The influence of solvent on labelled and free pyrene aggregation in novolac solutions and films

Laura L. Kosbar and Curtis W. Frank*[†]
*Departments of Chemistry and *Chemical Engineering, Stanford University, Stanford, CA 94305-5025, USA*
(Received 15 September 1989; revised 7 January 1991; accepted 16 January 1991)

The effects of various casting parameters were measured for films of novolacs (cresol-formaldehyde resins) containing pyrene groups either covalently bound to the polymer chain or physically dispersed in the novolac matrix. Aggregation of the dispersed pyrene was observed, as measured by excimer fluorescence and crystallite formation of the pyrene. The phase separation was enhanced in static-cast films over spin-cast films. Pyrene aggregation in films was also affected by the choice of casting solvent even though no significant solvent effects were observed for the tagged polymer or free pyrene in solutions of the casting solvents. A minimum in the plot of the excimer-to-monomer ratio for the films *versus* the dipole moment of the casting solvent occurred at about the dipole moment expected for the novolac. Pyrene aggregation appears to be more dependent on the interactions of the casting solvent and the host polymer rather than on the interaction of either with the pyrene itself.

(Keywords: novolac; pyrene excimer; aggregation; solvent casting)

INTRODUCTION

The formation and homogeneity of solutions, whether in the solid or liquid phase, has been of interest to researchers since the very earliest days of chemistry. Theories to deal with polymer solution thermodynamics were first proposed by Flory[1] and Huggins[2] around 1941. These theories encompass the interactions of the polymer with the small molecule solvent in which it is dissolved. Often the systems of interest are more complicated than just a single solute in a single solvent, however. Many applications involve multicomponent systems such as solutions of two polymers, or a polymer and small molecule solute in a solvent. The properties of films cast from such solutions may be dependent on the choice of casting solvent. In coatings the solvent provides for appropriate rheological properties and may be essential in improving the compatibility of materials that otherwise might tend to phase separate during casting. Although the solvent is essentially removed during the casting process, it may still play a crucial role in determining the final film characteristics. The casting technique, e.g. static, spin or Langmuir Blodgett, may also have an impact on the physical properties of the film.

One application that is dependent on films cast from multicomponent solutions involves resist materials used in semiconductor manufacturing. Most positive resist materials used in the semiconductor industry are composed of a polymer matrix and a small molecule or polymeric material that is radiation sensitive (the 'sensitizer'), dissolved in an appropriate solvent. The most common positive resists employ a novolac (cresol-formaldehyde) resin with a diazonaphthoquinone (DNQ) sensitizer in diglyme (bis 2-methoxyethyl ether), Cellosolve (2-ethoxyethanol) or a similar solvent[3]. A thin film (0.5–2 μm) is cast by depositing the resist solution on a flat substrate and spinning at high speeds (3000–8000 rev min^{-1}). The spinning causes rapid evaporation of the casting solvent and creates films of uniform thickness. The films are exposed with an electron beam or ultra-violet (u.v.) radiation, and the exposed areas are dissolved to form fine (0.5–5 μm) patterns in the film, which are then used to define the semiconductor devices.

The multicomponent resists allow incorporation of many desirable features that may not be available from a single material. The novolac polymer matrix has good film forming characteristics, imparts high resistance to reactive ion etching and is very soluble in the developing solution. However, novolac is not photosensitive so a sensitizer is added that undergoes a chemical reaction and converts to its acidic form upon irradiation. The unexposed sensitizer acts as a dissolution inhibitor for the polymer matrix, while the exposed sensitizer aids in polymer dissolution in the basic developing solution, leading to pattern definition. Common photoresists may contain fairly high concentrations of sensitizer, as much as 15–50 wt%[3,4]. Also, the polymer and the sensitizer are often marginally chemically compatible; hence, aggregation of the sensitizer may be of concern. Even distribution of the sensitizer in the spin-cast film is important in assuring the uniform dissolution of the exposed regions, or retention of the unexposed regions. Aggregation of the sensitizer could cause the resist to remain in the exposed regions, allow pockets of polymer to dissolve out of the unexposed region, creating pinholes in the film, or result in images with rough edges, as shown schematically in *Figure 1*. These problems would result

---

[†] To whom correspondence should be addressed

0032-3861/92/010141-11

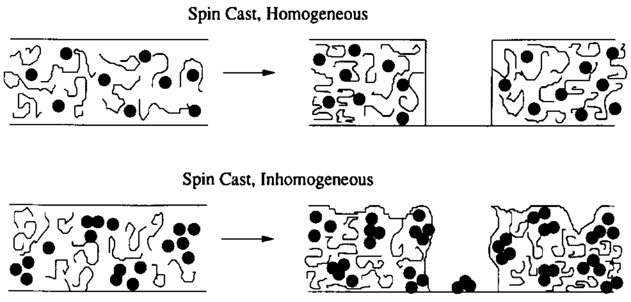

Figure 1 Schematic representation of the effects of sensitizer aggregation (●) on the performance of a lithographic resist. Aggregation of the sensitizer may cause pitting of the surface, uneven edges on images and possibly organic material left in exposed areas

in a reduction in device yield. The uniformity of film development will continue to increase in importance as image dimensions drop well into the submicrometre region where thinner films and smaller linewidth tolerances will be required. The homogeneity of a resist film on the molecular level is difficult to determine using conventional techniques, however.

Several techniques that have been developed to measure the homogeneity of solid solutions range from simple methods such as measures of optical clarity or of glass transition temperatures, to the more sophisticated techniques of light, X-ray or neutron scattering[5,6]. The simpler techniques tend to be fairly insensitive to film inhomogeneities on a small scale, and the scattering techniques, while they are much more sensitive, are more difficult to perform and often require facilities with restricted access. An alternative technique that combines high sensitivity and relatively simple sample preparation and equipment is fluorescence spectroscopy[7,8]. As a specific example, excimer formation measurements have been employed extensively to investigate polymer–polymer interactions in solid polymer blends[9–17]. In particular, Gashgari[9] found that the extent of excimer formation of an aromatic vinyl polymer blended with a non-fluorescent host polymer could be correlated with the solubility parameter (δ) difference of the two polymers to predict the compatibility of the polymer blend.

In this paper, we have used excimer fluorescence to evaluate the homogeneity of multicomponent films analogous to photoresists. The matrix resin is a novolac, but pyrene is used in place of the DNQ sensitizer. Pyrene has high fluorescence quantum yield, long excited state lifetime, and the ability to form excimers. The pyrene excimer-to-monomer ratio, I_E/I_M, can be used as an indication of the local concentration of pyrene. We have studied the distribution of pyrene in two types of films—those in which the pyrene was tagged onto the novolac backbone and those in which free pyrene was in solution with the novolac. Variations of I_E/I_M in films cast with both free and tagged pyrene using different casting solvents allow us to evaluate the effect of casting solvent on film homogeneity.

EXPERIMENTAL

Materials

The alcohol, ether–alcohol, and polymer solvents were obtained from Aldrich Chemical Company and included methanol (MeOH), ethanol (EtOH), 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE), 2-butoxyethanol (BOE), tetrahydrofuran (THF), ethyleneglycol dimethyl ether (EGDME), ethyleneglycol diethyl ether (EGDEE), bis 2-methoxyethyl ether (MOEE), and bis 2-ethoxyethyl ether (EOEE). All of the solvents were spectral grade except for EGDEE and EOEE. The spectroscopic grade solvents were used as received, and the other solvents were distilled prior to use. The pyrene and pyrene butyric acid (PBA) were also obtained from Aldrich and were purified by recrystallization from toluene. The novolac sample, which was synthesized from pure *m*-cresol and formaldehyde, was provided by Kodak. The material is quite polydisperse with $M_w = 13\,000$ and $M_w/M_n = 8.5$, as measured by gel permeation chromatography using polystyrene standards. The polymer was purified by two precipitations from THF into hexane. Pyrene tagged novolac was prepared by the previously described reaction[18] of PBA chloride with the phenolic groups on the polymer, resulting in pyrene covalently bonded to the polymer backbone through an ester linkage. The samples used in these experiments had molar ratios of tagged pyrene to monomer units of 0.196 or 0.050, as measured by u.v. absorption.

Sample preparation and viscosity measurements

The intrinsic viscosities ($[\eta]$) of the novolac in various solvents were measured using Ubbelohde type viscometers. Flow times of polymer solutions with concentrations of 1–6 g dl^{-1} were measured at 25.0 ± 0.01°C. Flow times were all above 100 s, so no kinetic corrections were required. At least three polymer concentrations, as well as the pure solvent, were examined for each solvent. The $[\eta]$ values were calculated from the average of the intercepts of ($\ln \eta_r/c$) and η_{sp}/c *versus* c, where η_r is the relative viscosity, η_{sp} is the specific viscosity and c is the concentration (in g dl^{-1}).

The solutions for spectroscopic analysis were prepared to have 1×10^{-5} M chromophores for both the free and tagged pyrene. The solutions of tagged pyrene were prepared from the novolac with 0.050 mol ratio tagged pyrene, yielding solutions with $\sim 1.8 \times 10^{-6}$ M polymer chains for chromophore concentrations of 1×10^{-5} M. The solutions were degassed with argon prior to measuring the spectra. The films for fluorescence measurements were cast from solutions containing 20 wt% solids, with a chromophore concentration of 0.20 mol ratio pyrene. The spin-cast films (~ 1 μm thick) were prepared by flooding a glass disc with the solution and spinning it at 4000 rev min^{-1} for 90 s on a Metron System Inc. LS-8000 spinner. Some of the films were then placed under vacuum for up to 16 h, but no changes in I_E/I_M were observed. Ultraviolet spectra of the spin cast films and the casting solutions indicate no loss of pyrene during casting. The static-cast films were prepared by placing ~ 0.3 ml of solution on a glass disc, allowing it to air dry, and then drying the films under vacuum overnight.

Fluorescence instrumentation and measurements

Fluorescence spectra were measured on a Spex Fluorolog 212 spectrofluorometer with a 450 W xenon arc lamp and a Spex DM1B data station. All spectra were corrected by comparison to a rhodamine reference solution. Solution spectra were measured at right angles, exciting the samples at the wavelength that gave maximum emission of the monomer. This occurred at 336 nm excitation for pyrene and 343 nm for PBA and the pyrene tagged novolac. The I_M was measured as the fluorescence intensity of the 0–0 transition of the chromophore, which was observed at 373 nm for pyrene and 376 nm for PBA and the tagged pyrene. The I_E was measured at 475 nm for all the samples. The fluorescence measurements are reported as I_E/I_M. Spectra of the films were obtained using front face fluorescence with the emission measured at a 20° angle with respect to the excitation beam. The films were excited at 342 and 348 nm for the pyrene and PBA/tagged pyrene, respectively, and the I_M was measured at 375 and 378 nm. The I_E was again measured at 475 nm. Excitation spectra were recorded for films with various concentrations of pyrene to evaluate self absorption and the presence of preformed excimer sites in the films. There were no significant deviations in the position or shape of the excitation spectra for samples with high concentrations of pyrene from those with lower pyrene concentrations, indicating minimal concentration related effects for these samples.

RESULTS

Solution measurements

Excimer formation in solution should be a diffusion controlled process[19], and I_E/I_M should be proportional to T/η (or $1/\eta$ for constant temperature) where η is the bulk viscosity. To test this for our system, the intensities of the monomer and the excimer peaks for solutions of pyrene, PBA and pyrene tagged novolac in various solvents were measured, and the ratios of I_E/I_M are plotted against the inverse of the solvent viscosity[20] in *Figure 2*. The excimer ratios of pyrene and PBA were measured to determine whether the chromophores themselves exhibited any solvent specific interactions and to compare with the excimer intensity of the tagged novolac. The excimer ratios for pyrene and PBA are very small at this concentration and indicate little dependence on solvent viscosity. The I_E/I_M values for pyrene are all between 0.0080 and 0.0133, and those for PBA are all between 0.0055 and 0.0088. Neither exhibit any observable specific solvent effects.

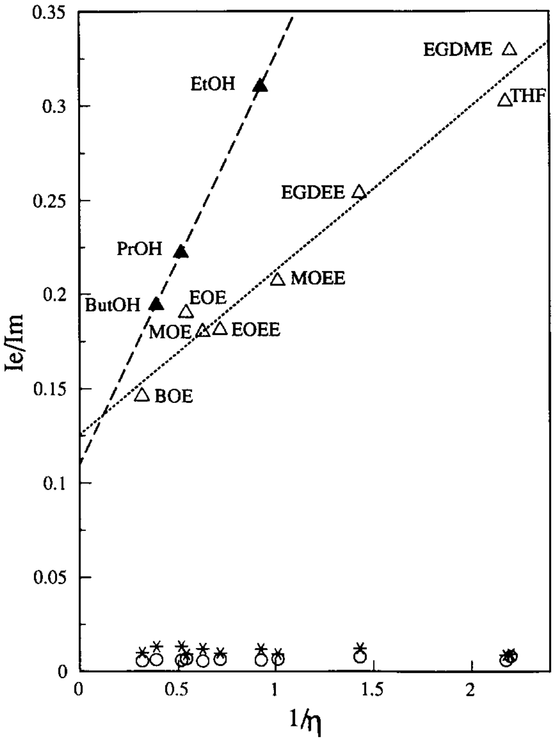

Figure 2 I_E/I_M of pyrene chromophores in solution as a function of the inverse of the solvent viscosity: (∗) pyrene; (○) PBA; (▲) 0.05 mol ratio pyrene tagged novolac in alcohols; (△) 0.05 mol ratio pyrene tagged novolac in ethers and ether-alcohols. All solutions had a chromophore concentration of 1×10^{-5} M

Table 1 Intrinsic viscosity of novolac in various solvents, calculated radius of gyration and approximate chromophore separation

Solvent	Intrinsic viscosity ($dl\,g^{-1}$)	Radius of gyration (Å)	Chromophore separation (Å)
MeOH	0.047	24.0	27
EtOH	0.050	24.4	28
ButOH	0.047	24.0	27
MOE	0.054	25.1	29
EOE	0.066	26.8	31
THF	0.051	24.6	28
EGDME	0.057	25.5	29
MOEE	0.056	25.4	29
EOEE	0.057	25.5	29

The I_E/I_M values for the pyrene tagged novolac are much larger than those for the equivalent concentration of free pyrene or PBA, as expected due to the existence of regions with a higher local chromophore concentration. The excimer ratio increases with decreasing viscosity, as expected. The excimer ratio is slightly higher, however, for all of the alcohols than it is for the other solvents with similar viscosities, and there is a steeper dependence on $1/\eta$. The tagged polymer was only slightly soluble in MeOH, even though the untagged polymer dissolves readily in this solvent, so MeOH was not used for the tagged polymer.

The intrinsic viscosities of the untagged novolac in several of the solvents are reported in *Table 1*. There is some variation in $[\eta]$ for the different solvents, with the alcohols yielding the lowest values of $[\eta]$ and the ether-alcohols generally having the highest values. The observed intrinsic viscosities are very close to those predicted from the literature Mark–Houwink constants for phenol-formaldehyde (PF) resins. Tobiason[21] found $[\eta] = 0.00661[M_N]^{0.28}$ for PF resins in MeOH at 25°C, and Kamide and Miyakawa[22] reported that $[\eta] = 0.0073[M_N]^{0.28}$ for PF resins in THF at 30°C. Using these relations, we find the predicted values of $[\eta]$ for our polymer to be 0.051 and 0.057 for MeOH and THF, respectively. These are within 10% of our measured values, in spite of the temperature difference for the THF measurements.

One measure of chemical compatibility is the solubility parameter, δ, defined byHildebrand[23] as

$$\delta_i \equiv (\mathrm{CED})^{1/2} \equiv \left(\frac{\Delta E_i}{V_i}\right)^{1/2} \qquad (1)$$

where CED is the cohesive energy density, ΔE is the molar energy of vaporization of a compound and V is its molar volume. To treat the thermodynamics of regular solutions, the enthalpy of mixing may be expressed in terms of δ by

$$\Delta H_M = V_i v_1 v_2 (\delta_1 - \delta_2)^2 \qquad (2)$$

where v_1 and v_2 are the volume fractions and δ_1 and δ_2 are the δ values of the solvent and solute, respectively. Often the enthalpic contributions are characterized in terms of the binary interaction parameter, χ, as

$$\chi_{12} = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \qquad (3)$$

Hildebrand demonstrated that differences in δ were useful in predicting the solubility behaviour of many non-polar solvents. Solubility parameters have been applied with only fair success to polymer–solvent systems, however.

The measurements of $[\eta]$ of a polymer in various solvents may be used to evaluate δ. The polymer is expected to be the most extended when δ for the solvent most closely matches that for the polymer, thus, a plot of $[\eta]$ *versus* δ should have a maximum at the δ value of the polymer[24]. Such a plot for untagged novolac in various solvents is given in *Figure 3*. A maximum in $[\eta]$ occurs at a δ value of ~10 cal$^{1/2}$ cm$^{-3/2}$. Although this is less than the value of 11.3 reported by Hansen[25] for phenolic resins, he does indicate that there may be some error in his measurement. The difference could also be due to the presence of *m*-methyl groups on our cresol-formaldehyde novolac compared to the phenolic novolac resin.

Film measurements

There are several questions related to aggregation of small dye molecules in novolac matrices that are of lithographic significance. The questions of greatest interest to us were the effects of casting technique and solvent choice on the extent of dye aggregation. Even though the majority of the solvent evaporates during the casting process (spin-cast films retain ~1–3% residual solvent[26]) and so is not a major component of the final film, the interaction of the solvent with the polymer and the chromophore may impact the structure of the cast film. The choice of casting technique may also affect the time scale over which casting occurs, and so the extent to which the thermodynamic and kinetic solvent–polymer and solvent–pyrene interactions influence film structure.

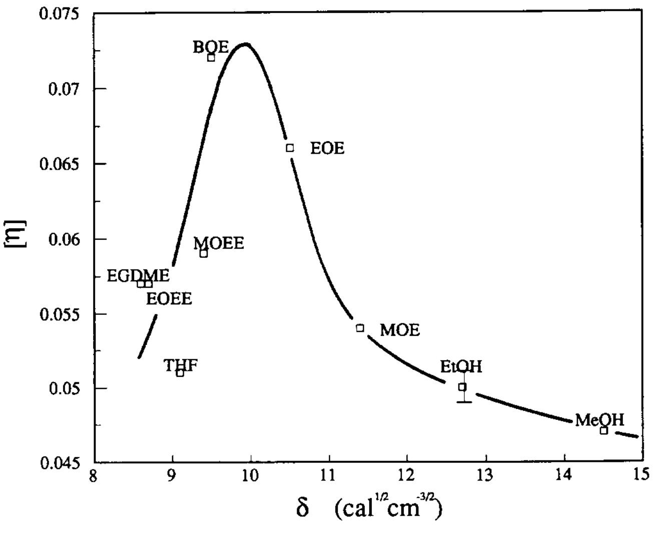

Figure 3 Intrinsic viscosity of untagged novolac in various solvents as a function of the solubility parameter of the solvent. The intrinsic viscosity is related to the size of the dissolved polymer coil

In order to evaluate the importance of the casting solvent on film homogeneity, films were cast from a series of solvents including the ethers THF, EGDME, EGDEE, MOEE and EOEE and ether-alcohols MOE, EOE and BOE. The differences in aggregation due to the casting solvent are expected to be the most obvious at higher pyrene concentrations, so the films were cast using either the novolac with the highest level of tagging, 0.20 mol ratio of pyrene to monomer, or from mixtures with an equivalent concentration of free pyrene. Films were also cast using 1.0 wt% of the 0.20 mol ratio pyrene tagged novolac in 99% untagged novolac. In this case, we are observing purely intramolecular excimer formation from isolated tagged coils.

The films were prepared using two different techniques—spin and static casting. The two methods differ in the length of time over which solvent evaporates and in the mechanical stress experienced during film formation. When films are static-cast, the casting process occurs over a much longer time span: 5–15 min as opposed to 5–30 s for spin casting. The slower static process should increase the likelihood that the system will achieve thermodynamic equilibrium prior to solidification, at which point the mobility of the components becomes severely restricted. The interactions between the solid components would be expected to be most important for static cast films. Due to the rapid solidification of spin cast films, the films cannot achieve a true thermodynamic equilibrium. The formation of the films may be affected much more by the interactions of the components with the solvent or the rate at which casting occurs.

If the rate of film formation is important, then aggregation might be expected to correlate with solvent properties such as boiling point, vapour pressure, evaporation rate or viscosity. If solvent–solute interactions are of prime importance, then aggregation may be correlated to solvent parameters such as the solvent polarity or δ. By comparison of different casting techniques, we can evaluate the relative importance of the various aspects of film formation. If phase separation of the components was thermodynamically favourable, it would be more likely to occur in the static-cast films. This was, in fact, observed as all of the static-cast films with free pyrene in novolac exhibited pyrene crystallite formation or visibly cloudy films. Only the spin-cast film prepared from MOE had a similar cloudy appearance. This indicates that in a thermodynamically controlled system, the free components will phase separate independent of the choice of casting solvent, within the set of solvents used in this study.

The excimer ratio is related to the local concentration of chromophores. If the chromophores aggregate during casting, the local concentration will increase. Thus, we expect that the excimer ratio will provide a measure of the compatibility of the polymer–chromophore–solvent system during film formation. This has been extensively studied by Gashgari, Semerak, Thomas and Tao in blends of amorphous polymers[9,17,28]. We attempted to correlate the excimer ratios measured for our films with solvent parameters related to the rate of solvent evaporation but found no correlation between I_E/I_M and boiling point, vapour pressure, evaporation rate or solvent viscosity. This indicated that the rate of film formation may not be a controlling factor in the homogeneity of these films.

Correlation of δ values with I_E/I_M has been used previously by Gashgari[9] for blends of poly(2-vinyl naphthalene) (P2VN) with various poly(alkyl methacrylates) prepared by static casting from toluene. Gashgari found that I_E/I_M varied with the δ of the host polymer using δ values calculated from Hoy's[29] group contributions. These calculated δ values give an internally consistent set of parameters, but tend to emphasize the dispersive rather than the polar or hydrogen bonding interactions. I_E/I_M for the P2VN guest polymer went through a minimum for host polymers that had δ values similar to P2VN, and increased as the difference in δ values increased. As in liquid solutions, the chains were believed to be more extended in the 'good' host polymer matrices, which had similar δ values and so the local concentration of chromophores was reduced. Conversely, high excimer ratios indicated higher incompatibility.

In the present investigations, the host polymer and the guest chromophore remain constant, and the excimer ratio will be used as a measure of the effects of casting technique and solvent on film formation. Unlike Gashgari's systems, our polymer and solvents have moderate polarities and hydrogen bonding capabilities. We have compared our I_E/I_M to experimental δ values that should include these interactions more accurately than the calculated values. The excimer ratios of the spin and static-cast films of tagged pyrene and the spin-cast films of the isolated tagged chains and novolac with free pyrene are plotted against the δ values of the casting solvents in *Figure 4*. The I_E/I_M values for the films with 1 wt% tagged polymer in untagged polymer have been multiplied by 100 so they can be compared on the same scale as the other films. The δ values of the solvents, along with literature values for PF resins[25,30] and pyrene (calculated from its heat of sublimation[31]) are tabulated in *Table 2*. The measurements of I_E/I_M for the static-cast films with free pyrene, which exhibited crystallite formation, varied widely even at different locations on a single film, probably due to variations in local pyrene concentration or structure. As a result, these measurements were not included.

There does appear to be a reasonable correlation between I_E/I_M for the spin-cast films and δ of the casting solvent. There appears to be less of a correlation for the static-cast films, however. This correlation is somewhat surprising because the final film contains, in principle, only the novolac and the pyrene. A minimum can be detected in the curves at δ values between 8.5 cal$^{1/2}$ cm$^{-3/2}$ and 9.5 cal$^{1/2}$ cm$^{-3/2}$. A δ of 9–9.5 cal$^{1/2}$ cm$^{-3/2}$ is in fair agreement with the maximum of ~10 cal$^{1/2}$ cm$^{-3/2}$ found from the $[\eta]$ values measured for the untagged novolac in a variety of solvents (*Figure 3*). The δ of pyrene, as calculated from its heat of vaporization[31], is ~10.6 cal$^{1/2}$ cm$^{-3/2}$. It has also been observed previously[32] that the measured δ of a material can vary slightly in different families of solvents. Since the minimum in I_E/I_M is close to that expected for both the polymer and pyrene, it is unclear whether the minimum is due to polymer–solvent or pyrene–solvent interactions. The minima for the films with free pyrene and those with isolated tagged chains are similar in location and shape, but there is a slight shift and broadening for the films of pure tagged polymer in the curves in *Figure 4*. We expected that the excimer fluorescence in the films with only 1% of tagged polymer will arise predominantly from intramolecular excimer

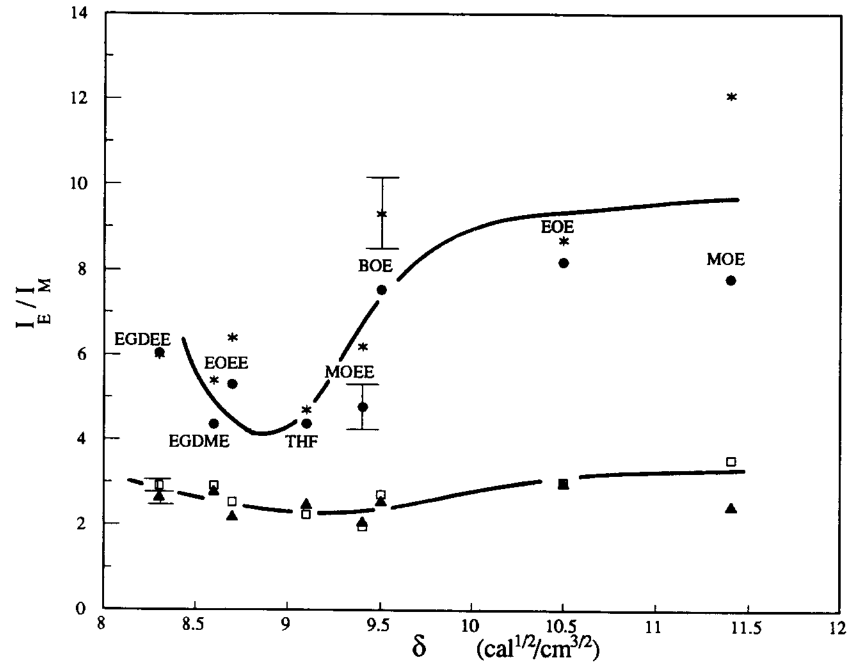

Figure 4 I_E/I_M of pyrene in films as a function of the solubility parameter of the casting solvent: (●) spin-cast films of 0.20 mol ratio of free pyrene in novolac; (▲) spin-cast films of 0.20 mol ratio pyrene tagged novolac; (□) static-cast films of 0.20 mol ratio pyrene tagged novolac; (*) spin-cast films of 1 wt% (0.20 pyrene tagged novolac) in untagged novolac. The data for the films with the mixture of tagged and untagged novolac have been multiplied by 100 so that they can be compared on the same scale with the other films

Table 2 Solubility parameters of solvents, phenolic resin and pyrene from the literature and calculated from equations (10)–(12)

	Solubility parameters ($cal^{1/2}\,cm^{-3/2}$)							
	δ_d		δ_p		δ_h		δ	
Compound	Lit.[28]	Calc.[29]	Lit.[29]	Calc.[28]	Lit.[28]	Calc.[29]	Lit.[9]	Calc.[29]
MEOH								
ETOH								
MOE	7.90	7.84	3.9	4.5	8.0	8.4	11.4	12.1
EOE	7.85	7.89	3.5	4.5	7.0	7.6	10.5	11.5
BOE	7.76	8.01	2.7	3.1	5.9	6.5	9.5	10.7
THF	8.22	7.89	3.1	2.8	3.9	2.6	9.1	8.9
EGDME	7.62		2.6			3.3	8.6	8.7
EGDEE	7.75		2.0			2.8	8.3	8.5
MOEE	7.89		2.4			3.4	9.4	8.9
EOEE	7.93		2.0			3.0	8.7	8.7
Phenolic resins	9.0	9.83	2.8	4.0	5.5	6.9	11.3[25]	12.3
Pyrene	11.5		0			0	10.6[36]	11.5

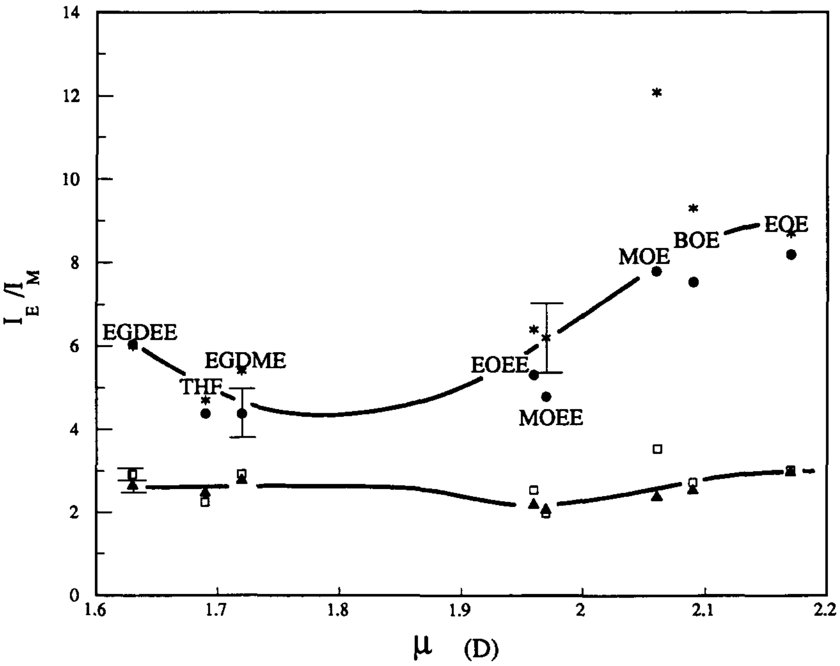

Figure 5 Dependence of I_E/I_M on the dipole moment of the casting solvent. Symbols as in *Figure 4*

formation, and so samples isolated chains. The excimer fluorescence from the films of pure tagged novolac must be primarily from intermolecular excimers or enhanced energy migration to the existing excimer-forming sites, as evidenced by the almost 100-fold increase in I_E/I_M. The intermolecular excimer formation is apparently less affected by solvent choice.

Both the solvents and the polymer used in this study have increased polarities and hydrogen bonding capabilities compared to the polymers studied by Gashgari[9]. In *Figure 5* we focus directly on these polar interactions, through correlation with the dipole moments of the solvents. The dipole moment of the solvents is directly related to δ_p, the polar contribution to the overall δ. All curves in *Figure 5* exhibit minima for solvents having dipole moments of ~1.80–1.90 D. Pyrene itself has no permanent dipole, and substituted pyrene might be expected to have a dipole moment similar to that of methyl or butyl naphthalene, which are in the range 0.37–0.75 D[33,34], so the minimum does not correlate with that expected from an interaction between the solvent and the chromophore. The dipole moment reported for PF resins in *p*-dioxane by Tobiason *et al.*[35] averages ~2.0 D, which is fairly close to the minima observed in our data. Tobiason *et al.* also reported that the dipole moments of the phenolic precursors were 0.1–0.2 D larger in dioxane than in benzene (which was the solvent used to measure all of the dipole moments of the casting solvents).

Taking this into account, the minima we observe in the I_E/I_M curves match very well with the predicted dipole moment of 1.8–1.9 for the polymer in benzene. This indicates that the value of I_E/I_M and hence the level of chromophore aggregation, is fairly independent of pyrene–solvent interactions, but rather depends on polymer–solvent interactions. This is supported by the observation that the minima for both the tagged and free pyrene films occur close to the same dipole moment, even though the dipole moments of the free and tagged pyrene probably differ by 0.4–0.7 D. If I_E/I_M were dependent on chromophore–solvent interactions, a shift in the position of the minima would be expected for the tagged *versus* free chromophores. The slight shift and broadening is again evident in the curves for the films of pure tagged polymer; however, the controlling factor appears to be similar in all cases.

The static-cast films of the tagged polymer in general have slightly higher values of I_E/I_M than the equivalent spin-cast films, but the differences are close to the experimental error. The static-cast film has a much longer casting time over which solvent evaporation occurs, and so a longer time for the thermodynamic effects which control component compatibility to take effect. Nevertheless, the level of aggregation is essentially the same as for the more rapid spin casting technique for the tagged films. By comparison, the aggregation in the films with free pyrene is much higher than for either the static or spin-cast films of the tagged polymer. The minimum also is much deeper for the spin-cast free pyrene films. As one moves away from the minimum, I_E/I_M increases much more quickly for the films with the more mobile free pyrene. The choice of solvent has a greater impact on the chromophore aggregation in these films. The static-cast films with the free pyrene all exhibited pyrene crystallization during casting, indicating the inherent immiscibility of the polymer–chromophore system at this concentration. The spin-cast films did not exhibit observable crystallization, presumably due to the speed at which the film is formed. For both the tagged and free pyrene, the spin-cast films are more homogeneous than the equivalent static-cast films.

In order to determine whether the trends observed above still occur at lower concentrations, films were spin-cast with 0.05 and 0.10 mol ratios for free pyrene in EGDEE, EOEE and EOE. The results are recorded in *Table 3*. Even though the excimer ratios are significantly reduced, the excimer ratio for EOEE is still lower than that for EGDEE and EOE, suggesting that the minimum still exists at the lower concentrations.

DISCUSSION

Solution studies

The measurements of the solutions of tagged novolac indicated that the samples dissolved in the alcohols had significantly higher levels of excimer formation than expected from the viscosity of these solvents. The excimer formation is affected by the local concentration of pyrene. It is possible that the polymer coil is more compact in the alcohols, resulting in an increase in the local concentration of pyrene. An estimate of the dimensions of a polymer coil can be derived from its $[\eta]$. In this way, we can evaluate whether the change in coil volume in the different solvents is sufficient to explain the deviations in I_E/I_M.

Table 3 I_E/I_M for spin-cast films of novolac with various levels of free pyrene

	Mole ratio pyrene/monomer		
Solvent	0.05	0.10	0.20
EOE	0.094	0.442	8.19
EOEE	0.077	0.395	5.31
EGDEE	0.088	0.524	6.05

The volume of a polymer coil is related to its $[\eta]$ by the relation[36]:

$$[\eta] = \Phi \frac{\langle R^2 \rangle^{3/2}}{M} = \Phi 6^{3/2} \frac{\langle S^2 \rangle^{3/2}}{M} \qquad (4)$$

where Φ is a universal constant, $\langle R^2 \rangle$ is the mean squared end-to-end distance, $\langle S^2 \rangle$ is the mean squared radius of gyration and M is the molecular weight. The universal constant does vary with the polydispersity of the polymer, with $\Phi = 2.7 \times 10^{23}$ for well fractionated polymers ($M_W/M_N \leqslant 1.25$) and $\Phi = 2.1 \times 10^{23}$ for poorly or unfractionated polymers ($M_W/M_N > 2.5$)[30].

Equation (4) is generally applicable for linear polymers. Polymers formed from *m*-cresol, however, are expected to have some branching due to the presence of three reactive sites on the *m*-cresol. It is also interesting to note that Mark–Houwink exponents determined by both Tobiason[21] and Kamide[22] for similar formaldehyde resins are 0.28. A value of the exponent of <0.5 is generally an indication of branching in the polymer chain[22]. Zimm and Stockmayer[37] developed a theory to predict the effect of branching on coil dimensions. They defined a variable, g, such that:

$$\langle g \rangle \equiv \frac{\langle S^2 \rangle_b^{1/2}}{\langle S^2 \rangle_l^{1/2}} \qquad (5)$$

where $\langle S^2 \rangle_b^{1/2}$ and $\langle S^2 \rangle_l^{1/2}$ are the root mean square radii of gyration of the branched and linear polymers, respectively. For a monomer with three active sites,

$$\langle g \rangle = \left[\left(1 + \frac{m}{7}\right)^{1/2} + \frac{4m}{9\pi} \right]^{-1/2} \qquad (6)$$

where m is the average number of branch units per molecule. Kamide and Miyakawa[22] determined that $m/M_N = 1.99 \times 10^{-3}$ for their PF resin. If we assume that the level of branching is similar for our cresol-formaldehyde resin, we would expect about three branches per chain for $M_N = 1500$ and a $\langle g \rangle$ value of 0.78. This assumption seems reasonable due to the close similarity of the monomers and the fact that our observed $[\eta]$ closely matched the prediction of their Mark–Houwink parameters.

We can now estimate the size of the polymer coils from their $[\eta]$ values. The results of these calculations are included in *Table 1*. If we make the crude assumption that the chromophores are evenly distributed in the coil volume, we can estimate the average distance of chromophore separation. These values are also recorded in *Table 1*. It is obvious that the differences in coil dimensions are not great in any of the solvents. The differences in the alcohols and the other solvents are not sufficient to account for the observed differences in I_E/I_M. Other interactions must come into play.

Several researchers[38–40] have noted deviations in I_E/I_M of pyrene end tagged polymers dissolved in water and methanol from the linear $1/\eta$ dependence exhibited for other solvents. They have proposed that hydrophobic interactions of the pyrene in these strongly hydrogen bonding solvents increases the probability of pyrene–pyrene interactions, and so increases I_E/I_M. Char *et al.*[38] have developed a model that employs a 'capture process' proposing that if two chromophores come within twice their capture radius of each other they will be attracted to each other and form an excimer. The capture radius varies with solvent, with a capture radius of ~6.5 Å for pyrene end tags in methanol. Two times the capture radius is about half of our predicted distance of chromophore separation. While the I_E/I_M ratios for the alcohols are higher than expected from their viscosity, they are not sufficiently elevated to support that large of a decrease in inter-chromophore separation. It is probable, however, that the higher alcohols have a smaller hydrophobic effect, and so a smaller capture radius, than methanol. This is supported by the fact that the tagged polymer would not completely dissolve in MeOH but it dissolved easily in the other alcohols. Hydrophobic interactions are probably responsible for much of the increased excimer ratio observed in the alcohols.

Excimer formation may also be modified by the mobility of the chromophores. The pyrene tags are randomly attached to the backbone of the novolac. Those attached to the middle of the chain may have more limited mobility than end tagged chromophores. This has been suggested by Dill's work on loop formation in linear polymers[41]. He predicted that internal loop formation was about two to almost 10 times less likely than end-to-end cyclization, depending on the size of the loop. The branching of the polymer may also create increased steric hindrance in the approach of two chromophores.

Film studies

Differences in the excimer ratio were observed in spin-cast films, even for casting solvents that did not exhibit specific interactions with the components in solution. The observed differences in excimer ratio did not correlate at all with the 'kinetic' casting parameters such as boiling point, vapour pressure, evaporation rate or solvent viscosity. There did appear to be a correlation with the casting solvents δ value and dipole moment, however.

Several attempts have been made to refine δ and to improve its predictive power, especially for polar solvents and solutes, and for systems in which hydrogen bonding is a significant factor[42]. Van Arkel and Vles[43] suggested an approach that explicitly includes dipole–dipole interactions such that

$$\delta^2 = \delta_p^2 + \delta_d^2 \qquad (7)$$

where δ_p is the portion of δ that is due to polar interactions and δ_d is the portion of δ that is due to purely dispersive interactions. Many attempts have been made to divide δ further by adding a third component, δ_h, which is due to hydrogen bonding interactions, yielding

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (8)$$

Hansen used this three-dimensional approach in determining the interactions of polymers with solvents and plasticizers[25]. Chen[44] found a two-dimensional approach to be useful in evaluating the interactions of solvents and polymers. In Chen's approach, he combined the dispersive and polar parameters into a single X parameter, similar to Flory's, such that,

$$X = \frac{V_1}{RT}\left[(\delta_{d,L} - \delta_{d,P})^2 + (\delta_{p,L} - \delta_{p,P})^2\right] \qquad (9)$$

where L and P stand for liquid (solvent) and polymer (solute), respectively. Chen plotted this X parameter against δ_h, assuming that the scale for X was twice the scale for δ_h. The interactions can then be judged from their radial separation distances on the plot, with good solvents lying closer to the solute than poor solvents. Unfortunately, it is difficult to determine the exact contribution to δ from the various types of interactions. In general, δ_d is related to the thermal expansion coefficient, α; δ_p is proportional to the dipole moment; and δ_h is related to measurements of hydrogen bonding, but exact relationships are difficult to determine.

Hansen[45] has reported experimentally derived values of δ_d, δ_p and δ_h for over 100 solvents, including MOE, EOE, BOE and THF, and for over 30 polymers and resins[25], including a PF resin. The values for the materials that are used in this study are included in *Table 2*. Koenhen[46] has proposed the following empirical expressions for relating various properties of materials to their δ values,

$$\delta_d = 9.55 n_D - 5.55 \qquad (10)$$

$$\delta_p = 50.1 \frac{\mu}{V^{3/4}} \qquad (11)$$

$$\delta_h = \sqrt{\frac{E_h}{V}} \qquad (12)$$

where n_D is the refractive index, μ is the dipole moment and E_h is the enthalpy of a hydrogen bond or donor/acceptor group. The constants were derived by fitting Hansen's solvent data. Hansen and Beerbower[47] report values of E_h to be ~20 kJ mol^{-1} for an alcohol group and ~2 kJ mol^{-1} for an ether group. The values for δ_h incorporate the greatest error[45]. The values of δ_d, δ_p and δ_h calculated from equations (10)–(12) for the solvents, pyrene and novolac are also reported in *Table 2*.

If I_E/I_M is indeed related to the solubility of novolac in the various solvents, then plots of the individual δ values might be expected to exhibit minima at the values for novolac. I_E/I_M values for the spin-cast films with free pyrene and the isolated tagged chains have been plotted against δ_d, δ_p and δ_h in *Figures 6A, B* and *C*. We have employed Hansen's experimental values of δ_d, δ_p and δ_h when possible, and have used the calculated values for the other solvents. There does not appear to be any correlation between δ_d and I_E/I_M (*Figure 6A*), which is not unexpected if the value of δ_d for novolac is ~9–9.8 cal$^{1/2}$ cm$^{-3/2}$ as predicted. Shallow minima appear in both *Figures 6B* and *C*. The minimum in *Figure 6B* occurs at about the value of δ_p calculated from equation (11) for novolac, although it is smaller than the value of 4.0 cal$^{1/2}$ cm$^{-3/2}$ found experimentally by Hansen. This is consistent with the minimum we observed earlier in the plot of I_E/I_M *versus* dipole moment at the experimental dipole moment of novolac (*Figure 5*). There is also a minimum observable in the graph of δ_h *versus* I_E/I_M at ~4–5 cal$^{1/2}$ cm$^{-3/2}$. This is lower than the value of 6.8 cal$^{1/2}$ cm$^{-3/2}$ calculated from equation (12) for novolac, but only slightly lower than the value of 5.5 cal$^{1/2}$ cm$^{-3/2}$ predicted by Hansen. As previously mentioned, calculated values of δ_h may be rather inaccurate.

In our ternary system, there are several interactions that may influence the homogeneity of the final film, including polymer–solvent, polymer–pyrene and pyrene–solvent interactions. We are interested in determining which of these interactions may be the most influential in controlling the formation of the polymer–pyrene films. We have plotted the solvent–solute interactions for both novolac and pyrene in *Figure 7* using the scheme proposed by Chen[44], including interactions for pyrene with novolac, in order to try and evaluate the relative importance of each type of interaction. We have used Hansen's δ values for the novolac, and the smallest molar volume for V in equation (9). We have included a few typical solvent/solute radii on the graph for comparison of novolac and pyrene interactions with the solvents and with each other. The novolac–solvent interactions appear to be much more favourable than either the novolac–pyrene or the pyrene–solvent interactions. The ether-alcohols are predicted to have a similar level of attraction to the novolac as the ethers. Novolac is approximately as good a solvent for pyrene as the ethers, and is significantly better than the ether-alcohols. The ether-alcohols exhibited the highest level of aggregation in the cast films.

Hansen[48] has suggested that to produce mutual solubility between polymer–polymer and polymer–pigment systems, the solvent must be most closely matched with the component that has the highest molecular weight. In fact, the δ values of our solvents are fairly closely matched to the novolac. He also suggests that the dye–solvent interactions should be small to enhance the dye–polymer interactions. If this were true in our case, we would expect the ether-alcohols to produce the most homogeneous films. Instead, we find optimum homogeneity, as measured by the excimer ratio, when the polymer–pyrene and solvent–pyrene inter-

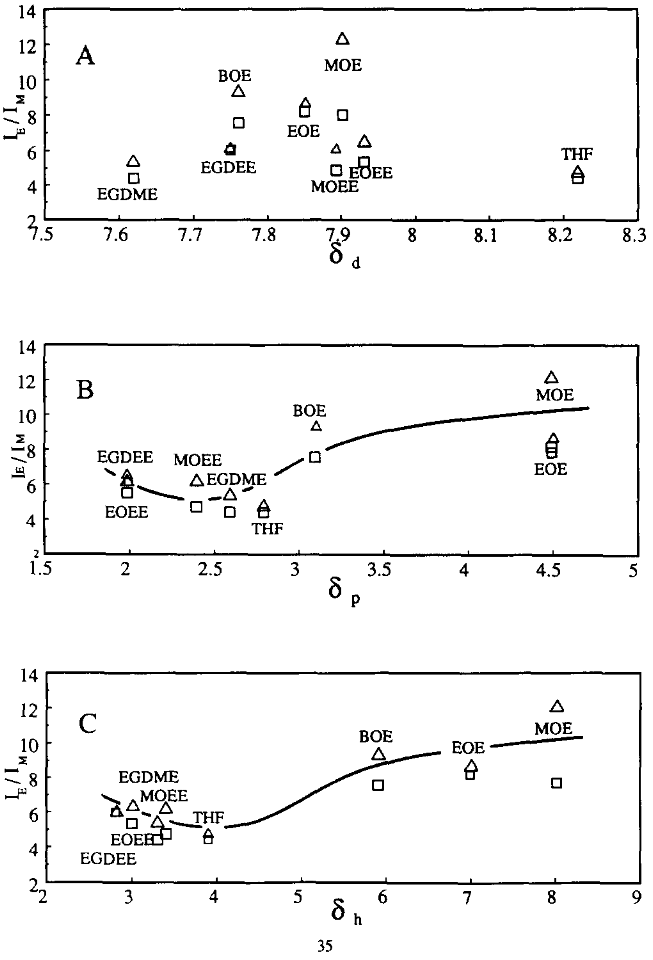

Figure 6 Dependence of I_E/I_M on (A) the dispersive solubility parameter, (B) the polar solubility parameter, (C) the hydrogen bonding solubility parameter of the casting solvents: (□) 0.20 mol ratio free pyrene in novolac; (△) 1 wt% (0.20 tagged novolac) in untagged novolac

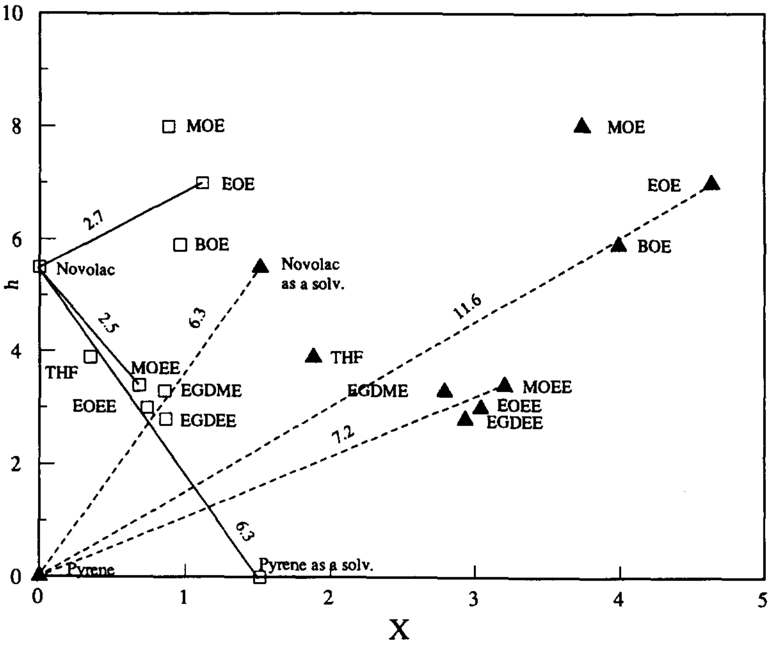

Figure 7 Relative affinity of pyrene and novolac for the various casting solvents and each other as predicted by their differences in χ and δ_h. The interactions are predicted to be related to the radial distance of the solvent from the solute. A selection of radii, in units of scale used for δ_h, are included for comparison

actions are predicted to be approximately equivalent. Frank and Zin[49] found that homogeneous films of polystyrene and poly(vinyl methyl ether) were formed when cast from a solvent that had similar interactions with both polymers, but that phase separation occurred when the extent of interaction of the solvent with the polymers was dissimilar. This observation does not explain our results either, since the interactions of the solvent with the polymer are much stronger than the pyrene–solvent interactions.

One way to interpret the excimer data with the apparent solvent–solute interactions is to consider the hydrogen bonding of the novolac more closely. It has been widely reported that novolacs have significant levels of intermolecular and intramolecular hydrogen bonding[50–56]. It has also been proposed that this intramolecular bonding can cause conformational changes in the novolac that tend to internalize the hydrophilic hydrogen-bonded portions, resulting in the exterior of the molecule being more hydrophobic[56]. The pyrene would have more favourable interactions with the more hydrophobic portions of the polymer. When dissolved in the ethers, the intramolecular hydrogen bonding would probably be stronger than that to the solvent. Hence, the solvent would do less to disrupt the polymer conformation. The pyrene also has about equal interactions with the polymer and the solvents. In the ether-alcohols, however, there should be increased hydrogen bonding between the polymer and the solvents, which may tend to orient the phenolic groups towards the outside of the polymer, decreasing its interactions with the pyrene. The ether-alcohols are predicted to be good solvents for the novolac, which is supported by our $[\eta]$ measurements. They are also poorer solvents for the pyrene, which would lead to a greater preference for pyrene–pyrene interactions over pyrene–novolac–solvent interactions, and hence promote pyrene aggregation during casting.

SUMMARY

For lithographic resists, the polymer and the sensitizer are relatively fixed by the requirements of processing, allowing limited options to improve compatibility through chemical modification. There is some flexibility in the choice of casting solvent, however. Our investigations have focused on whether the casting solution and the final film are affected by the choice of casting solvent, and if so, what physical parameter of the solvent is the most relevant in predicting film uniformity. These systems have also allowed us to observe the effects of various solvents on the extent of aggregation, as well as to compare different casting techniques.

Solvent specific effects were observed for the tagged novolac in solutions of alcohols. The effect has been observed before for pyrene end tagged polymers, and is suspected to be due to hydrophobic interactions of the pyrene molecules. Even though there did not appear to be solvent specific interaction of the tagged novolac in solutions of the ethers and ether-alcohols, differences did appear when films were cast from these solvents. The pyrene aggregates to a different extent in the various solvents. The aggregation of free pyrene in films cast from MOEE and EOE was dependent on both the concentration of the pyrene as well as the solvent. Aggregation of the free pyrene in both solvents appeared to differ significantly from that of pyrene tagged to the polymer backbone at concentrations of 0.06–0.10 mol ratio pyrene.

The level of aggregation varied with casting technique and choice of casting solvent. Spin-cast films exhibited less aggregation than equivalent static-cast films. In the extreme case, pyrene crystallites formed in static-cast films with free pyrene. The effect of solvent on film uniformity was dependent on δ, although the best correlation was found to be with the dipole moment of the solvent. The least aggregation occurs when the dipole moment of the casting solvent matches that predicted for the polymer matrix. This relation seems to be fairly independent of the characteristics of the chromophore. A comparison of calculated δ values, δ_d, δ_p and δ_h, also indicated a good correlation between δ_p and pyrene aggregation. The correlation with δ_h indicated that solvents that form strong hydrogen bonds may produce more aggregated films. This result indicates that improved uniformity in multicomponent films can be achieved by matching specifically the polar aspects of the solvent with the polymer matrix.

ACKNOWLEDGEMENT

This work was supported by the Semiconductor Research Corporation through the Sematech Center of Excellence in Lithography and Pattern Transfer.

REFERENCES

1 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660
2 Huggins, M. L. *J. Chem. Phys.* 1941, **9**, 440
3 Wilson, C. G. *ACS Symp. Ser.* 1983, **219**, 87
4 Bowden, M. J. *ACS Symp. Ser.* 1984, **266**, 39
5 Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New York, 1978
6 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
7 Semerak, S. N. and Frank, C. W. *Adv. Polym. Sci.* 1983, **54**, 31
8 Winnik, M. A. 'Photophysical and Photochemical Tools in Polymer Science', D. Reidel, Dordrecht, 1986
9 Frank, C. W. and Gashgari, M. A. *Macromolecules* 1979, **12**, 163
10 Semerak, S. N. and Frank, C. W. *Macromolecules* 1981, **14**, 443
11 Gashgari, M. A. and Frank, C. W. *Macromolecules* 1981, **14**, 1558
12 Semerak, S. N. and Frank, C. W. *Adv. Chem. Ser.* 1983, **203**, 757
13 Gelles, R. and Frank, C. W. *Macromolecules* 1983, **16**, 1448
14 Semerak, S. N. and Frank, C. W. *Macromolecules* 1984, **17**, 1148
15 Frank, C. W. and Zin, W. C. *ACS Symp. Ser.* 1987, **358**, 18
16 Gashgari, M. A. and Frank, C. W. *Macromolecules* 1988, **21**, 2782
17 Tao, W. C., Thomas Jr, J. W. and Frank, C. W. *Polymer* 1988, **29**, 1625
18 Kosbar, L. L., Kuan, S. W. J., Frank, C. W. and Pease, R. F. W. *ACS Symp. Ser.* 1989, **381**, 95
19 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley-Interscience, London, 1969, Ch. 7
20 Riddick, J. A., Bunger, W. B. and Sakano, T. K. 'Organic Solvents: Physical Properties and Methods of Purification', 4th Edn, John Wiley and Sons, New York, 1949
21 Tobiason, F. L., Chandler, C. and Schwartz, F. E. *Macromolecules* 1972, **5**, 321
22 Kamide, K. and Miyakawa, Y. *Makromol. Chem.* 1978, **179**, 359
23 Hildebrand, J. H. and Scott, R. L. 'The Solubility of Non-Electrolytes', 3rd Edn, Reinhold, New York, 1949
24 Spurlin, H. M. *J. Polym. Sci.* 1948, **3**, 714
25 Hansen, C. M. *J. Paint Technol.* 1967, **39**, 104
26 Thompson, L. F. and Bowden, M. J. *ACS Symp. Ser.* 1983, **219**, 161
27 Frank, C. W. and Gashgari, M. A. *Ann. NY Acad. Sci.* 1981, **366**, 387

28 Frank, C. W., Gashgari, M. A. and Semerak, S. N. 'Photochemical and Photophysical Tools in Polymer Science' (Ed. M. A. Winnik), D. Reidel, Dordrecht, 1986, pp. 523–546

29 Hoy, K. L. *J. Paint Technol.* 1970, **42**, 76

30 Burrell, H. 'Polymer Handbook, 2nd Edn' (Eds J. Brandrup and E. H. Immergut), John Wiley and Sons, New York, 1975, pp. IV337–359

31 Cox, J. D. and Pilcher, G. 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London, 1970, p.187

32 Semerak, S. N. and Frank, C. W. *Macromolecules* 1981, **14**, 443

33 McClellan, A. L. 'Tables of Experimental Dipole Moments', W. H. Freeman and Co., San Francisco, 1963

34 McClellan, A. L. 'Tables of Experimental Dipole Moments Volume 2', Rahara Enterprises, El Cerrito, 1974

35 Tobiason, F. L., Cain, G. H. and Anderson, J. W. *J. Polym. Sci., Polym. Chem. Edn* 1978, **16**, 275

36 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953, p. 611

37 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301

38 Char, K., Frank, C. W., Gast, A. P. and Tang, W. T. *Macromolecules* 1987, **20**, 1833

39 Oyama, H. T., Tang, W. T. and Frank, C. W. *Macromolecules* 1987, **20**, 1839

40 Cheung, S-T., Winnik, M. A. and Redpath, A. E. C. *Makromol. Chem.* 1982, **183**, 1815

41 Chan, H. S. and Dill, K. A. *J. Chem. Phys.* 1989, **90**, 492

42 Barton, A. F. M. 'CRC Handbook of Solubility Parameters and Other Cohesion Parameters', CRC Press, Inc., Boca Raton, 1983

43 Van Arkel, A. E. and Vles, S. E. *Trans. Faraday Soc.* 1946, **42B**, 81

44 Chen, S-A. *J. Appl. Polym. Sci.* 1971, **15**, 1247

45 Hansen, C. M. *IEC Prod. Res. Dev.* 1969, **8**, 2

46 Koenhen, D. M. and Smolders, C. A. *J. Appl. Polym. Sci.* 1975, **19**, 1163

47 Hansen, C. M. and Beerbower, A. 'Encyclopedia of Chemical Technology', Suppl. Vol., Wiley, New York, 1971, p. 889

48 Hansen, C. M. *J. Paint Technol.* 1967, **39**, 505

49 Frank, C. W. and Zin, W-C. *ACS Symp. Ser.* 1987, **352**, 18

50 Fahrenholtz, S. R. and Kwei, T. K. *Macromolecules* 1981, **14**, 1076

51 Yang, T. P., Pearce, E. M., Kwei, T. K. and Yang, N. L. *Macromolecules* 1989, **22**, 1813

52 Kim, H-I., Pearce, E. M. and Kwei, T. K. *Macromolecules* 1989, **22**, 3374

53 Sprengling, G. R. *J. Am. Chem. Soc.* 1954, **76**, 1190

54 Cairns, T. and Eglinton, G. *J. Chem. Soc.* 1965, 5906

55 Gupta, N. D. and Chatterjee, S. K. *J. Polym. Sci., Polym. Chem. Edn* 1974, **12**, 211

56 Templeton, M. K., Szmanda, C. R. and Zampini, A. *Proc. SPIE* 1987, **771**, 136