

Memory Effects in Collisional Polarization in Polystyrene, Xylene and Polystyrene Toluene Solutions

BY MUSA M. OMAR,[†] ALASTAIR M. NORTH, THOMAS G. PARKER[§] AND RICHARD A. PETHRICK*

Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, Glasgow G1 1XL

Received 13th September, 1982

Far-infrared ($10\text{--}250\text{ cm}^{-1}$) spectra of polystyrene in toluene, *m*- and *p*-xylene up to concentrations of 50% w/v are reported. Subtraction of the profiles for the pure components gives an excess loss associated with solvent–polymer collisional polarization. This increases with concentration up to 2%, decreases to 5% and then increases again. It is noted that these concentrations correspond to those at which hydrodynamic screening in the solvent flow velocity distribution starts increasing and then becomes constant, as evidenced in solution viscosity. An explanation of these variations in excess collisional polarization is offered in terms of the way in which the distribution of solvent molecular velocities affects the polarization *via* translation–vibration excitations. Perturbation of this distribution by prior inelastic collisions with polymer molecules then provides a ‘memory’ effect analogous to hydrodynamic screening.

In an earlier paper¹ the far-infrared spectra of polystyrene and its solutions in carbon tetrachloride, benzene and toluene were reported. Features observed in the region $10\text{--}250\text{ cm}^{-1}$ were ascribed to collisional polarization, the effective collision-induced dipole varying as $T^{1/2}$ in agreement with theory. More recently we have shown^{2,3} that for small molecules the magnitude of the induced polarization can be correlated with other quantities such as adiabatic compressibility. In polymer solutions the polymer–solvent interactions affect not only time-averaged thermodynamic properties but also time-dependent phenomena such as viscous flow.

When viscosity is studied as a function of polymer concentration one of the phenomena evidenced is the onset of ‘hydrodynamic screening’. For our present purposes we can consider this as occurring when the flow velocity distribution of solvent molecules impinging on one polymer molecule retains a perturbation induced by prior interaction with some other polymer chain. This ‘memory’ is usually considered as existing in the long-time tail of the solvent velocity time-correlation function. It is not at all clear whether such a ‘memory’, persisting over relatively long times, is evidenced in events as rapid as molecular collisions in liquids, and it is to this question that the present study is directed.

EXPERIMENTAL

Polystyrene [(B.D.H.), $\bar{M}_w = 110\,000$ and $\bar{M}_w/\bar{M}_n = 1.4$] was purified by repeated reprecipitation from toluene into methanol. The solutions used in this study were dried over molecular sieves prior to use. Low-molecular-weight liquids were purified as described previously.¹

[†] Present address: Department of Chemistry, Al-Fateh University, Tripoli, Libya.

[§] Present address: Hannah Research Institute, Ayr.

Far-infrared measurements were made using lamellar grating and Michelson interferometers.² Each interferogram was Fourier transformed after background subtraction and apodization,⁴ the spectra so obtained being stored and averaged. Absorption coefficients obtained from averaged spectra of at least six cell thicknesses had a precision of better than 5%. The spectra were recorded at 298 K, and the nature of the sample cell used in this study precluded significant variation of the temperature of the sample without causing problems of solvent loss.

RESULTS

Typical spectra obtained at 298 K are shown in fig. 1. In order to discern anomalous effects due to intermolecular interactions an 'excess loss' was calculated

$$\epsilon''_{\text{excess}} = \epsilon''_{\text{observed}} - [n_A^2 \epsilon''_A + 2n_A n_B (\epsilon''_A \epsilon''_B)^{1/2} + n_B^2 \epsilon''_B] \quad (1)$$

where ϵ''_A and ϵ''_B are the losses (imaginary permittivities) of the pure components of mole fractions n_A and n_B . The excess loss as defined above describes all additional dielectric losses found in the mixture which either are not present in the two pure components or do not add in a linear combination. This excess loss will therefore contain processes such as collisionally induced polarizations arising from cross-interaction of molecule A with B. The frequency and concentration dependences of the excess loss in dilute solutions of polystyrene in toluene and *m*- and *p*-xylene are shown in fig. 2. As the polymer concentration rises, the intensity of attenuation increases and then shows an unexpected decrease, before further increasing in line with the previous less detailed observations of polystyrene in toluene.¹ The amplitudes and frequencies of the maxima in $\epsilon''_{\text{excess}}$ are illustrated in fig. 3 and 4. More correctly the integrated intensities of the excess absorptions should be computed;² however, this introduces a large uncertainty because of the long tail in the loss interacting with a vibrational feature located at 160 cm⁻¹.

DISCUSSION

DILUTE SOLUTIONS (5% w/v)

Dilute solutions are defined as those in which there is no significant overlap^{5,6} of dissolved polymer coils, and usually exist when $[\eta]c \approx 1$, where $[\eta]$ is the intrinsic viscosity and c the concentration of the solution. In the very dilute regime each polymer molecule exhibits a totally independent effect on solvent flow velocity, but at the high concentrations interchain hydrodynamic screening is evidenced. This results in an increased viscosity over that predicted by extrapolation from the very dilute region, the divergence becoming marked at *ca.* 2% w/v (corresponding to $[\eta]c \approx 1$) in the solutions studied herein.

It is clear from fig. 2 and 3 that the decreased excess loss also becomes evident at the same concentration, and so it seems sensible to seek an explanation parallel to that for hydrodynamic screening.

It is sometimes overlooked that the interaction of radiation with the fluctuation of a collisionally induced dipole involves its formation and relaxation as well as its reorientation. The excitation mechanism in liquids is assumed to be the same as in translation-vibration energy transfer in gases,^{7,8} so that description of the intensity of interaction between radiation and the fluctuating dipole will contain a term of some form as

$$I_{\text{excitation}} = \int P_{\text{VT}} A_i A_j dt \quad (2)$$

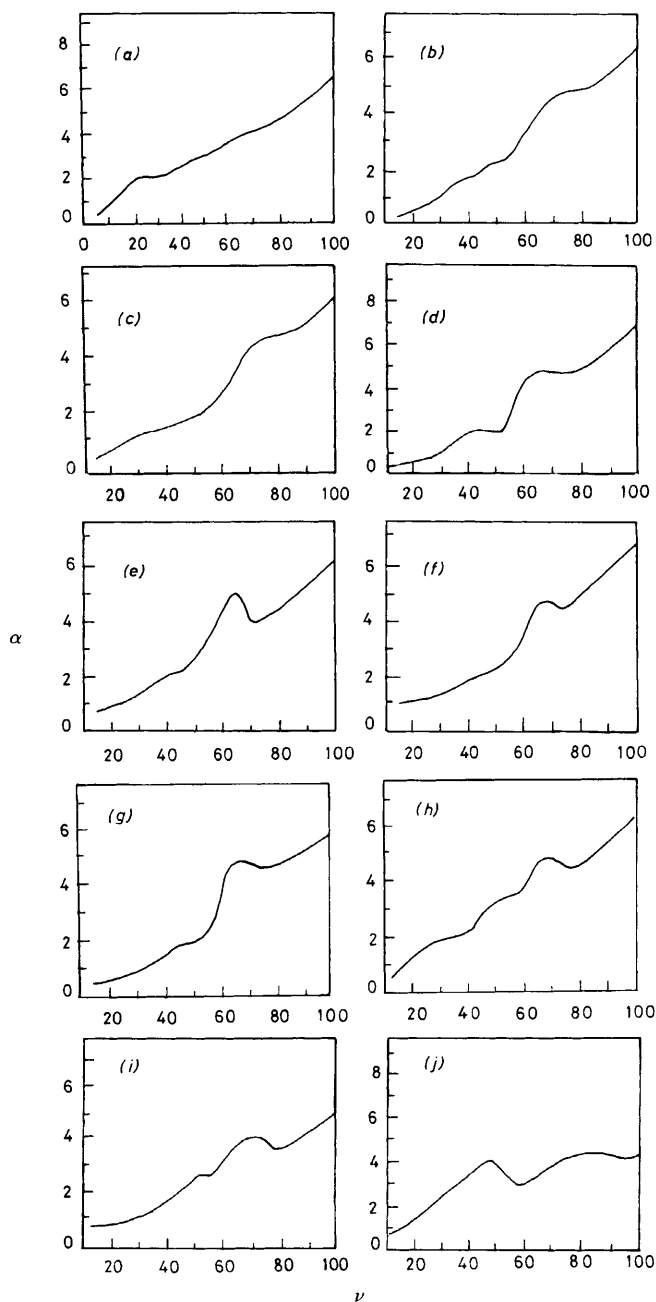


Fig. 1. Far-infrared absorption of solutions of polystyrene (PS) in *p*-xylene: (a) pure *p*-xylene; (b) 0.066 w/v% PS; (c) 0.12 w/v% PS; (d) 1.1 w/v% PS; (e) 4.4 w/v% PS; (f) 9.1 w/v% PS; (g) 26.4 w/v% PS; (h) 45.4 w/v% PS; (i) 56 w/v% PS; (j) pure polystyrene.

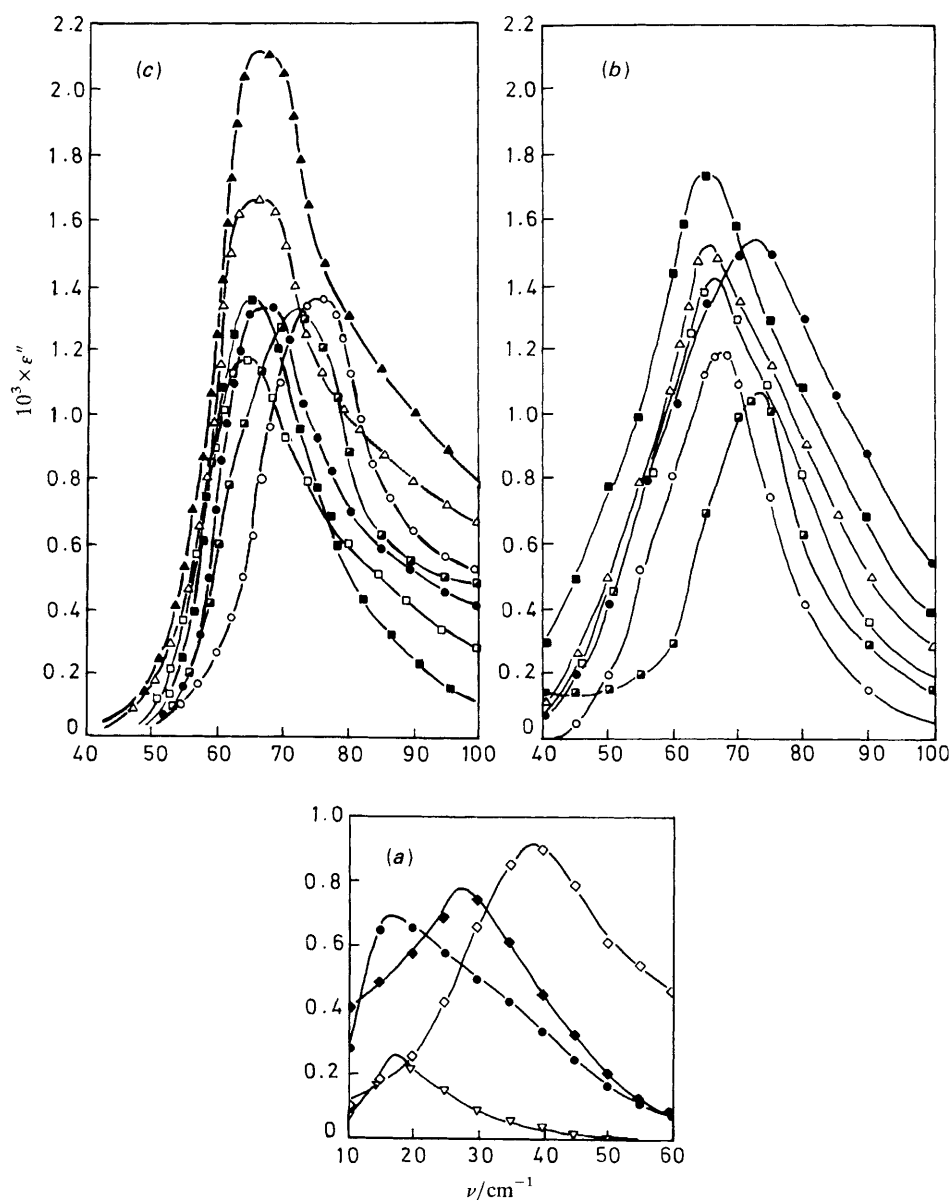


Fig. 2. Excess dielectric loss of dilute solutions of polystyrene (PS) in (a) toluene, (b) *m*-xylene and (c) *p*-xylene: \blacksquare , 0.066 w/v% PS/solvent; \circ , 0.12 w/v% PS; \bullet , 1.10 w/v% PS; \diamond , 2.03 w/v% PS; \blacklozenge , 3.56 w/v% PS; \square , 4.4 w/v% PS; ∇ , 4.98 w/v% PS; \triangle , 9.1 w/v% PS; \blacktriangle , 26.4 w/v% PS; \blacksquare , 50 w/v% PS.

where P_{VT} is the probability of formation of the polar excited state and $A_i A_j$ denotes the bimolecular nature of the collision process. The important point is that the probability function, P_{VT} , is compounded⁹⁻¹¹ of a collision frequency, the probability of energy transfer for a particular relative velocity of collision and a velocity distribution function. In this approach an average (over all molecules) effective

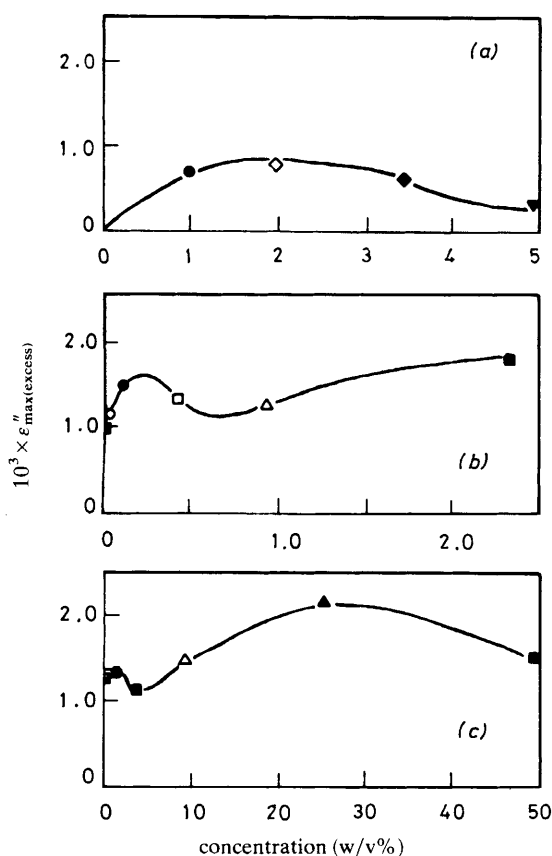


Fig. 3. Amplitude of the maximum excess dielectric loss (key as fig. 2).

dipole magnitude is replaced by an excitation (to a specific state) probability function. Consideration of the excess absorption then concentrates attention on i - j collisions (in this case between solvent and polymer) and particularly on their collision number and velocity distribution.

An explanation for the observed excess amplitude changes then emerges as follows. Below 1% w/v the loss amplitude reflects the non-ideal nature of the solvent-polymer inelastic collisions. That is, the excess function shows that the energy-transfer probability for a given collision velocity distribution is greater for the unlike collisions than predicted from the simple averaging of like collisions. This seems reasonable since it is perfectly possible for aromatic species attached to a chain backbone to show enhanced translation-vibration transfer (a broader profile of vibration frequencies) than when the species is an individual small molecule. Of course, the conformational form and translational position of the polymer chain are effectively frozen over these very short times. Above 1% w/v the frequency and integrated velocity function are reduced (either separately or as a combined function). This must be because the colliding molecules retain a lower velocity as a result of previous inelastic collisions. Since the effect becomes evident in this concentration range, an interchain phenomenon must be responsible and so the velocity reduction closely resembles that observed in flow as hydrodynamic screening.

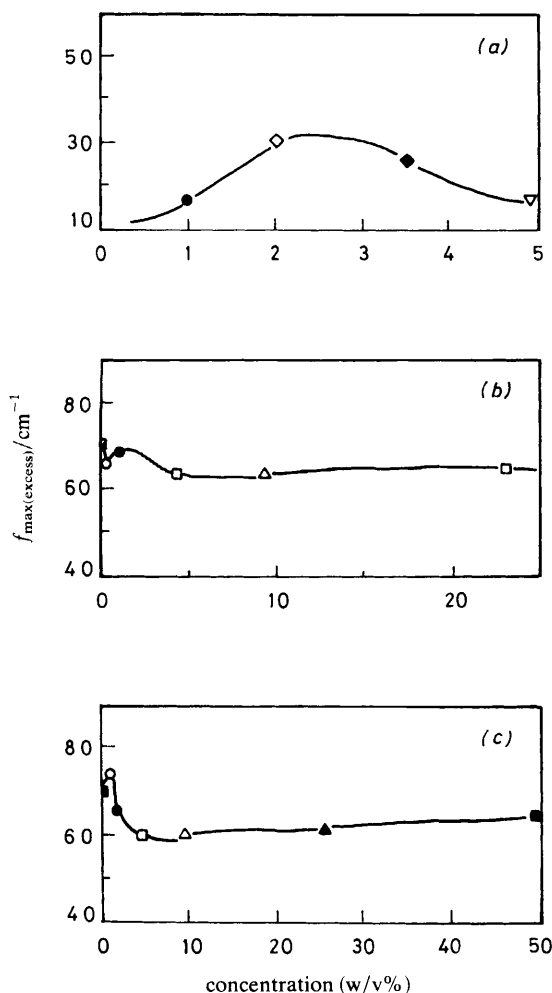


Fig. 4. Frequency of the maximum excess dielectric loss (key as fig. 2).

MORE CONCENTRATED SOLUTIONS

Once a concentration in excess of $[\eta]c > 5$ has been obtained, significant polymer coil interpenetration occurs and interchain hydrodynamic screening is little altered by increasing the concentration. The excitation probability function, P_{VT} , should then become invariant and the excess intensity of absorption will again (as in the very dilute region) become a function of the non-ideality of the collisions, reflected in $A_i A_j$. In accord with this hypothesis, the excess absorption increases above 5% up to at least 50% w/v. Thus in both concentration ranges the excess absorption amplitudes behave as predicted qualitatively from a velocity distribution deduced from hydrodynamic screening in flow viscosity. With the current system it is not possible to investigate the temperature dependence of the far-infrared absorption. It would be anticipated that changes in temperature, through their effect on the velocity distribution, should lead to changes in the probability of formation of the collisionally induced excited state. Further, in a polymeric system, the temperature

may also influence the conformational preference of the polymer and so the efficiency of the collisional interactions.

It must not be forgotten that the total band profile is the result of electromagnetic radiation interacting with both the formation (and annihilation) of polarization and its time-dependent distribution in space. While we have chosen to concentrate on the former aspect, treatments such as the 'itinerant oscillator'^{12,13} concentrate on the randomized libration-rotation behaviour in the latter stage. So far as we are aware, no model has been formulated to represent successfully concurrent excitation and libration. The excitation process can be modelled only imprecisely even for a gas (where the pair-interaction potentials are known). So the many-bodied problem of the liquid is even more complex, as can be concluded from the concentration dependences of fig. 3 and 4. Nevertheless, we feel that the behaviour evidenced in the excess functions (and particularly the excess amplitude changes when hydrodynamic screening becomes and then ceases to be important) is best explained through the influence of the velocity distribution on the probability of collisional excitational polarization.

M.M.O. thanks the Libyan Government for support.

- ¹ A. M. North and T. G. Parker, *Trans. Faraday Soc.*, 1971, **67**, 2234.
- ² D. V. S. Jain, A. M. North, M. M. Omar and R. A. Pethrick, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, in press.
- ³ D. V. S. Jain, A. M. North and R. A. Pethrick, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 1292.
- ⁴ J. Chamberlain, *Principles of Interferometric Spectroscopy*, ed. G. W. Chantry and N. W. B. Stone (Wiley, London, 1979).
- ⁵ M. V. Volkenstein, *Configurational Statistics of Polymeric Chains* (Interscience, New York, 1963).
- ⁶ P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- ⁷ J. A. Bucard and T. A. Litovitz, *J. Chem. Phys.*, 1971, **55**, 3585.
- ⁸ J. A. Bucard and T. A. Litovitz, *J. Chem. Phys.*, 1971, **54**, 3846.
- ⁹ K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, New York, 1959).
- ¹⁰ R. N. Schwartz, Z. I. Slawsky and K. F. Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591.
- ¹¹ W. M. Madigosky and T. A. Litovitz, *J. Chem. Phys.*, 1961, **34**, 489.
- ¹² C. J. Reid and M. W. Evans, *Molecular Interactions* ed. H. Tatajczak and W. J. Orville Thomas (Wiley, London, 1982), vol. 3, p. 409.
- ¹³ J. H. Calderwood and W. T. Coffey, *Proc. R. Soc. London, Ser. A*, 1977, **356**, 269.

(PAPER 2/1577)