BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 18, pp. 3427–3433, 1995

0032-3861/95/$10.00+0.00

polymer papers

Dielectric relaxation of some flexible copolymers in dilute solutions

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(Received 9 February 1993; revised 8 September 1994)

Dielectric measurements were carried out for some methyl methacrylate (MMA) and styrene (St) related polymers and copolymers in dilute solutions at a frequency range from 1 kHz to 18 GHz. The dielectric data revealed the existence of three absorption regions. The absorption region associated with the side-chain relaxation for MMA–St copolymer with a low content of MMA units, showed a diffusion-controlled relaxation which can be interpreted in terms of Kramer's theory but for large friction limits. On the other hand, all other polymers and copolymers investigated behaved according to Kramer's theory but for small friction limits. This type of polymer was found to be little affected by solvent viscosity and its dipolar relaxation process is very similar to that caused by the internal rotation of the flexible chain. In addition to the relaxation associated with the side-chain rotation, two more distinct relaxation processes are detected. That in the low frequency region is found to be due to conformational rearrangement of the main chain, while that at higher frequency could be attributed to the inner mobility of the side groups.

(Keywords: dielectric relaxation; dilute solution; flexible copolymers)

INTRODUCTION

The dielectric properties of solid polymers have been of great interest to many workers. The close relation between the mechanical properties and electrical behaviour warrants such interest, in addition to the direct application to the problem of electrical insulation.

The study of dielectric permittivity and loss in dilute solutions has fewer applications, however it offers important information concerning the molecular conformation under both equilibrium and dynamic conditions. This could be very helpful in throwing light on the conformation of macromolecules in solutions.

There are two types of polymer that exhibit dielectric relaxation independent of chain length[1,2]. The first type is polymers with dipoles attached rigidly perpendicular to the chain backbone, and the second is polymers with dipoles in the flexible side chains. The copolymers used in this study belong to the second type of polymer.

The nature of the relaxation processes in polymers has been investigated intensively and explained by a variety of authors[1,3–5]. However, a limited range of frequencies was usually used. Therefore, more extensive and systematic studies seem to be necessary to clarify all the different mechanisms involved in the relaxation process.

In this study we prepared two kinds of copolymers: (1) styrene (St) with methyl methacrylate (MMA), maleic anhydride (MA) and *N*-phenylmaleimide (NPMI); and (2) MMA with NPMI. We measured their dielectric properties over a wide range of frequency extended from 1 kHz to 18 GHz. The measurements were carried out in three non-polar solvents (benzene, toluene and dioxane) at temperatures between 20 and 40°C. In this study, the MMA unit was chosen as a flexible dipole unit while styrene was chosen as a rigid one. Similar measurements were previously done for these copolymers in the solid state[6,7] and also in dilute solutions[3,5], but in a limited frequency range which allowed only one absorption region—that associated with the side-chain rotation—to be detected.

EXPERIMENTAL

Copolymer synthesis

Copolymers were synthesized according to the procedures given previously[8], then purified and dried to constant weight at 60°C. The polymer composition was determined from elemental analysis for C, H and N carried out at the Microanalytical Unit in Cairo University. In the case of MMA–St copolymer, n.m.r. spectroscopy was used to measure the copolymer's composition.

Dielectric measurements

The dielectric properties were measured over a wide range of frequency extending from 1 kHz to 18 GHz. Up

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to 50 kHz a Schering bridge-type NF-decameter (Wissenschaftlich Technischer Werkstaten (WTW), Germany) was used. For frequencies between 50 kHz and 40 MHz, measurements were performed using a type 1245 A Q-meter (Marconi, UK). The cell used for both measurements was a cylindrical condenser, type NFL1 (WTW, Germany). The accuracy of measurements in ϵ' was 1% while for ϵ'' it was 3%. In the microwave region, for frequencies between 200 MHz and 18 GHz, a sweep-frequency spectrometer established in the National Research Center (Cairo, Egypt) was used; this instrument has been described elsewhere[9]. The generator was type 8620 C (Hewlett Packard, USA). The measuring cell, which has a coaxial transmission line, was completely filled with the solution being tested so that waves passed through a layer of constant length. The transmitted waves were detected, amplified and recorded by an $X-Y$ recorder.

Electrical conductivity measurements

The conductivity σ was measured using a OM4516/01 power supply unit (Philips, Holland) that gave a stable d.c. voltage between 0 and 250 V with a maximum permissible loading current of 1 mA. The potential difference (V) across the cell and the current (I) flowing through it were measured by a URI BN 1050 multimeter (Rhode and Schwarz, Germany). The electrical conductivity σ was calculated from the volume resistivity ρ using the relation[10]

$$\frac{1}{\sigma} = \rho = 3.6\pi CR \qquad (1)$$

where C is the capacitance of the cell in air (pF) and R is the measured resistance (V/I). The cell used for electrical conductivity measurements was that used for dielectric measurements in the frequency range 1 kHz–40 MHz.

Both dielectric and conductivity measurements were carried out at 20, 30 and 40°C using an ultrathermostat. The temperature was constant to within 0.1°C.

RESULTS AND DISCUSSION

Methyl methacrylate–styrene copolymers

Figure 1 shows the frequency (f) dependence of the dielectric permittivity ϵ' and dielectric loss ϵ'' in dioxane at various temperatures for MMA homopolymer (PMMA) and two MMA–St copolymers containing different mole fractions of MMA (x). ϵ' is found to decrease with increasing frequency. Three absorption regions have been detected from the absorption curve relating ϵ'' to $\log f$. To a first approximation, these three absorption regions can be represented by three Fröhlich terms[11] with relaxation time τ_i and distribution parameter P_i. Fitting of the data was carried out by a computer program. As an example of the analysis, the absorption curves (at 20°C) calculated for the MMA–St copolymer with $x = 0.666$ is illustrated in *Figure 2*. From this figure it is seen that, at lower frequencies, the addition of the absorptions does not agree well with the experimental measurements except after the subtraction of losses due to the d.c. conductivity, $(\epsilon'')_{dc}$. These losses are calculated by an equation given elsewhere[12].

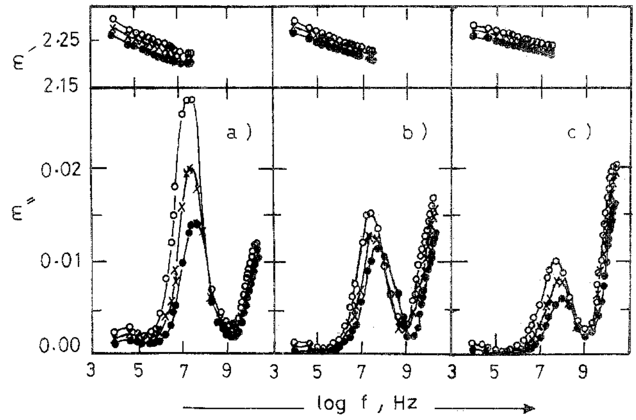

Figure 1 Frequency dependence of dielectric permittivity ϵ' and dielectric loss ϵ'' of (a) PMMA, (b) MMA–St copolymer with $x = 0.66$ and (c) MMA–St copolymer with $x = 0.064$ in dioxane at 20°C (○), 30°C (×) and 40°C (●)

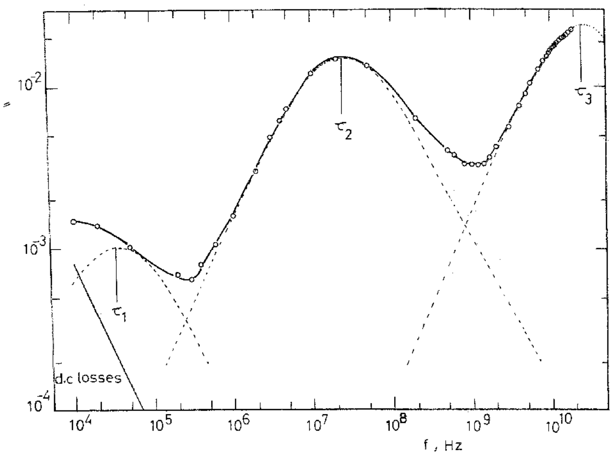

Figure 2 Absorption curve of MMA–St copolymer with $x = 0.666$ in dioxane at 20°C

The dielectric experiments reveal the existence of three distinct relaxations in the frequency range investigated and the results obtained are given in *Table 1*.

For MMA homopolymer and MMA–St copolymers with $x = 0.666$ and 0.064 in this work, the values of the relaxation time τ_{II} obtained in dioxane solution are comparable to those found in the literature in benzene[3,13] and toluene[3] solutions. In these copolymers, it is expected that the styrene units will screen the MMA units for two reasons: (1) the MMA unit lies approximately between two styrene units, as a consequence of the increased tendency for alternation when the product of the monomer ratios, r_{MMA} and r_{st} respectively, is small (about 0.23)[14]; and (2) the MMA unit is smaller than the styrene side group.

From the temperature dependence of τ_{II}, the apparent activation energy ΔH_{AII} has been calculated using the Eyring and Kauzmann equation[15]. τ_{II} was plotted against $1/T$ and ΔH_{AII} was calculated from the slope of the resulting straight line; values are given in *Table 1*. From this table it can be seen that both ΔH_{AII} and τ_{II} decrease with decreasing content of MMA units. A similar finding has been reported previously[9,10].

The observed relationship between the relaxation time τ and the activation energy ΔH_A can be expressed by:

$$\tau = \tau_0 \exp(\Delta H_A/RT) \qquad (2)$$

Table 1 Relaxation data of PMMA and MMA–St copolymers in dioxane at different temperatures. x is the mole fraction of MMA units in the copolymer chain; τ_i and P_i are the relaxation time and the distribution parameter for the three Fröhlich terms; I_2 and τ_0 are the moment of inertia and the relaxation terms of the moving units (side-chain rotation); ΔH_A is the activation energy for the three different mechanisms

		P_i			$\epsilon''_{i\,\max}$/conc.			τ_i (s)			ΔH_A (kJ mol^{-1})				
Material	t (°C)	I	II	III	I	II	III	I ($\times 10^6$)	II ($\times 10^9$)	III ($\times 10^{12}$)	I	II	III	I_2 ($\times 10^{38}$ g cm^2)	τ_0 ($\times 10^{13}$ s)
PMMA	20	1.6	2.0	0.0	0.181	1.807	0.699	4.10	9.36	7.96	1.58	1.48	0.60	0.4	2.03
conc. = 1.66%	30	1.6	2.0	0.0	0.145	1.205	0.681	2.99	1.12	6.63					
	40	1.6	2.0	0.0	0.121	0.781	0.651	1.80	4.08	5.68					
MMA–St	20	2.0	2.0	0.0	0.060	0.904	1.066	4.68	6.36	7.58	1.60	1.44	0.55	0.3	2.20
conc. = 0.68%	30	2.0	2.0	0.0	0.057	0.783	1.012	3.18	4.68	6.37					
$x = 0.666$	40	2.0	2.0	0.0	0.048	0.699	0.892	2.12	3.18	5.09					
MMA–St	20	2.0	2.0	0.0	0.029	0.752	1.860	4.10	3.18	6.37	1.67	1.27	0.53	1.02	3.90
conc. = 1.33%	30	2.0	2.0	0.0	0.023	0.602	1.635	2.89	2.27	5.49					
$x = 0.064$	40	2.0	2.0	0.0	0.020	0.459	1.504	1.72	1.67	4.68					

where τ_0 has the dimension of time and R is the gas constant. Values of τ_0 were calculated and are also given in *Table 1*; these values are found to be comparable to those in toluene solution[3]. For MMA–St copolymer with a high content of MMA units, the value of τ_0 is very close to that for PMMA, while τ_0 for MMA–St copolymer with a low content of MMA units is about two times larger. This result suggests that τ_0 effectively distinguishes the relaxation mechanisms of the dipoles.

It seems reasonable, therefore, to discuss the relaxation process of such copolymers on the basis of the microBrownian motion of the polymer chain immersed in solvents of different viscosities. Several authors[16–18] have attempted to extend Kramer's theory of diffusion[16] to polymers. This theory determines the rate constant for a particle moving over a potential barrier in a viscous medium. According to Iwasa *et al.*[16], the dielectric relaxation process for PMMA in dilute solution can be adequately explained by this theory in the small friction limit. From an analysis of the conformational energy of PMMA, Tanaka and Ishida[19] indicated that the potential energy (U) for side-chain rotation has two minima. Thus if the relation $U(\theta) = 1/2E^*(1 - \cos 2\theta)$, where E^* is the barrier height, is assumed for side-chain rotation, the relaxation time τ becomes[16]

$$\tau = \left(\frac{I}{2E^*}\right)^{1/2} \exp\left(\frac{E^*}{K_B T}\right) \qquad (3)$$

where K_B is Boltzmann's constant and I is the moment of inertia of the moving unit. It is reasonable to discuss the relaxation process of the investigated copolymers in terms of equation (3). E^* in this equation is to be compared with the observed activation energy ΔH_A divided by Avogadro's number[16]. The moments of inertia of the moving units involved in the relaxation process were calculated and are given in *Table 1*. These values are comparable to those found previously[3] in toluene. The values of I estimated for the copolymer having high content of MMA units ($x = 0.666$) and for PMMA are of the order expected for the internal rotation of a single side chain[16]. Accordingly, their dielectric relaxation process is attributed mainly to internal rotation of the side chain, i.e. to the rotation of the flexible dipoles.

On the other hand, the moment of inertia of the copolymer with low MMA content ($x = 0.064$) is considered to be higher than the order expected for internal rotation of a single side chain. These features are different from those of PMMA with the same flexible dipoles[16,20] and very similar to those of poly(p-chlorostyrene) (PpCS) having rigid dipoles[21,22]. These results suggest that the relaxation process of this copolymer is of a diffusion-controlled type where the rate of migration of a moving unit is controlled not only by the barrier height as in case of low friction limit, but also by a friction force exerted by the viscous medium[3].

The above considerations lead to the conclusion that PMMA and the MMA–St copolymer with high MMA content exhibit the same relaxation mechanism which is mainly dependent on the strength of the intermolecular interactions, the dipolar relaxation being very similar to that caused by the rotation of a flexible side chain. On the other hand, the MMA–St copolymer having a low MMA content showed a diffusion-controlled relaxation process which can be interpreted in terms of Kramer's theory in the large friction limit.

In addition to the relaxation associated with the side-chain rotation, two more distinct relaxation processes are detected as shown in *Figure 1*. The low frequency relaxation, which is characterized by the relaxation time τ_I, could be the result of large-scale conformational rearrangement of the main chain (the so-called crankshaft motion) while the relaxation time τ_{III} at the higher frequency range may result from segmental rotation, i.e. the inner mobility of the side groups. Comparing the magnitudes of the loss peaks (ϵ''_m/conc.) given in *Table 1* for such processes, it can be noticed that the contribution of the first process is the lowest and decreases with decreasing MMA content in the copolymer. Meanwhile, the magnitude of the third process is found to be higher and increases with decreasing MMA content. The small value of ϵ''_m/conc. noticed for the relaxation process associated with the backbone motion is comparable with the result given before for PMMA[21].

From the temperature dependences of τ_I and τ_{III}, the apparent activation energies ΔH_{AI} and ΔH_{AIII} were calculated according to the relation given before[15] and the results are given in *Table 1*. From this table it is clear that the change in either ΔH_{AI} and τ_I or ΔH_{AIII} and τ_{III} with decreasing MMA content in the copolymer is not considerable compared with that associated with rotation of the side chain, where ΔH_{AII} and τ_{II} decrease upon decreasing the content of MMA units.

Maleic anhydride–styrene and N*-substituted maleimide–styrene copolymers*

Figure 3 illustrates the dependence of ϵ' and ϵ'' on frequency at different temperatures for representative samples of maleic anhydride–styrene (MA–St) copolymer, *N*-phenylmaleimide homopolymer (PNPMI) and NPMI–St copolymer in dioxane. *Figure 4* presents the same dependence for octadecyl maleimide–styrene (ODMI–St) copolymer in different non-polar solvents: dioxane, benzene and toluene. After subtraction of the loss due to the d.c. conductivity $(\epsilon'')_{dc}$, three distinct relaxation processes were detected in each case. The results of the analyses are given in *Tables 2* and *3*. The relaxation time τ_I for both maleic anhydride and maleimide copolymers could be assigned to the motion of the main chain. In dioxane solution, the τ_I values are not very different from each other, while a significant decrease is noticed with decreasing viscosity of the solvent (dioxane > toluene > benzene). This means that motion of the chain backbone is clearly associated with the solvent viscosity[16]. The higher values of τ_I noticed here than given above for MMA copolymers and homopolymer can be attributed to the stiffer main chain.

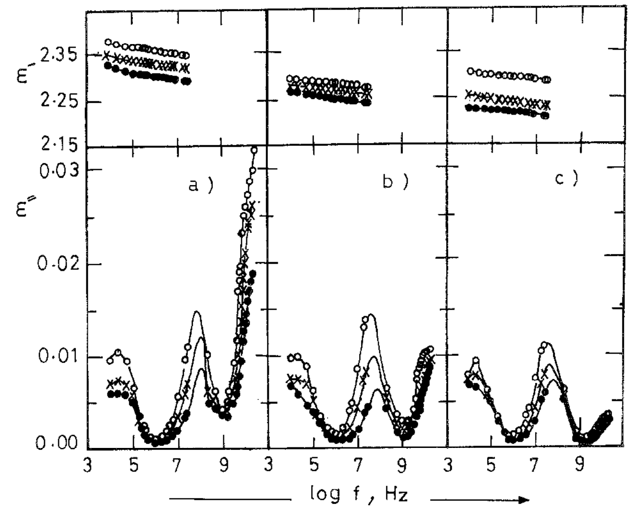

Figure 3 Frequency dependence of dielectric permittivity ϵ' and dielectric loss ϵ'' of (a) MA–St copolymer with $x = 0.500$, (b) PNPMI and (c) NPMI–St copolymer with $x = 0.500$ in dioxane at 20°C (○), 30°C (×) and 40°C (●)

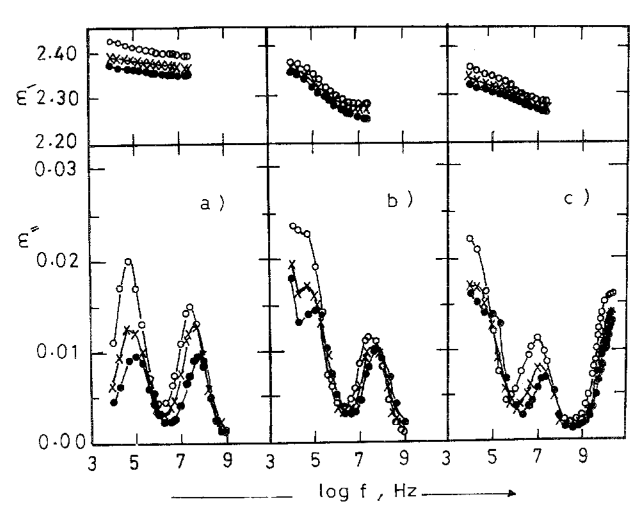

Figure 4 Frequency dependence of dielectric permittivity ϵ' and dielectric loss ϵ'' of ODMI–St copolymer with $x = 0.504$ in (a) toluene, (b) benzene and (c) dioxane at 20°C (○), 30°C (×) and 40°C (●)

From the results of ϵ''_m/conc. given in *Table 2* it is found that, in the case of MA–St and NPMI–St copolymers and NPMI homopolymer, the magnitude of the loss peak associated with motion of the main chain is still smaller than the contribution of the side-group motion. This trend is similar to that found for PMMA and MMA-St copolymer and is supported by other investigators[18,21]. On the other hand, the contribution of the main chain is larger than that of the side group in the case of ODMI–St copolymer. This interesting result can be attributed to the nature of this side group, which consists of a long chain of 18 carbon atoms and the absence of polarity. The side group is thus very flexible compared with the backbone, which is relatively rigid owing to the presence of the five-membered succinimide ring.

From the temperature dependences of τ_I, the apparent activation energies ΔH_{AI} were calculated using the equation given before[15] and the results obtained are collected in *Tables 2* and *3*. It seems that these energies are viscosity-dependent and vary from one substituent to another.

The second relaxation τ_{II} detected in the case of maleic anhydride and maleimide copolymers is due to the presence of the succinic anhydride or succinimide rings, respectively. This five-membered ring may provide enough free volume for orientation. To distinguish quantitatively whether the relaxation mechanism is (1) of a type which depends on the intramolecular interaction between the dipoles and their molecular medium or (2) a diffusion-controlled mechanism which satisfies

Table 2 Relaxation data of PNPMI, and NPMI–St and MA–St copolymers in dioxane at different temperatures. x is the mole fraction of NPMI or MA units in the copolymer chain, respectively; other symbols as given in *Table 1*

		P_i			$\epsilon''_{i\,max}$/conc.			τ_i (s)			ΔH_A (kJ mol^{-1})				
Material	t (°C)	I	II	III	I	II	III	I ($\times 10^6$)	II ($\times 10^9$)	III ($\times 10^{12}$)	I	II	III	I_2 ($\times 10^{38}$ g cm^2)	τ_0 ($\times 10^{13}$ s)
PNPMI	20	2.0	1.6	0.0	0.437	0.857	0.640	5.68	4.55	10.61					
conc. = 1.60%	30	2.0	1.6	0.0	0.366	0.554	0.543	3.95	3.18	8.84	1.51	1.36	0.60	0.5	2.55
	40	2.0	1.6	0.0	0.251	0.354	0.457	2.65	2.27	7.58					
NPMI–St	20	2.0	1.6	0.0	0.606	0.719	0.188	6.92	4.97	10.61					
conc. = 1.60%	30	2.0	1.6	0.0	0.425	0.563	0.168	4.68	3.32	8.84	1.75	1.44	0.79	0.2	1.71
$x = 0.550$	40	2.0	1.6	0.0	0.338	0.450	0.163	2.89	2.41	6.92					
MA–St	20	2.0	2.0	0.0	0.519	0.802	1.861	6.12	2.44	6.37					
conc. = 1.87%	30	2.0	2.0	0.0	0.396	0.642	1.631	4.18	1.76	5.31	1.48	1.34	0.77	0.2	1.39
$x = 0.500$	40	2.0	2.0	0.0	0.294	0.481	1.390	2.84	1.22	4.19					

Table 3 Relaxation data of ODMI–St copolymers in different solvents and at different temperatures. x is the mole fraction of ODMI units in the copolymer chain; other symbols as given in *Table 1*

			P_i			$\epsilon''_{i\,\mathrm{max}}$/conc.			τ_i (s)			ΔH_A (kJ mol^{-1})				
Material	Solvent	t (°C)	I	II	III	I	II	III	I ($\times 10^6$)	II ($\times 10^9$)	III ($\times 10^{12}$)	I	II	III	I_2 ($\times 10^{38}$ g cm^2)	τ_0 ($\times 10^{13}$ s)
ODMI–St		20	2.0	1.6	–	1.036	0.611	–	2.90	5.30	–					
conc. = 1.65%	benzene	30	2.0	1.6	–	0.777	0.570	–	1.77	3.41	–	1.72	1.53	–	0.1	1.36
$x = 0.504$		40	2.0	1.6	–	0.677	0.518	–	1.22	2.45	–					
ODMI–St		20	2.0	1.6	–	1.020	0.765	–	2.79	5.68	–					
conc. = 1.96%	toluene	30	2.0	1.6	–	0.633	0.657	–	2.27	3.98	–	1.75	1.51	–	0.1	1.74
$x = 0.504$		40	2.0	1.6	–	0.474	0.474	–	1.59	2.65	–					
ODMI–St		20	2.0	1.6	0.0	1.121	0.667	0.958	6.37	15.9	12.26					
conc. = 1.93%	dioxane	30	2.0	1.6	0.0	0.909	0.485	0.891	3.98	10.61	7.96	1.94	1.58	1.27	0.4	2.02
$x = 0.504$		40	2.0	1.6	0.0	0.848	0.412	0.848	2.45	7.23	6.37					

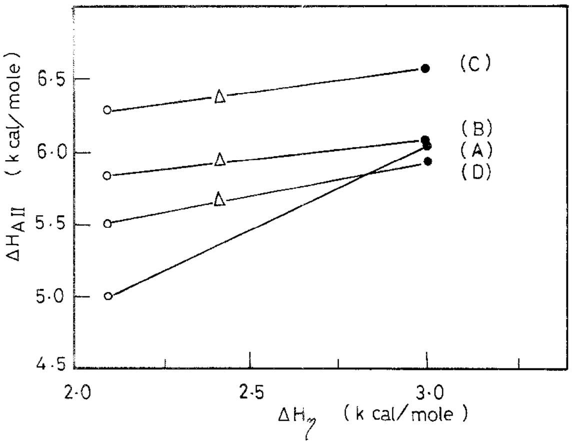

Figure 5 Relation between ΔH_{AII} and ΔH_η for (a) MMA–St copolymer with $x = 0.336^3$, (b) MMA–St copolymer with $x = 0.832^3$, (c) ODMI–St copolymer with $x = 0.504$ and (d) NPMI–MMA copolymer with $x = 0.148$. (O) Toluene, (Δ) benzene and (●) dioxane

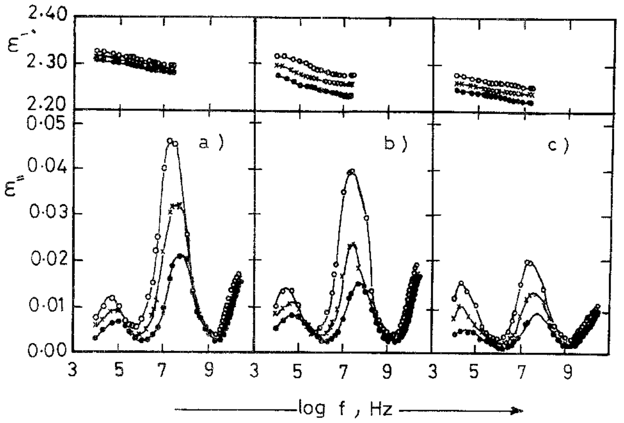

Figure 6 Frequency dependence of dielectric permittivity ϵ' and dielectric loss ϵ'' of MMA–NPMI copolymer with (a) $x = 0.600$, (b) $x = 0.420$ and (c) $x = 0.148$ in dioxane at 20°C (O), 30°C (x) and 40°C (●)

Stoke's law, the values of τ_0 were calculated using equation (2) and are given in *Tables 2* and *3*. Interestingly, it is found that these values are of the order of 2×10^{-13} s—the same as those for PMMA and the MMA–St copolymer with high MMA content—and satisfy mechanism (1) which is mainly dependent on the strength of the intramolecular interactions.

It therefore seems reasonable to discuss the relaxation processes of such orientations on the basis of equation (3) in which the frictional force has no role. The moments of inertia I of the moving units are listed in *Tables 2* and *3*. From these tables, it is seen that the values of I estimated do not exceed the value expected for the internal rotation of a single flexible side chain ($I = 1 \times 10^{-38}$ g cm^2) (ref. 23). So, their dielectric relaxation is attributed mainly to the internal rotation of the side group itself.

The values of ΔH_{AII} for ODMI–St copolymer, given in *Table 3*, are plotted as a function of the activation energy for the solvent viscosity ΔH_η (dioxane, benzene and toluene) in *Figure 5*. Each value of ΔH_η was determined from the plot of $\log \eta_0$ *versus* $1/T$, where η_0 is the solvent viscosity. It is of great interest to note that ΔH_{AII} changes very little with decreasing ΔH_η. This trend is similar to that found before[3] in the case of MMA–St copolymer having a high content of MMA units and contrary to that found for MMA–St copolymer with a low content of MMA units, in which ΔH_{AII} was dependent on solvent viscosity[3] (see *Figure 5*). This means that the dielectric relaxation phenomenon of these copolymers is not associated with the solvent viscosity but can be interpreted in terms of Kramer's theory in the small friction limit[16].

From the previous data it can be concluded that the dipolar relaxation process of MA–St, NPMI–St and ODMI–St copolymers in dilute solutions resembles that of NPMI homopolymer[24], which is mainly controlled by the intramolecular interactions between the dipole and its molecular environment[16].

Inversion of the substituted succinimide ring in the maleimide polymer and copolymers could be the mode responsible for the process associated with the relaxation time τ_{III}. This implies non-planarity of this system, with the nitrogen atom lying above or below the plane of the carbon framework. Such a hypothesis is supported by some structural evidence such as the non-planarity of *N*-(*p*-bromophenyl)succinimide[25]. The high value of τ_{III} detected in the ODMI–St copolymer could be due to the long side chain of the ODMI moiety. The structural similarity of the MA–St copolymer to the homomaleimide and its copolymers is evidence of the presence of the same relaxation mechanism which implies a non-planar ring system.

N-*phenylmaleimide–methyl methacrylate copolymer*

To study the relaxational processes of a copolymer containing two flexible dipoles, three samples of NPMI–MMA copolymer containing different contents of MMA

Table 4 Relaxation data of PMMA and MMA–NPMI copolymers in dioxane at different temperatures. x is the mole fraction of MMA units in the copolymer chain; other symbols as given in *Table 1*

Material	t (°C)	P_i I	P_i II	P_i III	$\epsilon''_{i\,\max}$/conc. I	$\epsilon''_{i\,\max}$/conc. II	$\epsilon''_{i\,\max}$/conc. III	τ_i (s) I (×10^6)	τ_i (s) II (×10^9)	τ_i (s) III (×10^{12})	ΔH_A (kJ mol^{-1}) I	ΔH_A (kJ mol^{-1}) II	ΔH_A (kJ mol^{-1}) III	I_2 (×10^{38} g cm^2)	τ_0 (×10^{13} s)
PMMA	20	1.6	2.0	0.0	0.181	1.807	0.699	4.10	9.36	7.96					
conc. = 1.66%	30	1.6	2.0	0.0	0.145	1.207	0.681	2.89	6.12	6.63	1.58	1.48	0.60	0.4	2.03
	40	1.6	2.0	0.0	0.121	0.783	0.651	1.80	4.47	5.68					
MMA–NPMI	20	2.0	2.0	0.0	2.010	7.705	3.350	4.19	6.92	5.90					
conc. = 0.60%	30	2.0	2.0	0.0	1.625	5.527	3.137	2.89	4.55	4.97	1.60	1.41	0.65	0.3	1.89
$x = 0.600$	40	2.0	2.0	0.0	1.172	3.655	2.965	1.87	3.36	4.08					
MMA–NPMI	20	2.0	2.0	0.0	2.000	5.734	2.541	4.68	6.12	5.90					
conc. = 0.68%	30	2.0	2.0	0.0	1.735	3.676	2.774	3.06	4.42	4.97	1.58	1.41	0.65	0.4	2.38
$x = 0.420$	40	2.0	2.0	0.0	1.213	2.206	2.647	2.12	3.00	4.08					
MMA–NPMI	20	2.0	2.0	0.0	2.444	3.419	1.961	4.27	5.13	5.96					
conc. = 0.59%	30	2.0	2.0	0.0	1.333	2.359	1.932	3.18	3.62	4.97	1.58	1.39	–	0.4	2.19
$x = 0.148$	40	2.0	2.0	0.0	0.872	1.538	1.367	2.21	2.53	4.81					

Table 5 Relaxation data of MMA–NPMI copolymers in different solvents and at different temperatures. x is the mole fraction of MMA units in the copolymer chain; other symbols as given in *Table 1*

Material	Solvent	t (°C)	P_i I	P_i II	P_i III	$\epsilon''_{i\,\max}$/conc. I	$\epsilon''_{i\,\max}$/conc. II	$\epsilon''_{i\,\max}$/conc. III	τ_i (s) I (×10^6)	τ_i (s) II (×10^9)	τ_i (s) III (×10^{12})	ΔH_A (kJ mol^{-1}) I	ΔH_A (kJ mol^{-1}) II	ΔH_A (kJ mol^{-1}) III	I_2 (×10^{38} g cm^2)	τ_0 (×10^{13} s)
MMA–NPMI		20	2.0	2.0	–	3.305	4.762	–	3.18	2.65	–					
conc. = 0.39%	benzene	30	2.0	2.0	–	2.991	3.641	–	1.99	1.81	–	1.58	1.36	–	0.2	1.48
$x = 0.148$		40	2.0	2.0	–	2.520	3.081	–	1.45	1.33	–					
MMA–NPMI		20	2.0	2.0	–	2.262	3.769	–	3.46	2.89	–					
conc. = 0.39%	toluene	30	2.0	2.0	–	1.708	3.015	–	2.21	2.04	–	1.56	1.32	–	0.3	2.19
$x = 0.148$		40	2.0	2.0	–	1.558	2.512	–	1.59	1.47	–					
MMA–NPMI		20	2.0	2.0	0.0	2.444	3.419	1.961	4.27	5.13	5.96					
conc. = 0.59%	dioxane	30	2.0	2.0	0.0	1.333	2.359	1.932	3.18	3.62	4.97	1.58	1.39	0.65	0.4	2.19
$x = 0.148$		40	2.0	2.0	0.0	0.872	1.538	1.367	2.21	2.53	4.81					

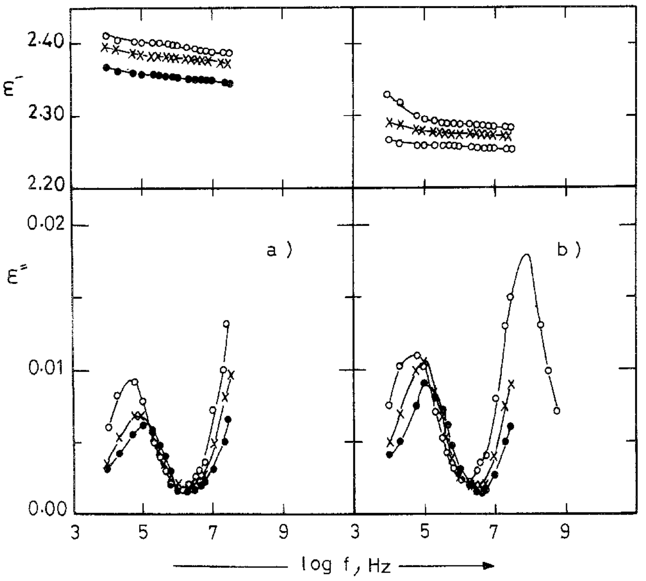

Figure 7 Frequency dependence of dielectric permittivity ϵ' and dielectric loss ϵ'' of MMA–NPMI copolymer with $x = 0.148$ in (a) toluene and (b) benzene at 20°C (○), 30°C (×) and 40°C (●)

units were prepared. *Figure 6* illustrates the dependence of ϵ' and ϵ'' on frequency at different temperatures for solutions of three copolymers containing 0.6, 0.42 and 0.148 mole fraction of MMA units, in dioxane. ϵ' is found to decrease with increasing frequency. After subtracting the losses due to the d.c. conductivity, the variation of ϵ'' with f is represented by three absorption regions. The values of τ_{II} given in *Table 4* are attributed mainly to the side-chain rotation responsible for the flexibility of these copolymers. So, it seems reasonable to discuss the relaxation processes of such orientations on the basis of equation (3) in which the frictional force has no role. The moment of inertia I was calculated for the three copolymers and is given in *Table 4*. The value of I is found to be of the order expected for the internal rotation of a single side chain, $I = 1 \times 10^{-38}$ g cm^2.

From the variation of τ_{II} with temperature, the apparent activation energy ΔH_{AII} was calculated and used to determine τ_0. Values of τ_0 are found to be of the order of 2×10^{-13} s.

The effect of solvent viscosity on the side-group motion has also been studied. The sample containing 0.148 mole fraction of MMA units was chosen and was dissolved in two additional solvents, benzene and toluene. The measured values of ϵ' and ϵ'' in these solvents are plotted against frequency in *Figure 7*. The activation energies ΔH_{AII} given in *Table 5* for this sample in the three different solvents are plotted as a function of the activation energy for the solvent viscosity ΔH_η in *Figure 5*. ΔH_{AII} decreases slightly with decreasing ΔH_η. This feature is very similar to that of ODMI–St copolymer and the MMA–St copolymer with high content of MMA units. From the data of ϵ''_m/conc. given in *Table 4* for such copolymers it may be seen that the contribution of the loss peak associated with the side-chain rotation decreases with decreasing MMA content in the sample. This trend is similar to that found in the case of MMA–St copolymer.

In addition to the relaxation associated with the side-chain rotation, two more distinct relaxation processes are detected. The low frequency relaxation τ_{I} can be attributed to the main-chain orientation while the relaxation time τ_{III} at the higher frequency range may result from inner mobility of the side groups in MMA, in NPMI, or both. τ_{I} is found to increase with increasing content of NPMI units in the copolymer, while no pronounced change in τ_{III} is noticed. On the other hand, it is found that τ_{I} decreases significantly upon decreasing the viscosity of the solvent.

From the values of ϵ''_{m}/conc. given in *Table 4* for such processes, it is found that the magnitude of the loss peak associated with main-chain rotation is small, but higher than that found in the case of MMA–St copolymers. This can be attributed to the presence of flexible dipoles in MMA–NPMI copolymer instead of the non-polar one in MMA–St.

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