ϵ'') of high NBM-content copolymers at 1 kHz

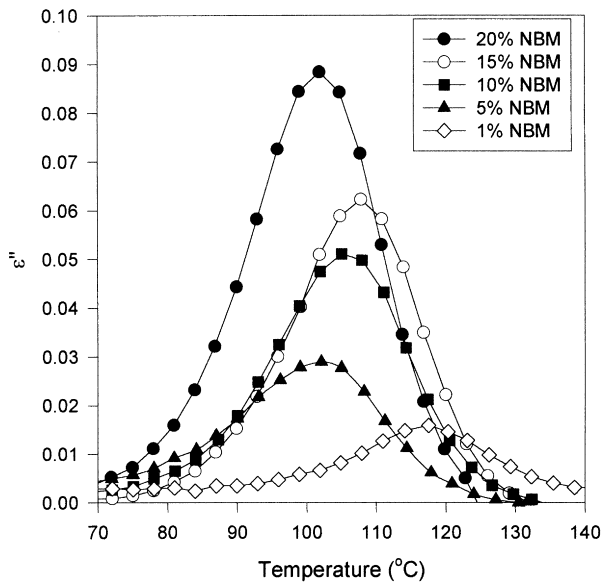


Figure 5 Isochronal dielectric relaxation loss curves (ϵ'') of low NBM-content copolymers at 1 kHz

The high styrene copolymers (Figure 5) show somewhat more complex behaviour, in line with the d.s.c. data in Table 1 and Figure 1. Although increasing styrene content still leads to peaks of a smaller magnitude, the NBM 10 and NBM 5 samples show a decrease in temperature with increasing styrene, rather than an increase, although the NBM 1 sample has the highest glass transition of all the samples measured. The appearance of the DRS plots look similar to Figures 4 and 5 if another measurement frequency is used, and in Table 1 and Figure 1 peak positions for isochronal curves measured at 10 Hz are presented. The dependency of the DRS data on NBM content is seen to be similar to the results of the d.s.c. technique. As would be expected, the higher frequency of the DRS technique (10 Hz in the case of Figure 1) leads to greater values of the glass transition temperature compared to d.s.c.

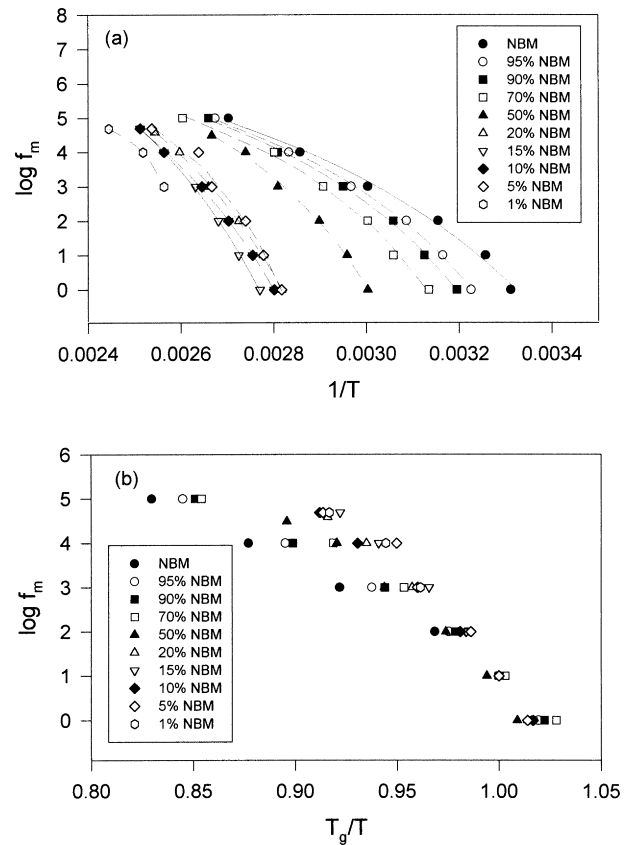


Figure 6 (a) Temperature dependence of the frequency maxima (f_m) for different high NBM copolymer compositions. The lines are results of fitting of the Vogel–Fulcher Equation (equation (6)) to the data. (b) Cooperativity plots of the data from part (a) obtained by plotting the same data as a function of normalised temperature, T_g/T , where T_g is the dielectric glass transition temperature obtained at 10 Hz

The locations of the frequency of maximum dielectric loss (f_m) as a function of reciprocal temperature are shown in Figure 6a. It can be seen that in most cases the data are curved downwards (rather than linear), indicative of the relaxation following a Vogel–Fulcher (VF)^{27,28} dependency which is indicative of the reduction of free volume as the glass transition is approached from above leading to longer relaxation times with decreasing temperature than would be expected from an Arrhenius-like behaviour. It should be noted that, despite the primary relaxation of PNBM being a combined $\alpha\beta$ -relaxation, it shows the slight downturn in frequency with decreasing temperature, giving it the character of an α -relaxation, as is seen in most of the copolymers.

With reference to the previous discussion on the coupling model in polymer relaxations^{5,6}, the data can also be plotted in terms of a reduced temperature, T_g/T , where in this case T_g is the dielectric glass transition at 10 Hz and leads to a common point at $\log f_m = 1$ and $T_g/T = 1$. It can be seen in Figure 6b that the data of the different copolymers overlay each other much more closely. That is, the rate with which the segments move is quite similar when compared at the same scaled temperature above their glass transition temperature. Of interest is the slope of the line at $T_g/T = 1$, which is a measure of the fragility or intermolecular cooperativity of the system. This has been defined as⁹

$$\text{COOP}(\tau_{\text{HN}}) = \frac{d \log(\tau)}{d(T_g/T)} \Big|_{T=T_g} \quad (5)$$

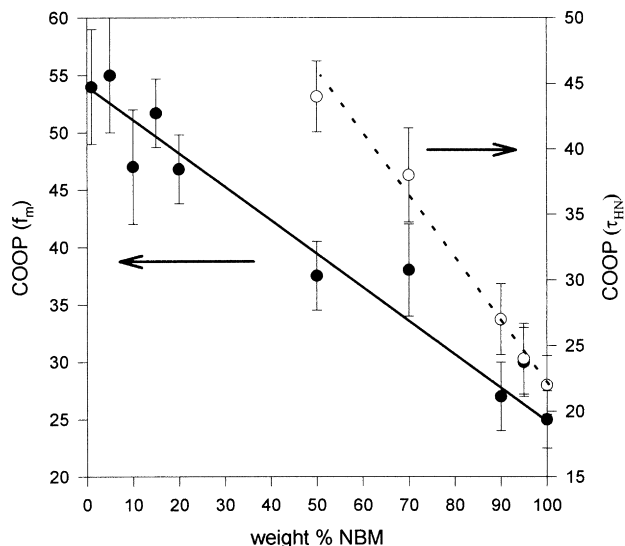


Figure 7 Cooperativity parameters defined in the text (such as in equation (5)) as a function of copolymer content. Both relate to the slope of a line tangent to the $T_g/T = 1$ point on a plot of either $\log f_m$ versus T_g/T ($\text{COOP}(f_m)$) or $\log \tau_{\text{HN}}$ versus T_g/T ($\text{COOP}(\tau_{\text{HN}})$)

Whilst the parameter in equation (5) is defined in terms of $\log \tau$ this can present problems in some systems. For example, in the copolymer material examined here the isothermal frequency scan is very poorly defined at high styrene content, as mentioned above, due to the low dipole moment. It was only possible to fit the Havriliak–Nagami Equation (equation (2)) at 50 wt.% NBM and higher, and the parameter $\text{COOP}(\tau_{\text{HN}})$ could thus only be fitted over this limited NBM composition range (the results are shown as open symbols in Figure 7). We have found²⁹ in work on a miscible polycarbonate/polyester blend system reported previously³⁰ that a plot of $\log f_m$ versus T_g/T shows the same trends and thus we propose its use in situations such as this where such curve fittings to frequency-scan data are not possible and relaxation times not obtainable. Due to the

inverse relationship between relaxation time and frequency the sign of the slope is changed, and thus $\text{COOP}(f_m)$ is defined as the mod of the slope of the $\log f_m$ versus T_g/T curve at $T_g/T = 1$. The $\text{COOP}(f_m)$ parameter is also shown in Figure 7.

It can be seen that in both cases (at least in the NBM-rich part of the composition) both parameters show an monotonic increase indicative of greater intermolecular coupling with increasing concentration of styrene units. The higher level of intermolecular coupling for PS compared to PNBM are expected given the ‘rougher’ profile of the PS chain and its protruding phenyl units³¹. It is interesting to note that the degree of coupling (as quantified by $\text{COOP}(f_m)$) seems to be linear with composition, as indeed is $\text{COOP}(\tau_{\text{HN}})$ in the limited range in which it can be determined.

This measure of intermolecular coupling can be compared with the other parameter often used to quantify coupling, β_{HN} . As before, it could only be determined from equation (2) for compositions of 50 wt.% NBM and higher. The value of the parameter related to the high frequency skewing of frequency-scan plots, γ_{HN} , was also determined. To allow a meaningful comparison between samples across the composition range, it is compared at a constant T_g/T value (in this case 1.0 was chosen), and all the results are shown in Figure 8 and data for a number of temperatures are shown in Table 2. β_{HN} initially decreases (relaxation spectrum broadens) from the NBM value with the addition of small amounts of styrene, possibly due to increased intermolecular coupling. However, in the concentration range in which β_{HN} could be measured (between 0 and 50 wt.% styrene), an increase in styrene content shows an increase in β_{HN} , which is opposite to what may be expected from increased coupling. Likewise, the copolymers do not have a relaxation broader than that of NBM homopolymer, as may be expected if there was large-scale blockiness in the copolymers. The values of γ_{HN} also vary monotonically with content at $T_g/T = 1$, decreasing with increasing styrene content, indicative of greater skewing in the frequency domain in that composition range.

Having determined the values of β_{HN} allows a point of

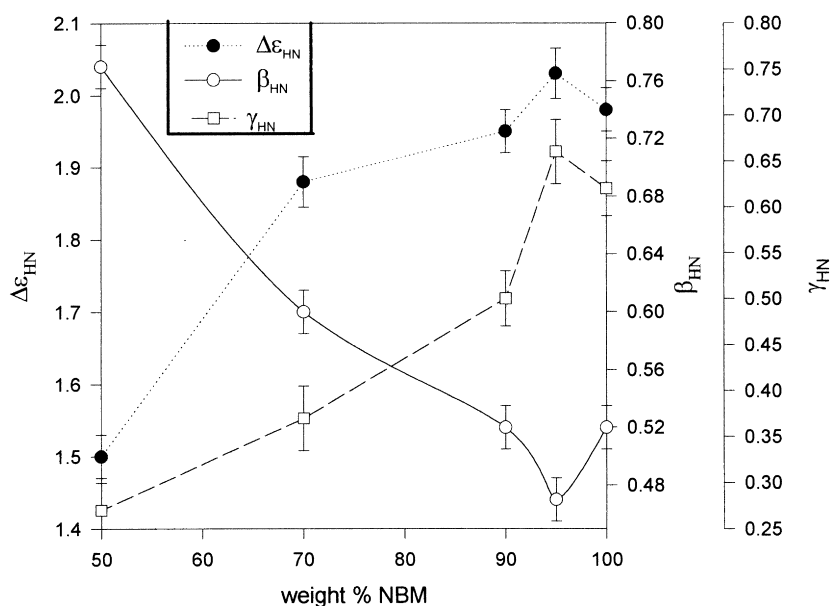


Figure 8 Parameters obtained by fitting the Havriliak–Nagami semi-empirical relaxation function (equation (2)) to isothermal frequency-scan data for the range of copolymer compositions for which this is possible (high NBM compositions). The parameters are: $\Delta\epsilon_{\text{HN}}$ (relaxation strength), β_{HN} (related to broadness of the relaxation) and γ_{HN} (indicative of high frequency skew). The points displayed as a function of composition are at constant $T_g/T = 1.0$

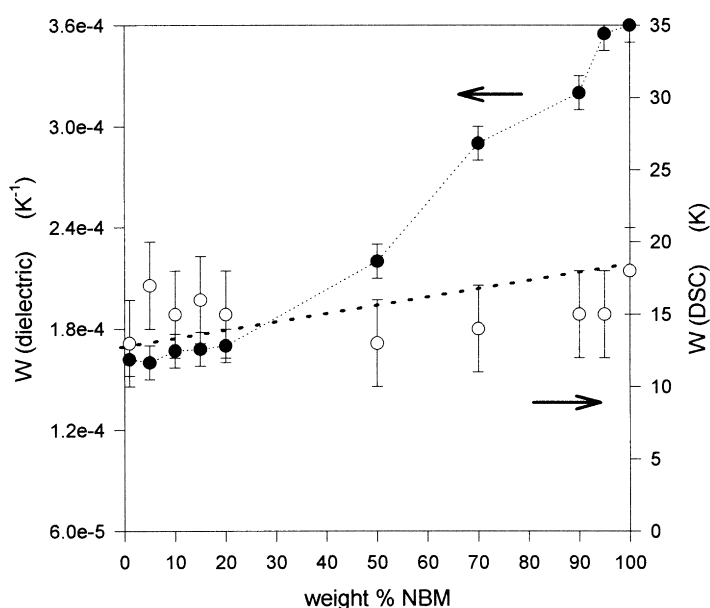
Table 2 Parameters relating to peak shape fitted from DRS frequency-scan data using equation (2)

Sample	T (°C)	γ_{HN}	β_{HN}
100% NB	28	0.58	0.60
	31	0.55	0.56
	34	0.62	0.52
	37	0.61	0.59
	43	0.62	0.56
95% NB	61	0.62	0.66
	39	0.80	0.41
	42	0.66	0.47
	45	0.66	0.46
	48	0.57	0.52
	51	0.49	0.55
	63	0.48	0.55
90% NB	78	0.63	0.52
	42	0.51	0.56
	45	0.48	0.54
	48	0.50	0.52
	51	0.52	0.50
	54	0.53	0.53
	57	0.55	0.54
	60	0.63	0.54
	63	0.43	0.63
	66	0.42	0.64
	69	0.42	0.66
70% NB	75	0.52	0.68
	78	0.48	0.70
	81	0.39	0.74
	51	0.38	0.58
	54	0.37	0.60
	57	0.37	0.61
	60	0.37	0.61
	63	0.30	0.67
	66	0.30	0.67
	69	0.24	0.72
	72	0.24	0.74
50% NB	75	0.24	0.74
	60	0.26	0.78
	65	0.28	0.77
	70	0.26	0.81
	75	0.24	0.79
	80	0.24	0.77
	85	0.22	0.77

comparison between our cooperativity data and those of other workers⁶. In that work with a range of homopolymers they found that there was a linear relationship between β_{HN} and COOP (τ_{HN}), with larger values of β_{HN} correlating with lower values of COOP (τ_{HN}). Our values of β_{HN} are of the order of 0.5 to 0.7. On their graph (Fig. 13 of Ref. 6), such values indicate the COOP (τ_{HN}) parameter should be approximately between 20 and 30, and this is shown in our data of Figure 7. Clearly, *n*-butyl methacrylate materials appear quite uncoupled. Ngai and Plazek⁶ make this point in terms of the longer side chain units plasticising the system and meaning that polymer backbones see an environment with a low concentration of backbone, but a higher concentration of the side group and thus intermolecular coupling will be less⁹. It should be noted that broadness is also determined in such frequency scans to some degree by the skew parameter, γ_{HN} . It can be seen in Table 2, that at the same time that the sample appears to become narrower with increasing styrene, its skew parameter also decreases.

To further investigate whether compositional and/or sequence fluctuations in the copolymers may lead to broader glass transition regions, the width of transitions seen by d.s.c. can be analysed. This was taken as the distance between the point at which the heat capacity deviates from its glassy value and returns to a straight line above T_g . This width (in K) is denoted W (d.s.c.) and is also shown in Figure 9. It can be seen that there is little change in the thermal broadness of the d.s.c. transition with composition. It thus appears that although coupling increases with the bulky styrene units, the range of environments is dictated by secondary interactions between polar units. This data confirms that compositional and sequence heterogeneity, if they exist, do not seem to play a significant role in the shape or temperature dependence of the transition.

Additional confirmation of broadness of the relaxation as a function of composition was sought by further analysing the data. Apart from the COOP parameters, another dielectric parameter readily measurable across the entire compositional range is the width-at-half height of an isochronal dielectric scan (such as those shown in Figures 4 and 5) at 10 Hz. In fact, it is more desirable to

**Figure 9** The broadness of the relaxation is quantified in two ways as a function of composition. W (dielectric) is the width-at-half-height of a reciprocal temperature versus dielectric loss (ϵ'') curve for 10 Hz and W (d.s.c.) is the breadth of the glass transition observed by differential scanning calorimetry

measure the width-at-half height of ϵ'' plotted against *reciprocal* temperature since, as noted by others^{13,32}, relaxation is an energy-activated process. The data of *Figures 4 and 5* were thus replotted in this manner and the width-at-half-height calculated and presented as parameter W (dielectric) with the units K^{-1} in *Figure 9*.

It can be seen from this that, as shown by the β_{HN} parameter, it appears to become narrower with increasing styrene content. Thus, although coupling has been found to *increase* with increasing styrene content, the width of the relaxation (as judged by the dependence of W (dielectric) on composition) is found to *decrease* by this analysis. This discrepancy probably lies in the fact that because the W (dielectric) parameter is measured at a range of temperatures, not only does the broadness of the relaxation change, but the activation energy does as well. Both parameters are dependent on the frequency of measurement (for example, low frequency relates to high activation energy) and thus the W (dielectric) parameter should strictly be compared at constant activation energy. Since this is difficult to determine, W (dielectric) is of limited use.

In the case of this copolymer, it appears β_{HN} is not related simply to the degree of intermolecular coupling. Nor, it seems, is compositional or sequence heterogeneity the predominant factor relating to broadness, as it is in blends³³ where dielectric spectra of miscible blends are broader than those of the homopolymers. Therefore, a different explanation for the change from the broader spectra of PNBM to increasingly narrower spectra with PS addition must be sought, an explanation not related only to compositional heterogeneity.

In homopolymers the broadness of the relaxation may also be dependent on the range of molecular environments in which the units find themselves. It may be that the range of environments caused by the polar dipoles and resultant secondary bonds in the NBM unit is responsible for such a distribution of relaxation times. By increasing the amount of non-polar styrene units this effect would be expected to decrease. The decreasing polarity is readily seen by determination of $\Delta\epsilon_{HN}$ from equation (2) at $T_g/T = 1$, the strength of the relaxation, which is related both to the density of dipoles taking part in the relaxation and conformational considerations. It can be seen in *Figure 8* that this decreases steadily from about 2.1 for NBM to lower values as it becomes more non-polar with increasing styrene. As before, values for materials with lower than 50 wt.% styrene could not be determined. Differentiating between intermolecular coupling and the range of molecular environments due to polar, secondary bonding is admittedly a difficult exercise as the two would be interrelated. The delineation may arise because the electrostatic interchain interaction dominates over the physical, interchain coupling in this instance.

In summary, it is worth noting that it is the COOP (τ_{HN}) parameter that is usually found to be the most indicative of coupling in a polymer system. It is found, for example, that even when a relaxation spectrum broadens for other reasons (such as crystallinity providing a restriction on chain motion)^{31,34} the temperature dependence of the relaxations relationship to intermolecular coupling remains and this gives us some certainty that the styrene unit is leading to greater, physical intermolecular coupling as expected from consideration of chain topology, despite the fact that relaxation broadness shows unexpected dependencies.

The $\log f_m$ versus $1/T$ data of *Figures 7a and 8a* could also be fitted to the VF equation^{27,28} which is of the

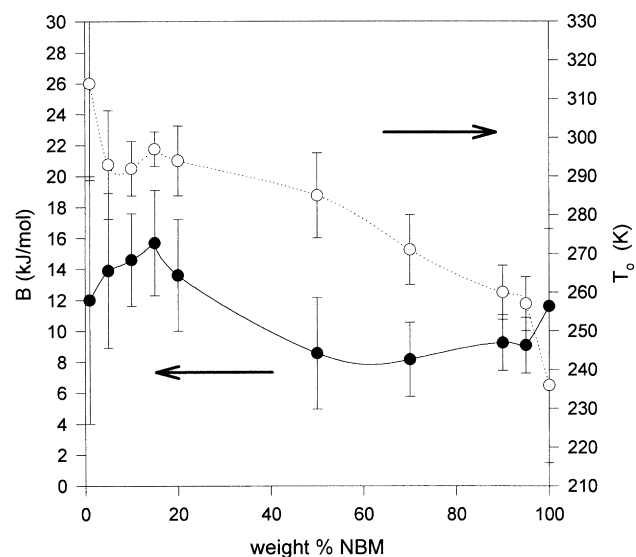


Figure 10 Vogel-Fulcher parameters B (related to activation energy) and T_0 as a function of copolymer composition, as determined from equation (6)

form

$$f_m = A \exp\left(-\frac{B}{R(T-T_0)}\right) \quad (6)$$

where A , B (kJ/mol) and T_0 (K) are fitted parameters. A is the pre-exponential factor, B is an effective activation energy and T_0 is the temperature at which there is a cessation of cooperative molecular motion and is usually thought to be some 50° below the glass transition temperature³⁵. The fit of equation (6) with the data is quite good, as can be seen across the composition range from the lines in *Figure 6a*. The values obtained for B and T_0 are shown in *Figure 10*. It can be seen that B remains relatively constant as a function of composition and that the energy of activation does not vary greatly between homopolymers, nor in the intermediate copolymer compositions. The error bars on the B data arise from the fact that the data in *Figure 6a* are not highly curved, and the fit would be better if a wider frequency range of measurement were available. The values of T_0 closely follow the T_g dependence observed in *Figure 1* and occur at values 50 – 60°C below the glass transition temperature, as expected.

CONCLUSIONS

The dielectric relaxation spectra of a full compositional range of a copolymer series has been investigated in which one of the components is polar. Whilst most of the glass transition temperatures of the copolymers lie between those of the homopolymers, the trend is not simple. Molecular weight differences between the different compositions do not fully explain these variations, and their variation may be due in part to non-randomness in sequence distributions.

The *n*-butyl methacrylate homopolymers primary relaxation is known to have an $\alpha\beta$ -character in that the bulky NBM sidegroup leads to a flexible main chain and the primary (α) and secondary (β) relaxations are merged within the frequency range being studied. Nonetheless, both PNBM and copolymers have a downward curvature of the $\log f_m$ versus $1/T$ curves, indicative of loss of free volume as the glass transition is approached from higher temperatures. From these curves the Vogel-Fulcher equation can be fitted

and a measure of the activation energy required for motion of the kinetic units can be determined and is found to be similar for both homopolymers and the intervening compositions.

To determine the degree of coupling and intermolecular interaction between chains the frequency or relaxation time dependence as a function of a reduced parameter, T_g/T can be examined, the so-called 'cooperativity' plots. The steeper these plots are at reduced temperature $T_g/T = 1$, the greater the degree of intermolecular coupling. Due to the very polarity of the styrene units it was not possible to fit the semi-empirical Havriliak–Negami function to isothermal, frequency-scan data at contents of less than 50 wt.% NBM. Therefore, in the same way in which either $\log \tau$ or $\log f_m$ (where f_m is the position of the frequency maxima) can be used to calculate activation energies, we constructed cooperativity plots across the whole composition range using dielectric loss maxima apparent for a series of frequency-multiplexed, temperature scans. It was found that with increasing styrene content the coupling smoothly changed between a lower value of PNBM and a greater value in PS. This is as expected with PS having a 'rougher' molecular profile due to the pendant phenyl ring, leading to greater interaction with neighbouring chains. Another common parameter used to quantify coupling is the β_{HN} parameter from the Havriliak–Negami equation which relates to relaxation broadness—in general, the lower the value of β_{HN} , the broader the relaxation spectrum, the greater the coupling. It was found that, in the compositional range in which the Havriliak–Negami equation could be sensibly applied, β_{HN} increased (relaxation spectra narrowed) with increased styrene. This is the opposite to what would be expected from coupling theory. Likewise, plots of dielectric loss against reciprocal temperature for the various compositions across the full compositional range also narrowed with increasing styrene.

In homopolymers and blends the broadness of the relaxation is often related not only to intermolecular coupling but also to the range of molecular environments in which the mobile units exist and, in the case of blends, to compositional fluctuation on a micro-level as well. This latter consideration would have led to an expectation that the copolymers would be considerably broader due to compositional or sequence distributions. We therefore propose that the narrowing of the relaxation distribution with decreasing polar NBM component is due to the reduction in polar, secondary-bond environments that may occur with high NBM content and that this is somewhat distinct to the physical intermolecular coupling caused by the pendant phenyl groups from the styrene moieties. Broadness of relaxation is clearly not solely determined by coupling and consideration of a number of parameters of the dielectric relaxation spectrum should be considered when investigating relaxational behaviour of copolymers.

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REFERENCES

1. Boyd, R. H. and Phillips P. J., *The Science of Polymer Molecules*. Cambridge University Press, Cambridge, 1993.
2. Utracki, L. A., *Polymer Alloys and Blends*, Hanser, New York, 1990.
3. Shears, M. F. and Williams, G., *J. Chem. Soc., Trans. Faraday Soc. II*, 1973, **69**, 608; Wetton, R. E., MacKnight, W. J., Fried, J.R. and Karasz, F. E., *Macromolecules*, 1978, **11**, 158.
4. Fischer, E.W. and Zetsche, A., *Acta Polym.*, 1994, **45**, 168.
5. Ngai, K. L., *Comments Solid State Phys.*, 1979, **9**, 127.
6. Ngai, K. L. and Plazek, D. J., *Rubber Chem. Tech. Rubber Reviews*, 1995, **68**, 376.
7. Williams, G. and Watts, D. C., *Trans. Faraday Soc.*, 1970, **66**, 80.
8. Havriliak, S. and Negami, S., *Polymer*, 1967, **8**, 161.
9. Kita, Y. and Koizumi, N., *Adv. Molec. Relax. Interact. Proc.*, 1979, **15**, 261.
10. Angell, C. A., in *Relaxations in Complex Systems*, ed. K. L. Ngai and G. B. Wright. Government Printing Office, Washington DC, 1985.
11. Roland, C. M. and Ngai, K. L., *J. Non-Cryst. Solids* **172–174**, 868, 1994.
12. Roland, C. M. and Ngai, K. L., *Macromolecules*, 1991, **24**, 5315.
13. McCrum, N. G., Read, B. E. and Williams, G., *Anelastic and Dielectric Effect in Polymeric Solids*. Wiley, London, 1967 (re-released by Dover Publications, New York, 1991).
14. Holzer, B. and Strobl, G., *Acta Polym.*, 1996, **47**, 40.
15. Sanchis, M.J., Martinez, E.S., Calleja, R.D., Pankratova, E.T. and Murin, I., *Polym. Int.*, 1996, **41**, 337.
16. Alvarez, F., Colmonero, J., Wang, C.H., Zia, J.L. and Fytas, G., *Macromolecules*, 1995, **28**, 6488.
17. Fitzgerald, J., Binga, T. D., Sorriero, L. J. and O'Reilly, J. M., *Macromolecules*, 1995, **28**, 7401.
18. Glatz-Reichenbach, J. K., Sorriero, L. J. and Fitzgerald, J. J., *Macromolecules*, 1994, **27**, 1338.
19. Schoenhals, A., Kremer, F. and Schlosser, E., *Phys. Rev. Lett.*, 1991, **67**, 999.
20. Fujioka, F., Noethiger, N., Beatty, C. L., Baba, Y. and Kaegmoto, A., in *Polymer Blends and Composite Materials*, ed. C. D. Han. ACS Advances in Chemistry Series., No. 206, American Chemical Society, Washington, 1984.
21. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
22. Ueberreiter, K. and Kanig, G. Z., *Naturforsch.*, 1951, **6a**, 551.
23. Yu, Z., Yashi, U., McGervey, J. D., Jamieson, A. M. and Simha, R., *J. Polym. Sci., Pt. B, Polym. Phys. Ed.*, 1994, **32**, 2637.
24. Santangelo, P. G., Ngai, K. L. and Roland, C. M., *Macromolecules*, 1993, **26**, 2682.
25. Ishida, Y. and Yamafuji, K., *Kolloid-Z.*, 1961, **177**, 197.
26. Williams, G. and Edwards, D. A., *Trans. Faraday Soc.*, 1966, **62**, 2091.
27. Vogel, H., *Phys. Z.*, 1921, **22**, 645.
28. Fulcher, G. S., *J. Am. Chem. Soc.*, 1925, **8**, 958.
29. Spall, S., Goodwin, A. A. and Simon, G. P. (unpublished results).
30. Spall, S., Goodwin, A. A. and Simon, G. P., *J. Polym. Sci., Part B, Polym. Ph.*, 1996, **34**, 2419.
31. Ngai, K. L. and Roland, C. M., *Macromolecules*, 1993, **26**, 6824.
32. Read, B. E. and Williams, G., *Polymer*, 1961, **2**, 239.
33. Wetton, R. E., MacKnight, W. J., Fried, J. R. and Karasz, F. E., *Macromolecules*, 1978, **11**, 158.
34. Ngai, K. L. and Roland, C. M., *Macromolecules*, 1993, **26**, 2688.
35. Matsuoka, S., *Macromolecules*, 1991, **24**, 2770.