polymer by the incorporation of metal. Shift in t_g also points to strong adhesion between the phases. Recently Aras, Sheldon and Lai[17] observed an increase in t_g of poly(vinylacetate) due to the impregnation of silica filler. They ascribed this increase due to the adhesion between the filler and the polymer.

In conclusion, dilatometric studies indicate the existence of a physical adhesion factor between the polymer and metal phases which causes segmental immobilization of the polymer. This may be responsible for the strengthening of the polymer matrix in the composite. Thermal analyses (d.t.a., d.t.g. and t.g.) have been taken up with a view to understanding the exact nature of the interaction between the matrix and the filler phases.

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Ion pair dissociation equilibria for iodonium and sulphonium salts useful in photoinitiated cationic polymerization

A. Ledwith and S. Al-Kass
*Donnan Laboratories, University of Liverpool, Liverpool L*69 3*BX, UK*
and D. C. Sherrington and P. Bonner
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

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During the past ten years, photochemically initiated curing of surface coatings has grown in importance and may be accomplished by both free radical (essentially acrylic systems) and cationic (essentially epoxide systems) processes[1].

Photochemically initiated cationic curing of epoxy systems involves photodecomposition of various aryl diazonium[2], diaryl iodonium[3], and triaryl sulphonium[4] salts having relatively stable non-nucleophilic anions such as PF_6^-, SbF_6^-, BF_4^-, etc. A notable feature of such photochemically-initiated polymerizations is the apparent effect of the anion on the extent and rate of epoxide consumption[3–5].

Pappas has shown[6] that iodonium salts and sulphonium salts exhibit different activities in the presence of various photosensitizers and rather similar differences are observed in rates of decomposition of the same salts when promoted by reducing organic radicals[7].

For any process occurring via charged species it is necessary to consider potential additional complications arising from ion pair dissociation equilibria[8], viz:

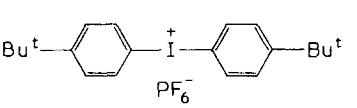
$$[\text{cation}][\text{anion}] \xrightleftharpoons{K_D} [\text{cation}] + [\text{anion}]$$

Except in special circumstances it is to be expected that free ions will be more reactive than ion pairs, although the influence of ion pairing on the precise mechanistic pathways for reactions of a photochemical excited ion is not easy to predict.

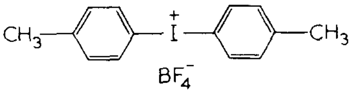
In earlier work[9–11] we have been concerned with the determination of ion pair equilibria and reactivities for salts or relatively stable organic cations and considered it useful, therefore, to attempt similar characterization for the initiating components of important cationic photocure systems.

Experimental details for the techniques of conductance measurement and solvent purification have been fully described in previous papers[9,10]. Analytical data for the salts investigated (I–III) are given in *Table 1.*

Values of K_D, λ_0, ΔH_0, and ΔS_0 for the salts I–III are equivalent conductance on salt concentrations in the solvents CH_2Cl_2 and CH_3CN by the method of Fuoss, with computerized iteration as previously described[9,11].



(I)



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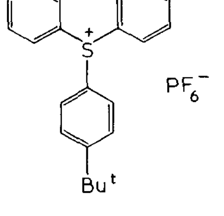

(III)

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Table 1 Elemental analysis data

Salt	%C		%H		%S		%I	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
1	44.8	44.6	4.95	4.87			23.3	23.6
2	41.4	42.5	3.40	3.56			31.7	32.1
3	56.9	56.9	4.91	4.99	6.91	6.90		

Table 2 Ion pair dissociation constants

Salt	Solvent	Temperature (°C)	$10^5 K_D$ (M)	λ_0 (mho cm^2 mol^{-1})	ΔH_0 (kJ mol^{-1})	ΔS_0 (kJ mol^{-1} K^{-1})
I	CH_2Cl_2	0	1.32	125	−4.9	−111
I	CH_2Cl_2	−41	1.93	68.9		
I	CH_3CN	0	276	165	−7.2	−76
I	CH_3CN	25	205	208		
II	CH_2Cl_2	0	0.47	119	−4.2	−119
II	CH_2Cl_2	−41	0.65	64.7		
II	CH_3CN	0	471	155	−5.4	−64
II	CH_3CN	25	386	190		
III	CH_2Cl_2	0	13.8	113	−5.2	−93
III	CH_2Cl_2	−41	20.7	65.5		
III	CH_3CN	0	441	152	−5.6	−66
III	CH_3CN	25	358	183		
III	Acetone	0	271	174		
III	10% THF/90% CH_2Cl_2	0	12.0	95.2		

These studies were made at two different temperatures and important data are summarized in *Table 2*.

Values of K_D, λ_0, ΔH_0, and ΔS_0 for the salts I–III are similar to those reported for related salts of several other types of carbocations[11,12] and to that reported[13] for $Et_3S^+BF_4^-$. It is important to note that for the iodonium salts the tetrafluoroborate II is much less dissociated in CH_2Cl_2 than the closely related hexafluorophosphate I. Interestingly, the sulphonium hexafluorophosphate III is approximately 10 times more dissociated in CH_2Cl_2 than the iodonium hexafluorophosphate I. In the considerably more polar solvent CH_3CN, values of K_D are orders of magnitude higher than corresponding values in CH_2Cl_2 and there is much less difference between the various salts. As expected, the greater solvating and dissociating power of CH_3CN smooths out molecular differences apparent in the less polar dichloromethane.

Solvent effects on ion pair dissociation equilibria are best explained by the Dennison–Ramsey treatment[14] which predicts a linear dependence of $\ln K_D$ on the reciprocal of dielectric constant (ε) of the medium. Data in *Table 2* for the salt III at 0°C indicate such a linear relationship for the solvents acetonitrile ($\varepsilon = 38.4$), acetone ($\varepsilon = 23.2$), dichloromethane ($\varepsilon = 9.92$), and 10% tetrahydrofuran–90% dichloromethane ($\varepsilon = 9.80$) and allow an average value of 13 Å to be calculated for the cation–anion contact distance in the ion pair. This value is significantly larger than that calculated for $Ph_3C^+SbCl_6^-$ (7.9 Å)[9] or $Et_4N^+SbCl_6^-$ (6.4 Å)[9] where the positively charged atom is taken from the first main row of the Periodic Table. The difference may be simply that sulphur is a second main row element, or that the sphere in a continuum model, on which the Dennison–Ramsey equation is based is too naive an approach.

In photochemically-initiated cationic polymerizations the primary process is generally assumed to be fragmentation of an appropriate excited state of the cationic component of the initiating salt, e.g. for diaryliodonium salts:

$$Ar_2I^+ \xrightarrow{h\nu} (Ar_2I^+)^* \longrightarrow ArI^{+\cdot} + Ar^\cdot$$

Precisely how the initially-formed cation radical fragment initiates polymerization is not clear and the equation, as written, does not show any of the many possible physical and chemical deactivation processes which might occur between anion and cation components of the initiating salt or its photofragments. Typical commercial photocure systems use mainly bulk epoxide as reaction medium, the polarity and dielectric constant of which is not likely to be higher than that of CH_2Cl_2 used in these studies. It follows, therefore, that values of K_D for the initiating salts in typical photocure layers will be in the range 10^{-4}–10^{-6} M. For a salt with $K_D = 10^{-5}$ M, the degree of dissociation will be approximately 50% at a salt concentration of 10^{-5} M. Above this concentration, which is orders of magnitude less than those employed commercially, the degree of dissociation will be drastically reduced and further, higher aggregates of the ions will be formed[8]. Thus extrapolation of photofragmentation patterns established for iodonium and sulphonium salts in polar media (e.g. acetone), where free ions predominate, to the much less polar photocurable epoxide coatings, where ion pairs and higher aggregates predominate, may not be justified. It is perhaps significant that tetrafluoroborate salts, which invariably yield inefficient photo-initiating systems, have the highest tendency to aggregate and thus afford maximum opportunity for anion deactivation of the photochemically excited cations and their photodecomposition products.

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On macro- and microviscosity of high polymer solutions

V. A. Bagdonaite and S. S. Juskeviciute
Vilnius State University, 232/34 Vilnius, USSR

and Yu. A. Shlyapnikov
Institute of Chemical Physics, USSR Academy of Sciences, 117334, *Moscow, USSR*

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The diffusion coefficient, D, in the liquid phase is related to the liquid viscosity η by the Stokes–Einstein equation:

$$D = \frac{RT}{6\pi r\eta} \qquad (1)$$

where r is the radius of diffusant molecule. So D may be used as a measure of the viscosity coefficient of the liquid media.

The high viscosity of the polymer solutions is due to the network formed by long chain molecules which contains a large amount of pure solvent in each cell. Viscosity depends both on the polymer molecular mass and the concentration. But the solvent properties in these cells depend only on the cell size, which is a function of the polymer weight concentration, and would be independent of the molecular mass of the polymer if the chain lengths were large enough to be compared with the cell size.

The difference between the measured viscosity of a high polymer solution and its microviscosity which affects molecular mobility within it has previously been reported[1,2].

The dependence of the diffusion coefficient of the low molecular mass compounds on the concentration of polystyrene in ethylbenzene, which is a low molecular mass model of the polymer monomeric unit, has been studied. Our aim was to verify the assumption that the polymer solution microviscosity is independent of the molecular mass of the dissolved polymer.

EXPERIMENTAL

The macroviscosity of concentrated polymer solutions were measured by the thick layer method[3,4], recording the reduction of the mild β-radiation intensity I caused by penetration of the labelled compound into the substance studied. As low-molecular mass probe compounds 2,6-di-tert-butyl-4-methyl phenol and 2,2'-methylene-bis(4-methyl-6-tert-butyl phenol), labelled with ^{14}C were used. All experiments were conducted at 20°C.

RESULTS AND DISCUSSION

According to the theory of ref 3, the radiation intensity–time curves expressed as I/I_0 vs. $t^{-1/2}$ possessed as asymptote passing through the coordinate origin (*Figure 1*). The asymptote slope, m, is related to the diffusion coefficient by:

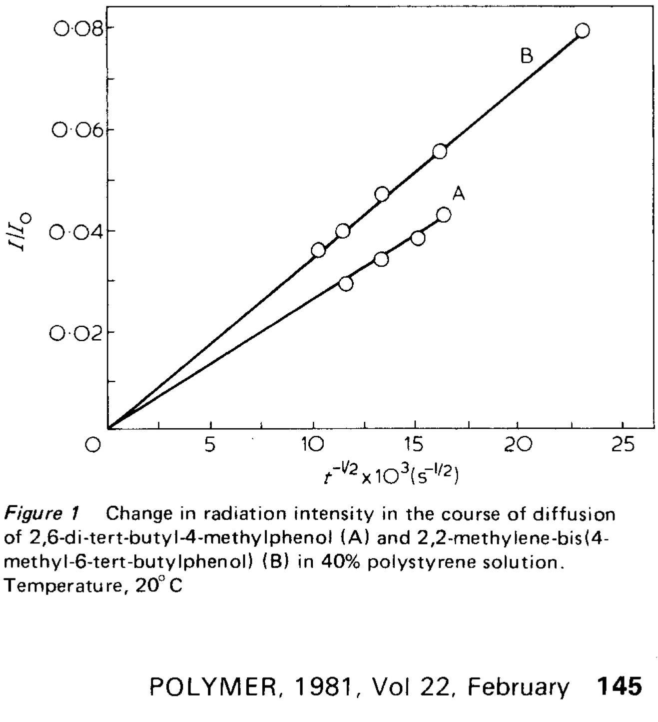

Figure 1 Change in radiation intensity in the course of diffusion of 2,6-di-tert-butyl-4-methylphenol (A) and 2,2-methylene-bis(4-methyl-6-tert-butylphenol) (B) in 40% polystyrene solution. Temperature, 20°C

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