Dielectric relaxation of poly(chlorostyrenes) and their copolymers in the primary transition region

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Dielectric relaxation measurements were carried out on a series of bulk poly(chlorostyrene) homopolymers and random copolymers over the frequency range from 50 to 100 kHz and at temperatures in the neighbourhood of the glass transitions of the polymers thus encompassing the α relaxation. Homopolymers examined were polystyrene (PS), poly(2-chlorostyrene) (P2CS), poly(3-chlorostyrene) (P3CS), and poly(4-chlorostyrene) (P4CS). Copolymers were poly(styrene-co-2-chlorostyrene) (PS2CS), poly(styrene-co-4-chlorostyrene) (PS4CS), and poly(2-chlorostyrene-co-4-chlorostyrene) (P2CS4CS). The dielectric data were analysed to yield dipole moments and Kirkwood–Fröhlich correlation parameters. The shapes of the dielectric loss curves were also taken into account. Glass transition temperatures were determined by differential scanning calorimetry (d.s.c.). It was concluded that the phenyl ring rotates freely in the α relaxation regions of PS, P4CS, and P3CS, but not in P2CS. The dipole moments of the copolymers are correlated with dyad distributions calculated from reactivity ratios.

INTRODUCTION

Dielectric relaxation measurements have been carried out on polystyrene, (PS), and many of its derivatives both in bulk[1–8] and solution[9–12] over wide temperature and frequency ranges. These investigations have established the existence of a number of distinct relaxation regions. In the bulk state there appear to be 4 main dispersions which are usually labelled α, β, γ, δ, in order of decreasing temperature, with the α process associated with the primary transition zone (glass transition) of the polymer. Despite the extensive dielectric studies as well as dynamic mechanical relaxation[6,13–17], and nuclear magnetic resonance[18–20] experiments there is still a lack of agreement about the detailed molecular mechanisms of the 4 relaxation processes referred to above.

In this paper we first present the results of an examination of the α relaxation region of bulk PS, poly(2-chlorostyrene), (P2CS), poly(3-chlorostyrene) (P3CS), and poly(4-chlorostyrene) (P4 CS). The α relaxations of P2CS and P4CS are similar while that of P3CS is much broader. It is shown that this can be accounted for on the basis of the rotation of the phenyl ring in P3CS which contributes to the α relaxation in this polymer. Although the phenyl ring is also presumably free to rotate in P4CS, this motion is not dielectrically active. It is postulated that steric hindrance prevents phenyl group rotation in P2CS.

Random copolymers of PS have also been the subject of extensive dielectric investigations[4,21–25]. The α relaxations of poly(styrene-co-2-chlorostyrene) (PS2CS), poly(styrene-co-4-chlorostyrene) (PS4CS), and poly(2-chlorostyrene-co-4-chlorostyrene) (P2CS4CS), are examined here. The shapes of the α relaxations of all the copolymers are similar to each other and to those of PS, P2CS, and P4CS. For all the copolymers the dependences of the dipole moments on composition are greater than predicted by simple additivity. These effects can be accounted for on the basis of intrachain angular correlations among dipoles which are dependent on the chemical sequence distribution of the copolymers.

EXPERIMENTAL

Materials

Atactic PS was obtained from the Monsanto Company, courtesy of T. Boyd. Chlorostyrene homopolymers and copolymers were prepared by free radical solution techniques, using the corresponding monomers purchased from the Aldrich Chemical Company. The distilled monomers were polymerized at 60°C for 10 h with 0.5 mol % azobisisobutyronitrile as initiator, and 40 mol % toluene as solvent and chain transfer agent. Conversion was 60% or less in all cases. Copolymer compositions were determined by elemental analysis for chlorine in the case of PS2CS and PS4CS and by quantitative analysis of solution infra-red absorbances for the P2CS4CS. Gel permeation chromatography (g.p.c.) indicated the production of high molecular weight materials with a polydispersity index of approximately 2.2. Characterization data are collected in *Table 1*. All polymers were purified by precipitation from dilute toluene solution into a large excess of stirred methanol; resultant powders were thoroughly dried *in vacuo* at 80°C

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Table 1 G.p.c. characterization data for the poly(chlorostyrenes) [molecular weights x 10^{-5}]

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$[\eta]^a$
PS	1.2	2.8	4.9	2.4	
P2CS	0.58	1.2	2.0	2.1	0.33
P3CS	0.63	1.3	2.0	2.0	0.38
P3CS	0.64	1.3	2.1	2.0	0.30
PS2CS[b]	0.46	0.94	1.5	2.0	0.30
PS4CS[b]	0.49	1.0	1.6	2.1	0.36
P2CS4CS[b]	0.75	1.6	2.6	2.1	0.41

[a] In toluene at 30°C [b] Representative data at approximately 50–50 copolymer composition. Complete data for all the copolymers are contained in Alexandrovich, P. S. *PhD Thesis* University of Massachusetts (1978) pp 49 and 50

Table 2 Homopolymer glass transition temperatures and dielectric parameters

Parameter	PS	P4CS	P2CS	P3CS
$^*M_n \times 10^{-5}$	1.2	0.64	0.58	0.63
T_g (°C)	104	131	131	93
ρ (g/cm^3)	1.048	1.226	1.245	1.243
ϵ_R	2.73	4.59	3.92	4.73
ϵ_u	2.69	2.95	2.99	2.72
μ_e^2 (D^2)	0.041	1.39	0.80	1.87
μ_0 (D)	0.36	2.21	0.56	1.91
g	0.32	0.28	0.33	0.51
Loss half-width (decades)	2.37	1.93	2.21	3.68
$\Delta H/\Delta L$	1.44	1.41	1.51	1.61

for 4 days. Samples for dielectric and calorimetric experiments were compression-moulded into films of the appropriate sizes.

Dielectric measurements

The dielectric constant ϵ' and loss factor ϵ'' for all materials were determined isothermally at 16 discrete frequencies in the range 50 Hz to 100 MHz. A General Radio model 1620A Capacitance Measuring Assembly was used in the dissipation factor mode. Samples of thickness approximately 0.04 cm were held in a three terminal Balsbaugh model LD-3 cell, with an active electrode diameter of 5.3 cm. The temperature of the sample assembly was maintained to within ±0.2°C by use of a specially constructed oven employing a Versatherm Proportional Controller. Approximately 1 h was required for the temperature to reach equilibrium between measurements.

Calorimetric measurements

Differential scanning calorimetry experiments were conducted with a Perkin–Elmer model DSC-2 instrument. Sample sizes of approximately 20 mg were used; a heating rate of 20°C min^{-1} was employed. D.s.c. glass transition temperature (T_g) values were determined as the temperature at which the heat capacity achieved one half of the total step change associated with the glass transition.

RESULTS AND DISCUSSION

Glass transition temperatures

Glass transition temperatures (T_gs) for the homopolymers are listed in *Table 2*. Both P2CS and P4CS have identical T_gs of 131°C but P3CS shows an anomalously low value of 93°C, lower even than that of the 104° of PS itself.

Dipole moments of homopolymers

Figure 1 is the Argand diagram for P2CS. It has been shown by Work[58] that the Argand diagrams constructed for P4CS over a range of temperatures do not give good superposition. Such effects were not observed in this work possibly due to our use of a more restricted temperature range. The limiting low frequency (ϵ_R) and high frequency (ϵ_u) dielectric constants were obtained from plots such as that shown in *Figure 1*. Effective dipole moments per repeat unit (μ_e) were then obtained from the Onsager equation[26].

$$\mu_e^2 = \frac{9kT}{4\pi N}\,\frac{(2\epsilon_R + \epsilon_u)(\epsilon_R - \epsilon_u)}{\epsilon_R(\epsilon_u + 2)^2} \qquad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, and N is the number of dipoles per unit volume. The calculations using equation (1) were carried out at 423K. However, N was calculated using available room temperature densities listed in *Table 2*. Densities of P2CS and P4CS were determined with a sodium nitrate/water density gradient column, as was that of PS[27]. The value for P3CS is from McCammon *et al.*[3]. Values of ϵ_R, ϵ_u and μ_e^2 are all collected in *Table 2*. Absolute values of the dielectric constant are probably in error by as much as 10% due to nonuniformity in sample thickness and inaccuracies in thickness measurements. However, the dielectric constants reported in *Table 2* are in good agreement with literature values. For example our value for ϵ_u for P4CS of 2.95 may be compared with the 2.7 reported by Curtis[1] and the 3.05 reported by Wetton *et al.*[28]. The uncertainty in μ_e is somewhat less than in the dielectric constant since the difference $\epsilon_R - \epsilon_u$ is the most important factor in equation (1).

The Kirkwood–Fröhlich correlation parameters, g[24], were calculated from:

$$g = \mu_e^2/\mu_0^2 \qquad (2)$$

where μ_0^2 is the square of the dipole moment of an 'isolated' monomer unit. Gas phase dipole moments of chlorinated

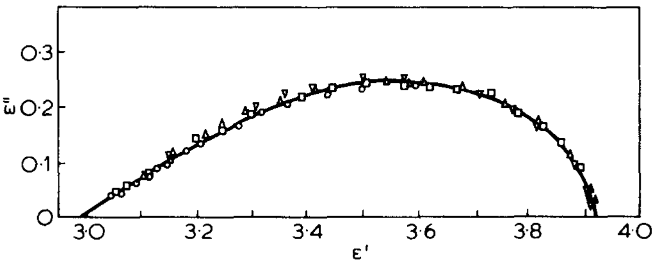

Figure 1 Argand diagram (Cole–Cole plot) for P2CS in the α relaxation region. ○, 151.4°C; □, 155.3°C; △, 160.2°C; ▽, 165.0°C

Table 3 Reactivity ratios and g_{12} values for the copolymers

Value	PS4CS	PS2CS	P2CS4CS
Number of samples	9	6	4
Monomer 1	4CS	2CS	4CS
Monomer 2	S	S	2CS
r_1	1.00	1.25	0.55
r_2	0.70	0.59	0.71
g_{12}	0.52	0.69	0.62
Standard deviation in g_{12}	0.05	0.07	0.03

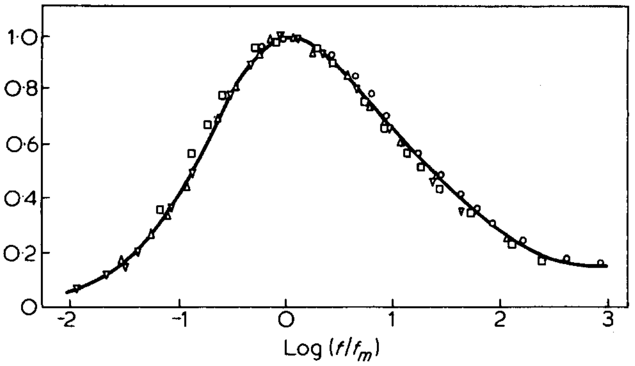

Figure 2 Frequency dependence of the normalized dielectric loss for P2CS in the α relaxation region. Key as in *Figure 1*

toluene were taken to be the appropriate values for μ_0. These values are also collected in *Table 2*. Those for toluene, 2-chlorotoluene and 4-chlorotoluene are literature values[30] while that for 3-chlorotoluene was calculated using group moments according to the method outlined by Smyth[31]. Similar group contribution method calculations for 2- and 4-chlorotoluene yield values essentially identical to the experimental values for these compounds cited in *Table 2*.

The value of $g = 0.3$ (± 0.03) for P4CS may be compared to the rotational isomeric state theory calculations of Saiz, Mark and Flory[32], and Mark[33]. These authors calculated the dipole moment ratio for isolated chains of P4CS:

$$D_\infty = \lim_{x \to \infty} \mu_x^2/\mu_0^2 \tag{3}$$

where D_∞ is identical to g in our notation. Their results yield a value of g of 0.55 for the atactic configuration. The disparity may be accounted for partly by their use of $\mu_0 =$ 1.9 D instead of our value of 2.21 D and by the fact that their calculations were carried out at room temperature. D_∞ decreases with increasing temperature and $\epsilon_R - \epsilon_u$ also decreases with temperature for bulk polymers[29]. It would thus appear that the g value for bulk P4CS reflects the conformational properties of the individual polymer chains.

An examination of *Table 2* reveals that g is the same for PS, P4CS and P2CS but is significantly higher than P3CS. This indicates less correlation between dipolar motion in P3CS than in the other polymers. As already discussed, the g values for PS and P4CS are accounted for on the basis of the conformational properties of the main chain as reflected by the isomeric state theory. It is likely that the g values for P2CS may be similarly accounted for although calculations are lacking. The higher value for P3CS indicates that either the conformational energies of the main chain of P3CS are different from those of the other polymers or that the dipole is not rigidly coupled to the main chain. This could be the case if the phenyl ring rotates freely in the α relaxation region of P3CS. Since the g value for P3CS is calculated from the polarization change accompanying the merged α and β relaxations, it would be higher for P3CS than for P4CS since rotation of the phenyl ring in P4CS produces no component of the dipole parallel to the main chain. However, the similarity between the g values of P4CS and P2CS can only be explained on the basis of the absence of phenyl group rotation in the α relaxation region in P2CS, presumably due to the steric hindrance introduced by the presence of the chloride group in the 2 position of the phenyl ring. If, however, rotation of the phenyl ring in the α relaxation region does not occur for any of these polymers, the observed differences in g can only arise from conformational energy differences among the various derivatives.

Shapes of dispersion curves for the homopolymers

Figure 2 shows the normalized frequency dependence of the dielectric loss of P2CS. The normalization was carried out by plotting the ratio ϵ''/ϵ''_m *versus* $\log(f/f_m)$ where ϵ''_m and f_m are the maximum loss magnitude and frequency of maximum loss, respectively, at a given temperature. *Figure 2* shows that temperature–frequency superposition is applicable over the temperature range investigated. The loss half-widths listed in *Table 2* are the distances in decades of frequency between the right and left hand branches of curves such as that in *Figure 2*, at half-height. PS, P2CS and P4CS all display similar dispersion curve shapes and widths in the α relaxation regions. The small differences in half-width in these polymers are probably not significant. PS in particular, because of its low dipole moment is difficult to determine accurately and various background effects may contribute appreciably to the observed loss width. P3CS on the other hand shows a loss half width more than a decade greater in frequency than the other polymers. The normalized frequency dependence of the dielectric loss in P3CS is shown in *Figure 3*.

In addition to the loss half-width it is possible to characterize the shapes of the dispersion curves by their asymmetry in frequency. The quantity $\Delta H/\Delta L$ which represents the ratio of the distance of the high frequency branch at half-height from $\log(f/f_m) = 0$ to that of the distance of the low frequency branch at half-height from $\log(f/f_m) = 0$, was used for this purpose and the results are collected in *Table 2*. For PS, P2CS, and P4CS, $\Delta H/\Delta L$ ranged from 1.4 to 1.5 which is consistent with the findings of Williams *et al.*[34] for a large number of amorphous polymers. P3CS on the other hand has a $\Delta H/\Delta L$ value of 1.61 showing considerably more asymmetry than the other polymers.

Dielectric loss curves are frequently fitted to the empirical Fuoss–Kirkwood expression[35] which involves one parameter, m:

$$\cosh^{-1}[H(0)/H(x)] = mx \tag{4}$$

where

$$x = \ln(f/f_m)$$

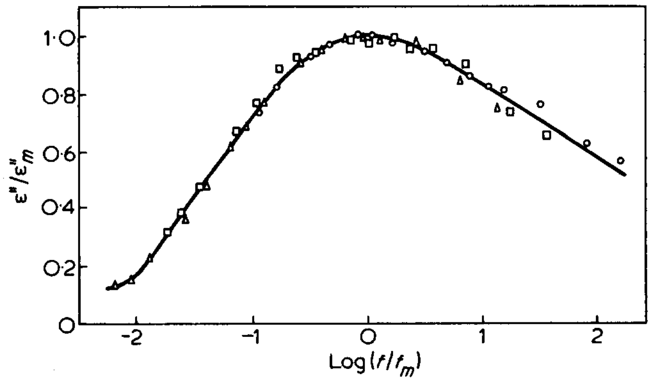

Figure 3 Frequency dependence of the normalized dielectric loss for P3CS in the α relaxation region. ○, 123.3°C; □, 129.7°C; △, 135.0°C

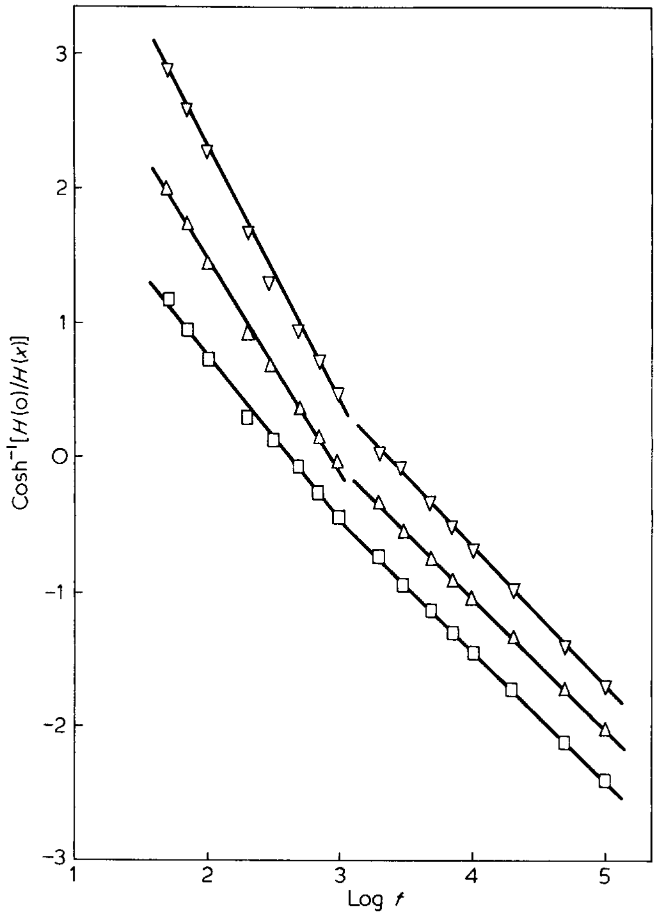

Figure 4 Fuoss–Kirkwood plots for the α relaxation of P2CS at various temperatures. □, 155.3°C; △, 160.2°C; ▽, 165.0°C

and

$$H(x)/H(0) = \epsilon''(2 + 1/\epsilon^2)/(\epsilon''_m(2 + 1/\epsilon_m^2))$$

Such a single parameter fit predicts Debye-type relaxation for $m = 1$ and symmetric loss curves no matter what the value of m. *Figure 4* is a plot of equation (4) for P2CS, and it can be seen that a straight line relationship is not obtained because of the asymmetry of the experimental data, indicating that equation (4) cannot be used to fit the data. In addition it is evident that the slopes increase with increasing temperature, reflecting a narrowing of the relaxation curve. The data in *Figure 4* fit two straight lines rather well, leading to two values of m. These values of m are plotted as a function of $T - T_g$ for PS, P2CS and P4CS in *Figure 5*. The three polymers all exhibit the same behaviour, reflecting the similarity of the shapes of their dispersion curves. Although P3CS exhibits qualitatively similar behaviour to that shown in *Figure 4* both the absolute values of its Fuoss–Kirkwood parameter and its temperature dependence are much lower than for PS, P2CS and P4CS. It is probable that the data in *Figure 4* are not of sufficient precision to warrant the use of two Fuoss–Kirkwood expressions but the conclusion that the shapes of the relaxation curves for PS, P2CS and P4CS are similar to each other and different from that of P3CS is still valid.

β *Relaxation and phenyl group rotation*

Generally, at least two distinct relaxation processes are observed in amorphous polymers[36–39] usually labelled α and β in order of decreasing temperature at a given frequency of observation. The α relaxation arises from microBrownian segmental motions accompanying the glass transition while the β relaxation is frequently attributed to local motions of the main chain or of side groups. Since the two processes in general possess quite different temperature and pressure differences, there is a region of high temperature and low pressure at which they merge and become indistinguishable. Such behaviour is not confined to polymers but also occurs in low molecular weight glass-forming materials[40,41] and thus such unique polymer properties as chain connectivity and specific side chain motions are not necessary to account for the presence of the α and β relaxations.

The presence of multiple relaxations in PS and its derivatives has been alluded to in the Introduction. Most studies have postulated some form of phenyl side group rotation involvement in all the sub-T_g relaxations. For example, the cryogenic δ relaxation (located at 55K at 10 kHz in PS) has been attributed by some authors to oscillatory motion of the phenyl ring coupled to the main chain[3,5,8,15,16]. Others believe the δ relaxation to arise from defects associated with the steric configuration of the polymer[6]. The γ relaxation (located at 180K at 10 kHz in PS) has also been attributed to phenyl group oscillation[6,42]. Reich and Eisenberg[43], on the basis of potential energy calculations, suggest that the γ relaxation may be due to actual rotation of the ring. Abe, Flory, and Tonelli[44], on the other hand, using the rotational isomeric state theory to perform conformational energy calculations, conclude that the phenyl ring is confined to a perpendicular arrangement *vis-à-vis* the main chain when the latter is in any of its preferred conformations. Tonelli[45] extended this work and asserts that phenyl group rotation can occur only when the backbone is in an extremely high energy conformation, present at less than 1% concentration at equilibrium. Tonelli postulates an activation energy in excess of 100 kcal mol^{-1} for phenyl ring rotation while Eisenberg and Reich suggest a figure of 8 kcal mol^{-1}. Tonelli also calculates an activation energy of 9 kcal mol^{-1} for a partial rotation of ±30°.

The β relaxation in P4CS has been assigned to phenyl group rotation by Fielding–Russell and Wetton[2]. This is based on the fact that no dielectric β relaxation is observable in P4CS (which has no component of the dipole per-

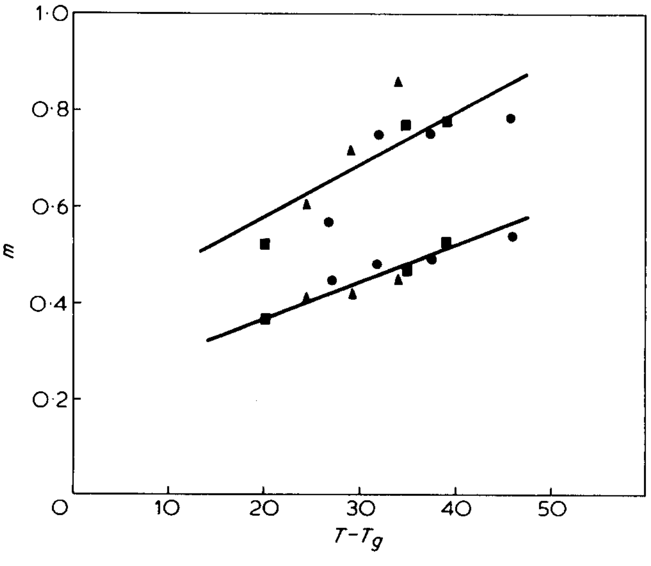

Figure 5 Dependence of the Fuoss–Kirkwood m parameter or $T-T_g$ for PS (■), P2CS (▲) and P4CS (●)

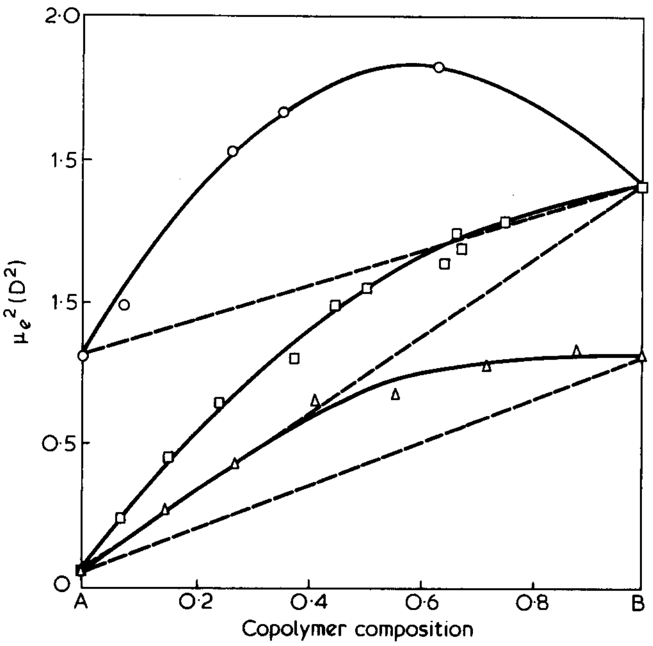

Figure 6 Composition dependence of the copolymer dipole moments

	A	B
○	2CS	4CS
□	S	4CS
△	S	2CS

pendicular to the axis of the ring) while a mechanical β relaxation does exist. Curtis[1] and Wetton *et al.*[2,7] have also studied the dielectric relaxation of P3CS and demonstrate the presence of a β relaxation in this polymer.

Yano and Wada[6] have observed both a mechanical and dielectric β relaxation in PS itself and they postulate local mode motions of the main chain to be the mechanism of the β relaxation.

N.m.r. data are in conflict concerning the rotation of the phenyl ring in PS and its derivatives. One school of thought concludes no rotation occurs[18,20] while the other contends that n.m.r. data are consistent with rotation of the ring at the same rate as the rearrangement of the chain backbone[46].

The postulate of phenyl ring rotation as the mechanism of the β relaxation in PS and its derivatives serves to explain all the experimental observations of this study. The broad relaxation in P3CS is interpreted as arising from a merged α and β process. Steric hindrance precludes phenyl group rotation in P2CS and the β process is not dielectrically active in PS and P4CS thus accounting for the similarities of the shapes of the α relaxation curves for these three polymers. The postulate of phenyl group rotation in P3CS contributing to a merged α and β relaxation also accounts for the higher g factor for this polymer than that for PS, P2CS and P4CS. Rotation of the phenyl ring in P3CS eliminates many of the angular correlations between dipoles no matter what the local main chain conformation may be. This is not true for PS and P4CS since the dipole is rigidly attached perpendicular to the chain in these polymers. Thus PS, P2CS, P3CS, and P4CS may all be assumed to have similar conformational energies and offer similar barriers to rotation about backbone bonds.

The low T_g of P3CS may also be associated with phenyl group rotation. This phenomenon may be associated with greater free volume in this polymer compared with the others because of the motion of the substituent in the 3 position or it may result from a modification to intermolecular interactions arising from the rotation of the 3-substituted phenyl ring. In view of the calculations of Tonelli[45] partial rotation of the phenyl ring cannot be ruled out as the mechanism of the β process.

Dipole moments of copolymers

Copolymer dipole moments and g factors were calculated by the method outlined below. To obtain N in equation (1) the densities were first derived using the assumption of volume additivity.

$$1/\rho = w_1/\rho_1 + w_2/\rho_2 \tag{5}$$

where w values are the weight fractions of the homopolymers and ρ are the corresponding homopolymer densities, the values of which are collected in *Table 2*.

N then followed from equation (6):

$$N = A\rho/(x_1 m_1 + x_2 m_2) \tag{6}$$

where A is Avogadro's number, x are mole fractions and m are comonomer repeat unit molecular weights. μ_e^2 was then calculated from equation (1). g was calculated from equation (2) as previously but now μ_0^2 was obtained from:

$$\mu_0^2 = x_1(\mu_{1,0})^2 + x_2(\mu_{2,0})^2 \tag{7}$$

where μ^0 are the appropriate isolated unit dipoles taken from *Table 2*.

Figure 6 presents the composition dependence of μ_e^2 for the 3 copolymers investigated. In all cases this composition dependence of μ_e is greater than predicted by simple arithmetic averaging. The composition dependence of g is plotted in *Figure 7* for PS4CS, in *Figure 8* for PS2CS, and in *Figure 9* for P2CS4CS. In *Figure 7* are also included the results of Mikhailov *et al.*[24] for PS4CS copolymers in solution. These data increase at lower 4-chlorostyrene content which may be due in part to experimental difficulties due to the decreased dipole moments of these copolymers. The values are also larger than those for the bulk case which

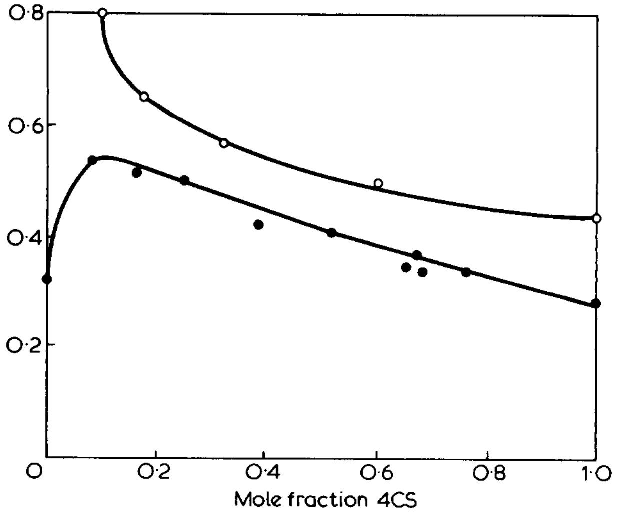

Figure 7 Composition dependence of the correlation parameter, g, for PS4CS both in solution and in bulk. ○, Mikhailov (solutions); ●, this work

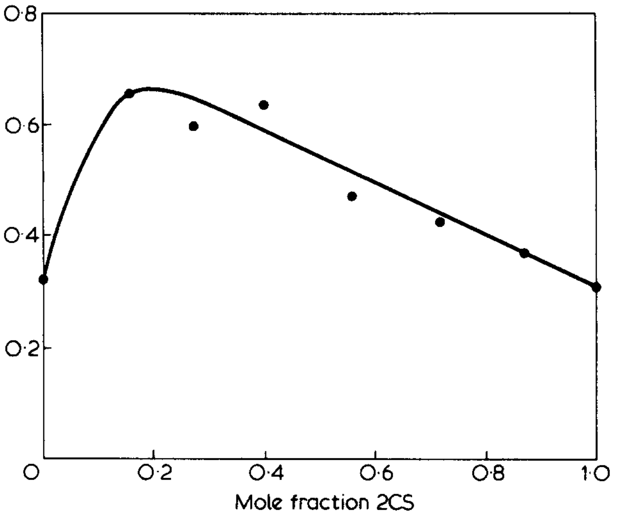

Figure 8 Composition dependence of the correlation parameter, *g*, for PS2CS

is accounted for by the use of lower μ_0 values in Mikhailov's work than those employed here. It may be concluded from *Figure 7* that strong evidence exists for the intrachain origin of the *g* factor in the bulk.

The behaviour outlined in *Figures 6–9* has received considerable experimental and theoretical attention, mostly for the solution cases[21–25,47–54]. The PS4CS copolymers have been studied most[21–25]. The increase in *g* is attributed to a loss of cancelling correlations among dipoles due to the dilution of the 4-chlorostyrene units by the relatively non-polar styrene units. These effects depend on chain conformation and calculations have been carried out using the rotational isomeric states model[47] which satisfactorily account for the observed composition dependence of *g*.

The composition dependence of *g* in this study of styrene copolymers can be largely accounted for on the basis of a very simple model in which the dipolar cancelling is assumed to arise from the geometry of dyads alone. The argument proceeds as follows.

Dyad fractions, F_{11}, F_{22}, and F_{12} can be calculated for random copolymers from copolymer compositions and reactivity ratios by well-known methods[55]. In this case reactivity ratios were determined from a least squares analysis of the Fineman–Ross[56] form of the copolymerization equation. Although in some cases conversion was as high as 60%, the copolymerizations were 'ideal' enough that compositional drift is unlikely to influence the estimates of the reactivity ratios. The reactivity ratios obtained are listed in *Table 3* and are in good agreement with available literature data[58]. Dipole moments were then calculated from equation (8):

$$\mu_e^2 = g_1 F_{11}\mu_{1,0}^2 + g_2 F_{22}\mu_{2,0}^2 + g_{12}F_{12}(\mu_{1,0}^2/2 + \mu_{2,0}^2/2) \quad (8)$$

where g_1, g_2, μ_{10}, μ_{20}, refer to the appropriate homopolymer values from *Table 2* and g_{12} is the correlation factor for the mixed dyads. [In this analysis, the experimental composition dependences of μ_e was fitted using g_{12} as an adjustable parameter.]

Values of g_{12} obtained from equation (8) for the copolymers are listed in *Table 3*. These values are all higher than the *g*s for the homopolymers in *Table 2*, which implies that the presence of comonomer units leads to a loss of cancelling correlations among dipoles along the chain. Such angular correlations among dipoles certainly must extend beyond dyads but consideration of dyad geometry alone is sufficient to account for most of the effect.

The stereochemistry of the chain is unknown but for racemic dyads the lowest energy conformation is (*trans, trans*) while for meso dyads it is (*trans, gauche+*). In either case this leads to the phenyl ring axes having preferred orientations of 120° to each other. The dipole moment for a dyad may be obtained from the dot product of the two-bond moment vectors:

$$\mu^2 = m_1^2 + m_2^2 + 2m_1m_2\cos\theta \quad (9)$$

where m_1 and m_2 are the dipole moments of the individual units, that is the μ_0 values collected in *Table 2*, and θ is 120° in this case. For the 4CS dyads application of equation (9) leads to a value of 2.2 D while two individual 4CS units would have a dipole moment of 4.4 D. Thus the *g* factor for 4CS dyads is 0.5. Similar considerations lead to a *g* factor of 0.8 for 4CS–S dyads. Thus the increase in *g* with increasing styrene concentration for both PS2CS and PS4CS is mainly due to dipolar cancellation in the mixed dyads, S–4CS. In the case of P2CS–4CS, the pronounced maximum in *g* is also due to the mixed dyads.

Shapes of copolymer dispersion curves

Half- and three-quarter frequency widths of the normalized dielectric loss in the α relaxation region are plotted in *Figure 10* for PS2CS. It is seen that the widths are independent of composition. Fuoss–Kirkwood parameters are also identical for all the copolymers and indistinguishable from the behaviour shown in *Figure 5* for the homopolymers. Thus the relaxation behaviour of the copolymers exhibits no evidence for a contribution of the β process to the α relaxation region and is consistent with the presence of a random distribution of comonomer units.

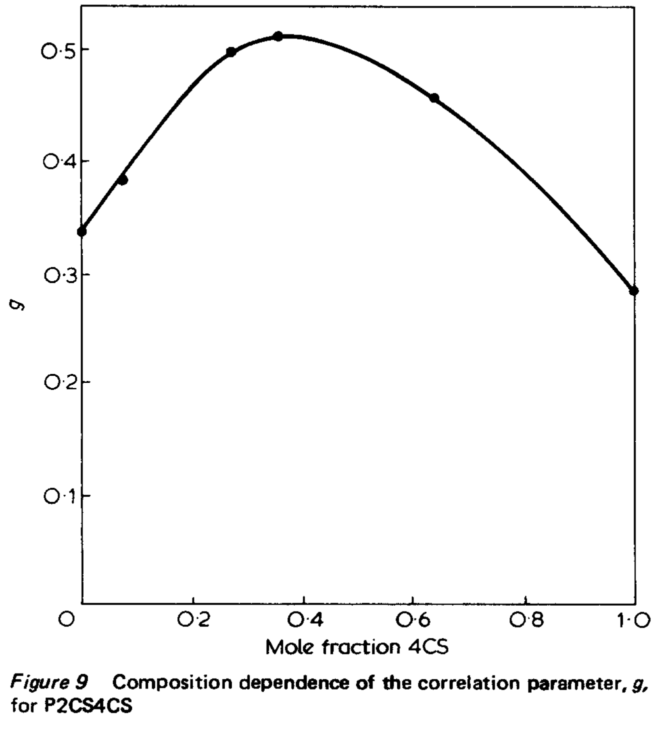

Figure 9 Composition dependence of the correlation parameter, *g*, for P2CS4CS

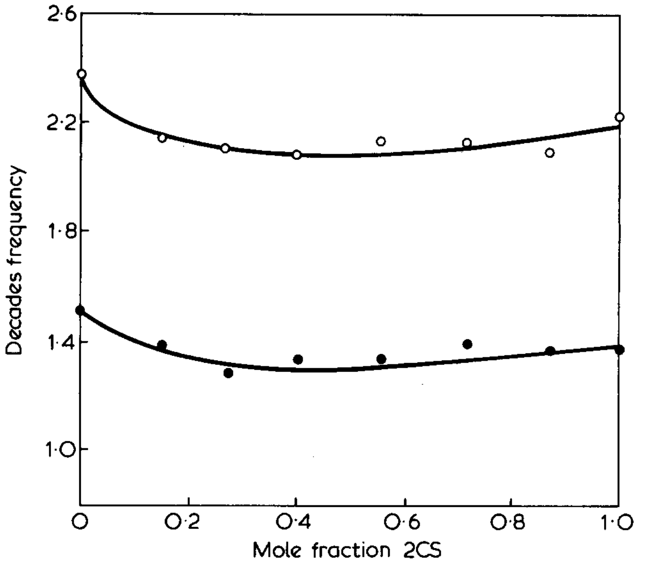

Figure 10 Composition dependence of the frequency widths of the dielectric loss in the α relaxation region for PS2CS. ○, 0.5 width; ●, 0.75 width

CONCLUSIONS

(1) The phenyl side group in PS, P3CS and P4CS undergoes essentially free rotation in the dielectric α relaxation region, while in P2CS the phenyl groups are presented from rotating by steric hindrance. This side group motion does not contribute to the α relaxation process but is responsible for the β process.

(2) The positive deviations of the composition dependence of the dipole moments of PS2CS, PS4CS and P2CS4CS may be largely accounted for on the basis of dyad geometry alone.

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