Spectroscopic studies of spin-coated dye-in-polymer films. On the relationship between compatibility and aggregation of small molecules in polymer matrices

Kock-Yee Law
Xerox Webster Research Center, 800 *Phillips Road,* W114, *Webster, NY* 14580, *USA*
(*Received* 29 *December* 1981; *revised* 26 *February* 1982)

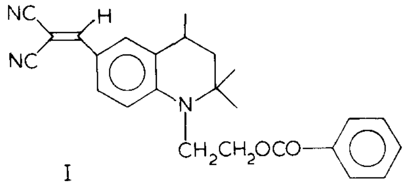
Dye-in-polymer (DIP) films of various concentrations of I (a *p-N,N*-dialkylaminobenzylidenemalononitrile derivative) in four polymers of different dye–polymer compatibilities have been prepared by spin-coating technique using a wide range of coating speeds (600–8000 rpm). The aggregation of dye molecules in polymer matrix was studied by electronic spectroscopy. The dye–polymer compatibility of various DIP systems was examined by d.s.c. Our results indicate that there exists a saturated concentration of I in each polymer and this saturated concentration decreases as the dye–polymer compatibility decreases, e.g. it decreases from ~20% in poly(vinyl acetate) and in poly(isobutyl methacrylate) to ~10% in styrene/isobutyl methacrylate (8:2) copolymer to ~5% in polystyrene. At dye concentrations lower than this saturated concentration, the degree of dye aggregation is not sensitive to varying spin-coating speeds. At dye concentrations higher than this saturated concentration, the degree of dye aggregation depends on the degree of dye–polymer incompatibility and on the spin-coating speed. The significance of the present work in solvent coating technology of small molecule/polymer systems, in general, will be discussed. Finally, the T_g's of various DIP systems were found not to correlate with the dye concentration (by weight). This is attributable to the strong dye–dye interaction of I inside the polymer matrix.

Keywords Spin-coating; dye aggregation; dye–polymer compatibility; dye–polymer film

INTRODUCTION

Spin-coating has long been recognized in the fabrication of semiconductor devices in industry. Applications in photoresist[1], electron resist[2] and magnetic disc[3] have already been documented in the literature. Studies on the uniformity of spin-coated films and the dependence of film thickness upon dispense volume, dispense spin-speed and spin-coating speed of the substrate have been advanced by O'Hagan and Daughton[4], and Givens and Daughton[5]. These authors found that the average film thickness of a spin-coated film is independent of the dispense spin-speed and of the dispense volume, but is a strong function of the spin-coating speed. All these coating parameters have also been studied theoretically by Washo[6]. Because of the unique characteristic of spin-coated films, the combination of high uniformity and high reproducibility, it has recently been used as a fabrication technique for organic dye-in-polymer optical disc[7,8].

We[9] have recently reported a study on the photochemistry of *p-N,N*-dialkylaminobenzylidenemalononitriles. The S_1 state of this class of meterials is a charge-transfer π,π^* state which undergoes predominantly radiationless decay *via* molecular relaxation. This molecular relaxation can be slowed down *via* increasing the molecular rigidity of the chromophore[9], increasing the solvent viscosity of the medium[10], or decreasing the ambient temperature[9]. Because of the technological significance of *p-N,N*-dialkylaminobenzylidenemalononitrile, I, in ablative optical recording [7a], I was further studied in a wide range of concentrations ranging from 1% to 60% by weight in poly(vinyl acetate) matrices[11]. Spectroscopic results showed that, below 20% dye loading, the dimeric species of I exist in equilibrium with the monomers, with an equilibrium association constant of 1.56 M^{-1}. Further increase in dye concentration leads to the formation of higher aggregates. The fluorescence quantum yields (φ_f) of the dye monomer, dimer and higher aggregates were determined to be ~0.01, ~0.1 and 0.066, respectively. The higher φ_f of the dimer and the higher aggregates was attributed to the decrease in rate of radiationless decay of I due to the restricted molecular relaxation resulting from the binding of dye molecules.



I

Owing to the spectral differences in the monomer emission (emission maximum, λ_F, ~490 nm) and the dimer or higher aggregates emission (λ_F ~590 nm), very small change in monomer concentration (to form dimer or higher aggregates) will be magnified by a factor of 7–10 in the long wavelength emission intensity. In the present work we make use of our previous spectroscopic results to investigate the aggregation of I in various spin-coated

0032—3861/82/111629–09$03.00

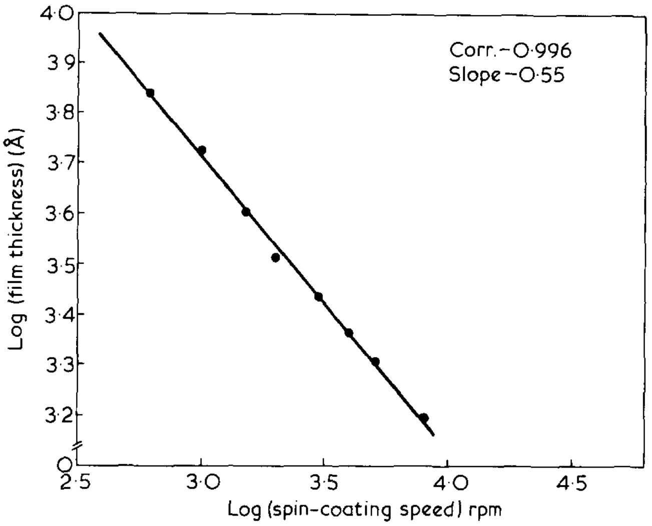


Figure 1 Plot of log (film thickness) *versus* log (spin-coating speed)

dye-in-polymer films. The coating characteristics of these spin-coated films are shown to be very similar to those previously reported by others[4,5]. Since it is known that the microscopic structure of dyes in polymer matrix may have a profound effect on the performance of a given device[12,13], fundamental understanding of the effect of various coating parameters on the resulting dye aggregation in polymer matrix will certainly have an impact on solvent coating technology. We here describe an investigation on the effects of dye–polymer compatibility and of the evaporation rate of coating solvent, which is controlled by the spin-coating speed, on the degree of aggregation of I in various dye-in-polymer systems. An empirical relationship between dye–polymer compatibility and spin-coating speed is obtained and the technological implication of the present work is discussed.

EXPERIMENTAL

Materials

Compound I was obtained from Eastman Chemicals and was purified as described previously[9]. Styrene/isobutyl methacrylate (8:2) copolymer (S-iBMA) ($MW = 44500$, $M_n = 16644$), was by courtesy of Dr B. Grushkin (Xerox Webster Research Center). Poly(vinyl acetate) (PVAc) was B12 grade from St. Lawrence Company; poly(isobutyl methacrylate) (PiBMA) was secondary standard from Aldrich ($MW = 369000$, $M_n = 128000$); polystyrene (PS) was from Polysciences Inc. ($MW = 20000$); and 1,1,2-trichloroethane (technical grade), methylene chloride (spectral grade) and 3-pentanone (practical) were from Fisher. All these materials were used as received. Glass substrates (2″ x 2″) were bought from Corning (7059) and were washed by soapy water and distilled water (twice) in an ultrasonic bath; they were then cleaned by ethanol vapour (refluxed over 95% ethanol) before use.

Preparation of dye-in-polymer (DIP) films

Various coating solutions of dye I and polymers (of known dye–polymer ratio) in 1,1,2-trichloroethane (or 3-pentanone) were prepared by vibrating the dye–polymer materials in an ultrasonic bath until a clear solution was achieved. The concentration of the coating solution, which ranges from 1 to 6%, is chosen in such a way that the thickest spin-coated DIP film prepared from a given coating solution will have an absorbance of $\lesssim 0.25$ at the excitation wavelength (400 or 410 nm). Each of these solutions was filtered through a 0.2 μm Millipore filter, then spin-coated at varying speeds (600–8000 rpm) onto precleaned 2″ x 2″ glass substrates using a Headway Research Photo-resist spinner (Model 1-EC-101). Uniform and optically clear films were obtained. The absorbance and the thickness of the resulting films were measured using a Cary 17 spectrophotometer and a Tallystep instrument, respectively.

DIP films for differential scanning calorimetry (d.s.c.) measurements were prepared by solvent casting 5% methylene chloride solutions of known dye–polymer ratios onto pre-cleaned glass substrates. The resulting films were dried slowly at room temperature for ~14 h and then vacuum-dried at ~50°C for another 48 h. Controlled experiments indicated that films prepared by these procedures were solvent free.

Luminescence measurements

Fluorescence emission and fluorescence excitation spectra were recorded by front surface illumination on a Perkin-Elmer MPF 4 spectrofluorimeter which was equipped with a differential corrected spectra unit (d.s.c.u.-2). The optical densities of all the dye-in-polymer samples were $\lesssim 0.25$ at the excitation wavelength. Controlled experiments showed that the polymer films themselves did not show any absorption or emission under the experimental conditions.

Analysis of absorption and fluorescence emission spectral data

The absorption coefficient (α) of I in polymer matrix is given by:

$$\alpha = \frac{\text{(optical density)}}{\text{(dye concentration)(film thickness)}}$$

For a given set of spin-coated DIP films (prepared from the same coating solution at varying spin-coating speeds (600–8000 rpm)), the film thickness increases as the spin-coating speed decreases (*Figure 1*). In the present study, the α of I of each individual film was not calculated, instead, it was examined by plotting the optical density (o.d.) at a given wavelength as a function of film thickness. Selected examples are shown in the insets of *Figure 2*. Straight lines having intercept very close to zero indicate that the α of I is unchanged for a given set of spin-coated films. Any deviation from this linearity indicates changes of the α of I, implying that the morphology of I changes as the spin-coating speed varies.

The φ_f of I is known to be very sensitive to its immediate surrounding[10] in the matrix and this issue will be addressed elsewhere[14]. Only relative φ_f is considered in the present work. The relative φ_f of I for a given set of spin-coated films is evaluated by plotting the relative fluorescence emission intensity (I_f) at the emission maximum as a function of the o.d. at the excitation wavelength. Examples are given in the insets of *Figure 3*. A linear relationship with an intercept close to zero indicates a constant φ_f value for a given set of spin-coated films. However, any deviation from this linearity will serve as a gauge for detecting any aggregational changes of I as the spin-coating speed decreases.

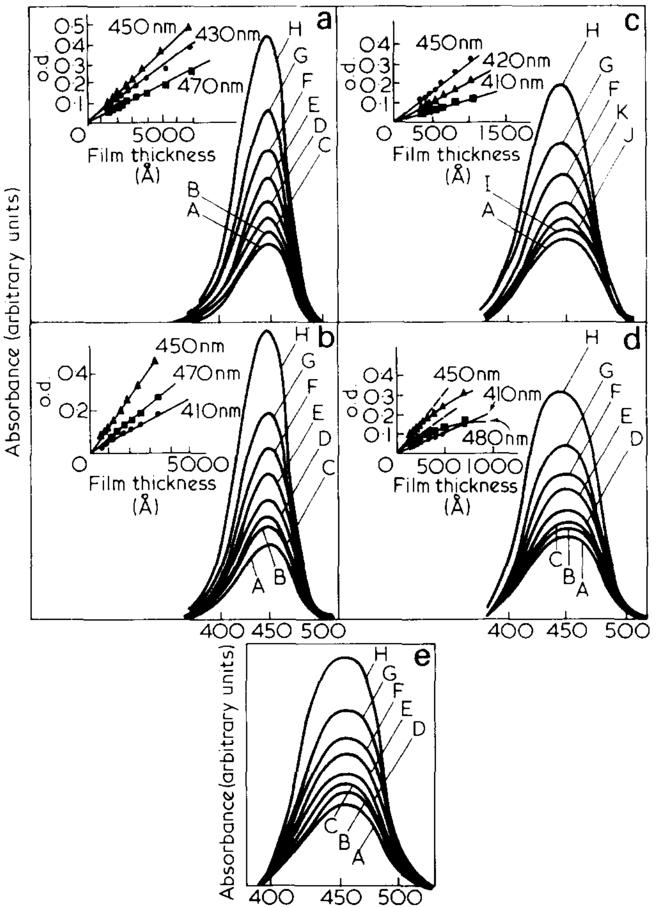


Figure 2 Absorption spectra of spin-coated DIP films of I in PVAc at (a) 5%, (b) 10%, (c) 20%, (d) 40%, and (e) 60% dye loading A, 8000; B, 5000; C, 4000; D, 3000; E, 2000; F, 1500; G, 1000; H, 600; I, 4500; J, 3500 rpm, and K, 2500 rpm)

Differential scanning calorimetry (d.s.c.)

Glass transition temperatures (T_g) were determined by d.s.c. using a Dupont 990 Thermal Analyser provided with a low temperature attachment for subambient operation. Various samples (~10 mg) were weighed on a Perkin-Elmer autobalance. A scan rate of 5°C/min was used throughout the runs. The T_g was taken as the intercept of the sloping part of the curve with the extrapolated low temperature baseline (from the second scan).

RESULTS AND DISCUSSION

Preparation of spin-coated dye-in-polymer (DIP) films

As indicated in the introductory section, spin-coating has been a versatile process for coating uniformly thin film on round substrates. Recent studies by Givens and Daughton on a polyimide solution (PIQ, from Hitachi Chemical Company) indicate that the average film thickness obtained by spin-coating is independent of the dispense speed of the substrate and the dispense volume of the coating solution[5]. Brief examination on these two parameters indicates that similar independence is also observed for the DIP films prepared in the present work. Also in good agreement with the previous work[4,5], the average film thickness of the spin-coated film is a strong function of the final spinning speed of the substrate. *Figure 1* gives a typical example of this kind by plotting log (film thickness) *versus* log (spinning speed) using a 5% dye–polymer (1:9) 3-pentanone solution. The linear correlation of the straight line is −0.996 and the slope is −0.55. Similar characteristics were also obtained from other coating solutions throughout the present study. Theoretical modelling of the spin-coating process has been advanced by Washo[6], who calculated and experimentally showed that, for a steady state Newtonian fluid, the slope of the log (thickness) vs. log (spin speed) plot should be −0.67. The slopes of all the dye–polymer coating solutions presently studied are in the range of −0.4 to −0.6. This indicates that the spin-coating process investigated here does not behave in a Newtonian manner, but is in good agreement with other low viscosity coating solutions reported in the literature which give slopes ranging from −0.4 to −0.7[1,15,16].

Spectroscopic studies of spin-coated DIP films: (I) In PVAc

Absorption. The absorption spectra of I at 5% and 10% dye loading in PVAc matrices as a function of spin-coating speed are shown in *Figures 2a* and *2b*, respectively. The absorption maximum (λ_{max}) at each dye concentration remains constant for films prepared at varying spin-coating speeds. The α of I of each individual film is examined by the o.d. *versus* film thickness plot as presented in the insets of *Figures 2a* and *2b*. Straight lines having intercepts very close to zero are obtained. These results indicate that the absorption spectra of I at 5% or 10% dye loading are superimposable and lead us to conclude that the aggregation of I in PVAc is independent of spin-coating speed at these two concentrations.

The absorption spectra of spin-coated DIP films at 20% 40% and 60% dye loading are shown in *Figures 2c*, *2d* and *2e*, respectively. In contrast to those observed at lower dye concentrations, where λ_{max} is constant within a family of spin-coated films, λ_{max} shifts to shorter wavelengths, from 453 to 447 nm, from 456 to 449 nm and from 460 to 450 nm at 20%, 40% and 60% dye loading, respectively, as the spin-coating speed decreases from 8000 to 600 rpm. Since a similar blue shift was previously observed for films of increasing dye aggregation in PVAc matrices[11], we attribute the blue shift presently observed to the formation of higher (or more) aggregates of I. These results suggest that higher (or more) aggregates of I are formed when DIP films are spin-coated at lower speeds at these three concentrations.

At 20% of I in PVAc, the α of I of each individual film is constant from 400 to 500 nm (inset of *Figure 2c*), indicating that the induced aggregational change of I by varying spin-coating speeds is relatively small compared with those at higher dye concentrations (40% and 60%). A slightly different result was obtained previously where we did not observe any changes in either λ_{max} or α of I as the spin-coating speed decreases at this concentration[11]. This difference is attributable to the use of methyl ethyl ketone (a more volatile solvent compared with 3-pentanone and 1,1,2-trichloroethane) as a coating solvent in our previous work. As seen in the present work (see later for discussion), the use of a more volatile coating solvent may produce a quenching effect on the aggregation of I during the film formation, and this may occur even at the lowest spin-coating speed (~1000 rpm) previously used because of the high volatility of methyl ethyl ketone. Consequently, no aggregational changes of I induced by spin-coating could be seen.

At 40% dye loading, the α of I (inset of *Figure 2d*) is constant when the DIP film is spin-coated at speeds

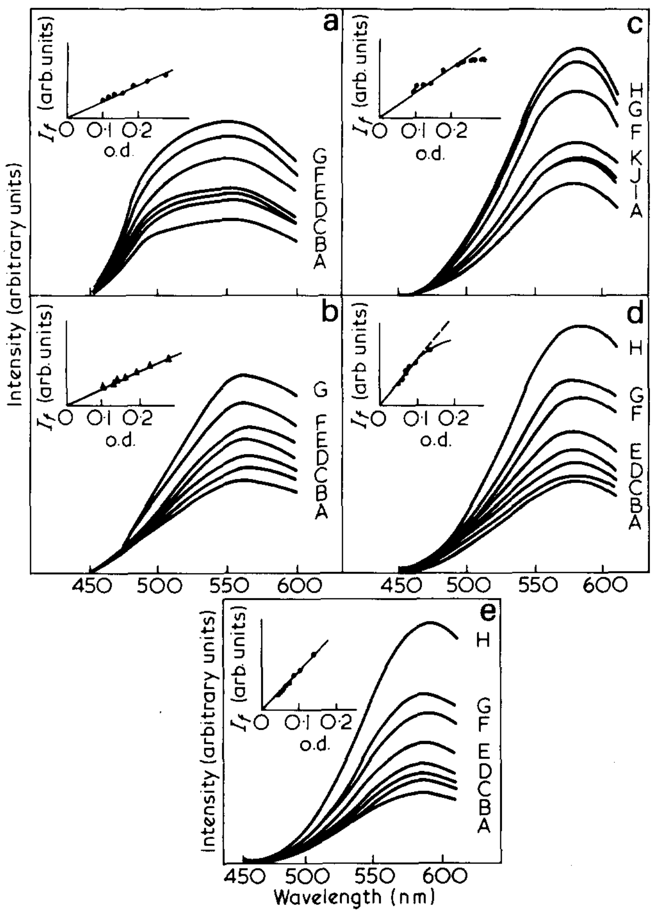


Figure 3 Fluorescence emission spectra (corrected) of spin-coated DIP films of I in PVAc at (a) 5%, (b) 10%, (c) 20%, (d) 40% and (e) 60% dye loading (A, 8000; B, 5000; C, 4000; D, 3000; E, 2000; F, 1500; G, 1000; H, 600; I, 4500; J, 3500; and K, 2500 rpm)

>3000 rpm and decreases as the spin-coating speed decreases at lower coating speeds (<2500 rpm) at absorption wavelengths >420 nm. As a result, the absorption spectra of I obtained from films coated at various speeds are no longer superimposable; they are blue shifted and less intense as the spin-coating speed decreases.

At 60% dye loading, owing to the large error involved in the film thickness measurement[17], the α of I of each individual film cannot be analysed.

Fluorescence. Figures 3a and *3b* show the relative fluorescence emission intensity of I in PVAc at 5% and 10% dye loading, respectively. The excitation wavelength was either at 400 nm or 410 nm where all the aggregated species of I have a very similar absorption coefficient[11]. Plots of I_f *versus* o.d., which are used to determine the relative φ_f of I of each individual DIP film, are shown in the insets of *Figures 3a* and *3b*. The observed linear relationship at dye concentrations $<20\%$ indicates that φ_f of I is independent of the spin-coating speed. These results suggest that at any given I concentration of dye loading $<20\%$, the degree of aggregation of I is unchanged as the spin-coating condition varies.

Figures 3c and *3d* show the fluorescence spectra of I at 20% and 40% loading in PVAc, respectively, as a function of spin-coating speed. The relative φ_f of I (insets of *Figures 3c* and *3d*) indicates that φ_f is constant for films spin-coated at speeds >1500 rpm and starts decreasing for films spin-coated at lower speeds. Since we have previously shown that the φ_f of the dimer and of the higher aggregates of I are 0.1 and 0.066, respectively, in PVAc matrix[11], the decrease in φ_f observed at 20% and 40% dye loading can therefore be interpretated as the conversion of dimer to higher aggregates during spin-coating when a lower spin-coating speed is used. This result confirms the conclusion derived from the absorption spectral data that I forms more (or higher) aggregates as the spin-coating speed decreases in the low speed range at these two concentrations.

The fluorescence spectra for films coated at varying spin-coating speeds at 60% dye loading are shown in *Figure 3e*. The relative φ_f of I (inset of *Figure 3e*) is constant over a wide range of coating conditions. Since absorption spectral data clearly indicate the spin-dependence of the aggregation of I at this concentration, the constant φ_f observed merely reflects the similarity in microenvironment of I in various highly aggregated states which have escaped dectection by fluorescence spectroscopy.

Excitation. The fluorescence spectra of various DIP films were also examined, but no further information is gained. For instance, at any given monitoring wavelengths, films at the same dye concentration ($\lesssim 20\%$) gave identical excitation spectra regardless of the spin-coating speed, which indicate the same degree of aggregation of I in these films (see *Figure 4a* and *4b*). However, at dye concentrations $\geqslant 40\%$, the excitation spectra (at any monitoring wavelengths, see examples in *Figures 4c* and *4d*) of films spin-coated at lower speeds are generally blue shifted and broadened compared with those films coated at higher spin-coating speeds. On the basis of our previous work[11], these results also suggest that I forms more (or higher) aggregates when the DIP film is spin-coated at lower speeds at these dye concentrations.

(2) In PiBMA

The electronic spectra of I at 10%, 20% and 40% dye

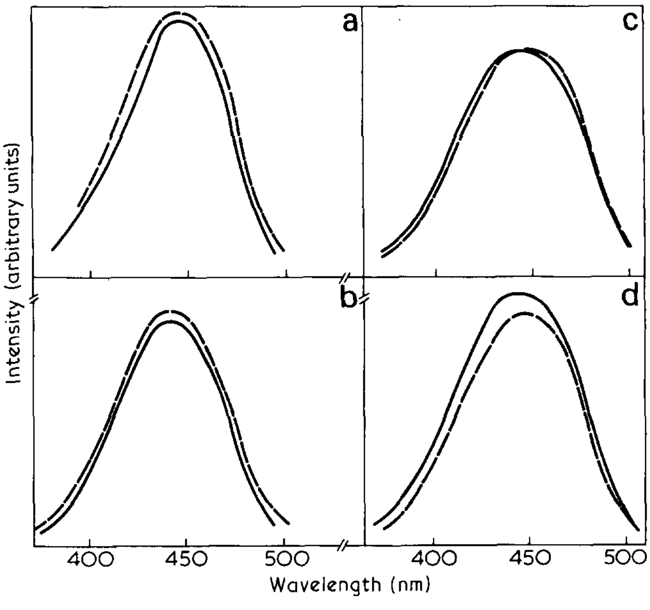


Figure 4 Fluorescence excitation spectra (corrected) of I in PVAc (a) 5%, monitored at 520 nm; (b) 5%, monitored at 590 nm; (c) 40%, monitored at 520 nm; and (d) 40%, monitored at 590 nm (spin-coated at 1000 (——) and 8000 rpm (– – – –)

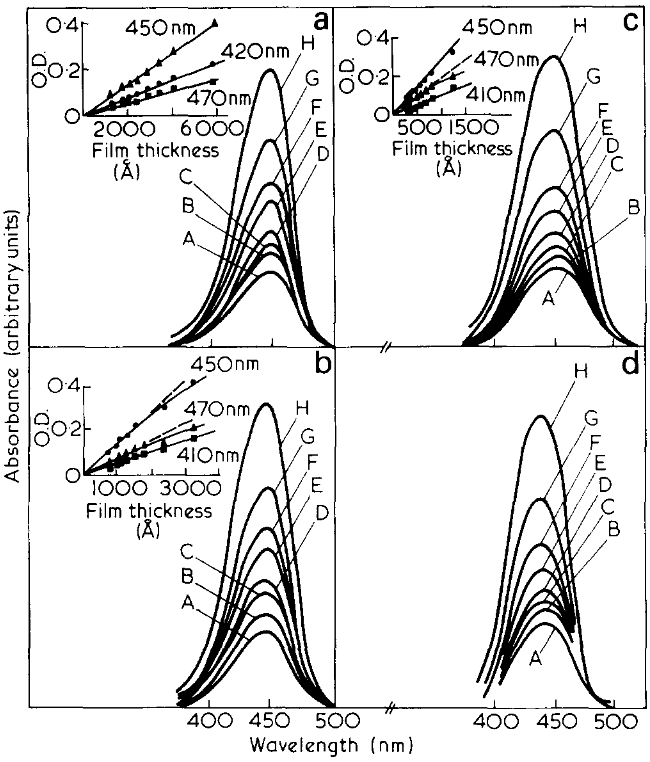


Figure 5 Absorption spectra of spin-coated DIP films of I in S-iBMA (8:2) at (a) 5%, (b) 10%, (c) 20%, and (d) 40% dye loading (A, 8000; B, 5000; C, 4000; D, 3000; E, 2000; F, 1500; G, 1000; and H, 600 rpm)

loading in PiBMA films prepared under a wide range of spin-coating speeds were examined. Owing to the similarity in local environment of I in PiBMA compared with that in PVAc, λ_{max} and λ_F (fluorescence emission maximum) of I at a given dye concentration are very similar in these two polymers. The spectroscopic results of I in PiBMA are summarized as follows.

At 10% or 20% dye loading, in each case, λ_{max}, α, λ_F and φ_f of I remain the same as the spin-coating speed varies. The fluorescence excitation spectra for films coated at varying spin-coating speeds at each dye concentration (10% or 20%) are superimposable. All these results indicate that, at any dye concentration of $\leqslant 20\%$, the aggregation of I in PiBMA matrix is not sensitive to the spin-coating speed.

At 40% dye loading, λ_{max} of I shifts to shorter wavelengths, from 455 to 449 nm, as the spin-coating speed decreases from 8000 to 600 rpm. Although analysis of the absorption coefficient of each individual film cannot be performed due to the large error involved in film thickness measurements[17], the blue shift of λ_{max} of I gives clear evidence on the formation of more (or higher) aggregates of I as the spin-coating speed decreases. The φ_f of I of each film, which is analysed *via* a I_f vs. o.d. plot, is constant also. This again, may either reflect the minute change in the degree of aggregation of I as the spin-coating speed changes or the similar φ_f of I in various aggregated states. Further evidence on the formation of more (or higher) aggregates of I as the spin-coating speed decreases comes from the excitation spectra, e.g. excitation spectra of DIP films spin-coated at low speeds are always broader than those spin-coated at higher speeds. Thus, we concluded that the aggregation of I is also spin-speed dependent at 40% dye loading in PiBMA.

(*3*) *In S-iBMA* (*8:2*)

As shown in our previous work[9], I forms strong intramolecular CT complex in the ground state. The solubility of I in non-polar solvent is therefore quite low. In this section, we attempt to decrease the solubility (or compatibility) of I in polymer matrix by introducing a non-polar component, namely styrene (S), in PiBMA matrix using a random copolymer S-iBMA (8:2).

Absorption. Figure 5a shows the absorption spectra of spin-coated DIP films of I in S-iBMA (8:2) at 5% dye loading. Both λ_{max} and α of I (inset of *Figure 5a*) remain constant upon changes in spin-coating speed. This result suggests that the aggregation of I is not changing as the spin-coating speed varies at 5% loading in S-iBMA (8:2) matrix.

Figures 5b, *5c* and *5d* show the absorption spectra of spin-coated DIP film of I in S-iBMA (8:2) at 10%, 20% and 40% dye loading, respectively, At these three concentrations, λ_{max} of I shifts from 450 to 448.2 nm, from 455 to 450 nm and from 459 to 450 nm at 10%, 20% and 40% dye loading, respectively, as the spin-coating speed decreases from 8000 to 600 rpm. The α of I at 10% and 20% dye loading (see insets of *Figures 5b* and *5c*) is constant at each concentration when the DIP film is spin-coated at speeds >2000 rpm, and starts to decrease at lower spin-coating speeds (<2000 rpm). Since we also observe similar blue shift in λ_{max} and similar decrease in α of I upon dye aggregation in PVAc matrices, we accordingly conclude that, in S-iBMA (8:2) matrices at 10% and 20% dye loading, the degree of aggregation of I is held constant when the film is spin-coated at speeds >2000 rpm and speed dependent, forms more (or higher) aggregates of I as the spin-coating speed decreases in the low spin-speed range (<2000 rpm).

Fluorescence. The same sets of films were also studied by fluorescence spectroscopy. The fluorescence spectra of films prepared at varying spin-coating speeds at 5%, 10%, 20% and 40% dye loading are presented in *Figures 6a*, *6b*, *6c* and *6d*, respectively. Unlike absorption spectroscopy where the monomer, the dimer and higher aggregates of I absorb in a similar spectral region, the fluorescence emission bands of the monomer, the dimer and higher aggregates of I emit quite differently in the visible region: λ_F (monomer) ~490 nm and λ_F (dimer or higher aggregates) ~590 nm. The fluorescence spectra, therefore, allows us to estimate qualitatively the degree of aggregation of I in various polymers. Comparison of the fluorescence spectra in *Figures 6a–6d* with those in *Figures 3a–3d* indicates that the relative fluorescence emission intensity at ~490 nm to that at ~590 nm (I_{490}/I_{590}) is always smaller in S-iBMA (8:2) at the same dye concentration. These results suggest that more dimer and higher aggregates of I are formed in S-iBMA (8:2). This is what would be expected since there are fewer polar sites available in S-iBMA (8:2) matrix. Consequently, the interaction between I (a polar molecule) and S-iBMA (8:2) is relatively weak; and results in a higher degree of aggregation of I in S-iBMA (8:2) generally.

The relative φ_f of I remains constant for films spin-coated at varying speeds at 5% dye loading (inset of *Figure 6a*) and becomes sensitive to the spin-coating speed at 10%, 20% and 40% dye loading. At these three concentrations, φ_f is constant for films spin-coated at speeds >3000 rpm and decreases as the spin-coating

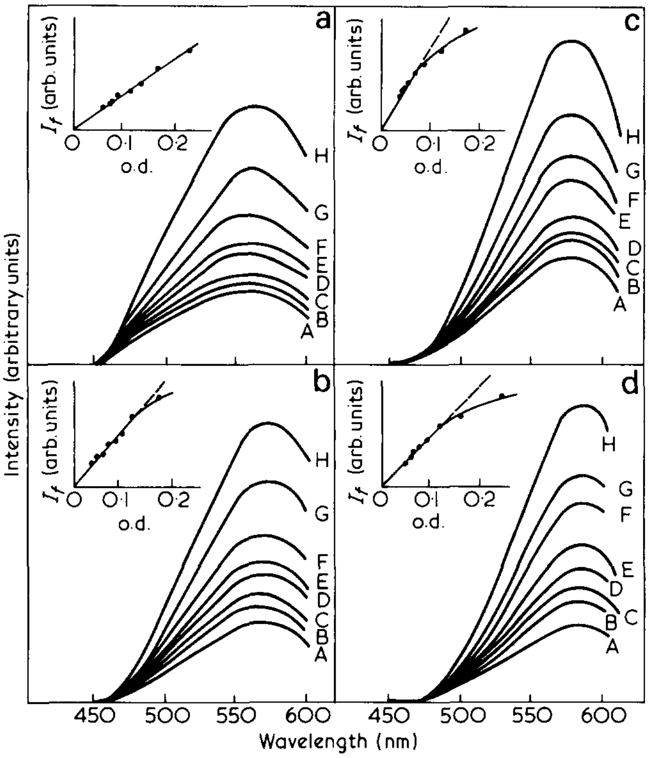


Figure 6 Fluorescence emission spectra (corrected) of spin-coated DIP films of I in S-iBMA (8:2) at (a) 5%, (b) 10%, (c) 20%, and (d) 40% dye loading (A, 8000; B, 5000; C, 4000; D, 3000; E, 2000; F, 1500; G, 1000; and H, 600 rpm)

speed decreases at lower spin-coating speeds (<2500 rpm). The fluorescence spectral data thus suggests that the degree of aggregation of I is unchanged upon varying spin-coating conditions at 5% dye loading and becomes sensitive to spin-coating conditions at higher dye concentrations: more aggregates are formed as the spin-coating speed decreases. This is in excellent agreement with the conclusion deduced from the absorption spectral data.

The excitation spectra of these films were also studied. The spectral results are consistent with the absorption and fluorescence spectral data.

(4) In PS

The solubility (or compatibility) of I in polymer matrix is further decreased by using PS as a binding matrix. Three dye concentrations, 5%, 10% and 20% have been studied and the results are discussed as follows.

At each dye concentration, λ_{max} of I in PS exhibits a very small blue shift as the spin-coating speed decreases, e.g. λ_{max} shifts from ~451.5 to 450 nm, from 452 to 450 nm and from 446 to 440 nm at 5%, 10% and 20% dye loading, respectively, when the spin-coating speed changes from 8000 to 600 rpm. The α of I (analysed by the o.d. vs. film thickness plot) at each dye concentration does not show any visible changes as the spin-coating speed decreases. This is presumably due to the minute aggregational changes of I under various coating speeds since the blue shift of λ_{max} within a family of spin-coated DIP films already gives positive evidence on the aggregational change of I (form more or higher aggregates) as the spin-coating speed decreases.

The fluorescence spectra of these films were also examined. I exhibits only long wavelength emission (λ_F ~590 nm), which is attributed to the dimer or high aggregates emission of I, even at a very low dye loading, e.g. 5% in PS. This is consistent with the trend that more aggregates of I are formed as the dye–polymer compatibility decreases. The order of increasing the number of aggregates in polymer at a given dye concentration is PVAc ~PiBMA→S-iBMA (8:2)→PS.

The relative φ_f of I is constant, regardless of the spin-coating speed at either 5% or 10% dye loading. The constant φ_f at these two concentrations probably indicates that the induced aggregational changes of I by spin-coating is very small, since the fluorescence excitation spectra, which are in agreement with the absorption spectral data, clearly show broadening as the spin-coating speed decreases.

At 20% dye loading, φ_f of I is basically constant for films spin-coated at speeds >2500 rpm and decreases as the spin-coating speed decreases at the lower spin-coating speed range. Moreover, similar broadening effect on the fluorescence excitation spectra (regardless of the excitation wavelength) is also observed when the spin-coating speed is reduced. These results, together with the absorption spectral data, firmly indicate the formation of more (or higher) aggregates of I as the spin-coating speed decreases at this dye concentration.

In summary, spectroscopic results of I in PS clearly indicate that the aggregation of I in PS is very sensitive to the spin-coating speed at all the dye concentrations studied. Within a family of spin-coated films, the degree of aggregation is unchanged when the film is spin-coated at speeds >3000 rpm; more (or higher) aggregates are formed when the film is spin-coated at speeds lower than 2500 rpm.

D.s.c. measurements

The glass transition temperatures (T_g) of various DIP systems were determined by d.s.c. Typical d.s.c. traces as a function of I concentration, using I in PVAc as an example, are shown in *Figure 7*. The d.s.c. results are

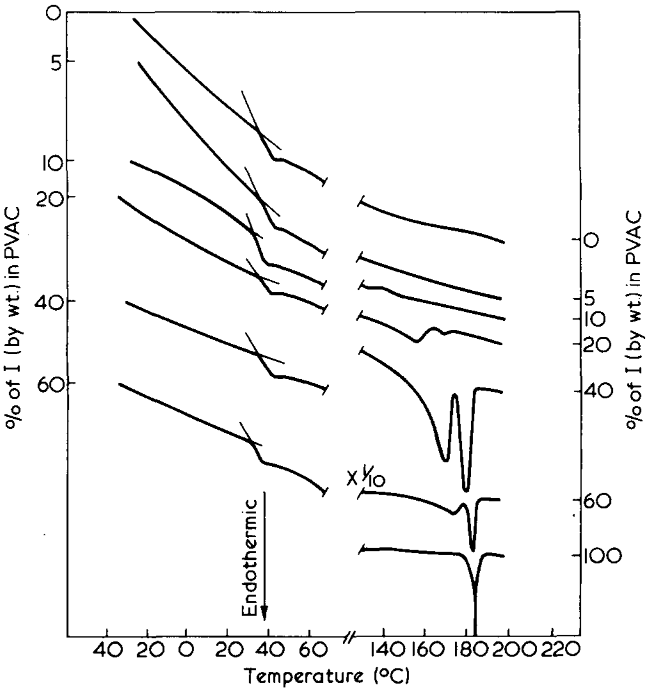


Figure 7 D.s.c. scans of I in PVAc

Table 1 D.s.c. results of various DIP systems

Polymer	PVAc			PiBMA			S-iBMA (8:2)			PS		
1 conc. (% by wt.)	T_g^a	m.p.^{b}	Film quality	T_g^a	m.p.^{b}	Film quality	T_g^a	m.p.^{b}	Film quality	T_g^a	m.p.^{b}	Film quality
0	35	–	clear	52	–	clear	78	–	clear	42	–	clear
5	34	–	clear	51	–	clear	73	–	clear	44	159, 169	cloudy
10	30	–	clear	50	–	clear	71	–	clear	44	178	cloudy
20	33	156	clear	50	164	clear	70	175, 184	cloudy	44	171, 180	cloudy
40	34	170, 180	cloudy	51	171, 181	cloudy	78	179, 184	cloudy			
60	32	172, 177, 183	cloudy									
100	–	186										

^{a} Glass transition temperature, in °C, within ±2°C
^{b} Melting point (peak), in °C, within ±1°C

Table 2 Relationship between effect of spin-coating speed and dye concentration in various polymer matrices

Polymer 1 conc. (% by wt.)	Effect of spin-coating speed			
	PVAc	PiBMA	S-iBMA (8:2)	PS
5	none	none	none	√
10	none	none	√	√
20	√	√	√	√
40	√	√	√	
60	√	√		

tabulated in *Table 1*. The apparent film quality and the melting points (m.p.) of various DIP systems are also included.

The results in *Table 1* indicate that I does not show any glass transition relaxation in the temperature range examined, −120° to 200°C[18]. The m.p. of I measured by d.s.c. is 186°C which is in good agreement with the reading obtained from a hot stage m.p. apparatus (186° − 188°C).

The effect of plasticizers (or small molecules) on the dynamic (T_g) relaxation of many polymers has been investigated[19]. In some cases the T_g of a small molecule/polymer system exhibits a single correlated motion. The T_g decreases as the small molecule concentration increases and follows the Fox equation[20,21]. In some other cases (e.g. polar polymer and non-polar plasticizer), the T_g relaxation is not correlated and does not follow any relationship, but the T_g is affected by the presence of the second species[22].

In the present work, since I does not exhibit any T_g relaxation, only a single T_g is anticipated in each DIP system. However, any interactions between I and the polymer should be reflected by changes on the T_g as the dye concentration increases. Moreover, the absence of the m.p. of I in some DIP systems also give indication on the formation of solid solution between I and the polymer at certain dye concentration. In the case of phase separation, where I crystallizes out of the polymer matrix, dye–polymer interactions can also be seen *via* the depression of the m.p. of I.

In polar polymers such as PVAc and PiBMA, the interaction between I and the polymer is expected to be strong. As seen in *Table 1*, below 20% dye loading in these two polymers, the solvent cast DIP films are optically clear. The T_g's, however, only decrease slightly as the dye concentration increases and do not follow the Fox equation. The absence of the m.p. of I does suggest that I forms solid solutions with PVAc or PiBMA at dye concentrations <20%. Since spectroscopic results indicate that I exists in a monomer ⇄ dimer equilibrium in these DIP systems[11], the small plasticizing effect and the lack of correlation observed here are presumably due to the stronger dye–dye interaction as compared to the dye–polymer interaction in these matrices.

Above (or at) 20% in PVAc or PiBMA, I crystallizes out of the polymer matrix and the solvent cast DIP films are no longer optically clear. D.s.c. shows one or more melting peaks of I at each concentration, which are attributable to the different plasticized states of solid I. Spectroscopically, we observed the formation of higher aggregates of I at these concentrations. The spectroscopic and d.s.c. results are thus consistent with each other. Since I starts to crystallize out of the polymer matrix above 20% dye loading, 20% can, therefore, be regarded as a saturated concentration in these two polymers (PVAc and PiBMA).

Very similar characteristics on T_g's and m.p.'s are also observed for DIP systems of I in S-iBMA (8:2) and PS (see *Table 1*). The important point here is that, as the dye–polymer compatibility decreases, from PVAc and PiBMA to S-iBMA (8:2) to PS, the saturated concentration of I decreases from $\sim$20% to $\sim$10% to $\lesssim$5%, respectively.

Interpretative discussion on the relationship between spin-coating speed and dye–polymer compatibility

Combining the results of absorption, fluorescence emission and excitation spectroscopic studies, we have been able to study the effect of spin-coating speed on the aggregation of I at various dye concentrations in polymers of decreasing dye–polymer compatibility, PVAc $\sim$ PiBMA > S-iBMA (8:2) > PS. The results are summarized in *Table 2*.

Comparison of the results in *Tables 1* and *2* clearly shows that whenever the solvent cast DIP film is not optically clear, or a melting point is observed, we consistently observed a spin-speed dependence on the degree of aggregation of I when the DIP film is spin-coated at low speeds (<2500 rpm). These results can be explained as follows. Since I only exists in monomeric form in all the coating solutions studied, the aggregation of I in the final film will therefore strongly depend on how I is distributed during the film formation. At dye concentrations below the saturated concentration, the thermodynamic interaction between I and the matrix polymer controls such a distribution, the aggregation of I is thus independent of the spin-coating speed. In fact, the shape of the fluorescence emission band of a solvent cast

DIP film (zero spin-coating speed), which should be very sensitive to the monomer, dimer distribution, is nearly identical with a spin-coated DIP film at the same dye concentration.

At dye concentrations above the saturated concentration, owing to the strong dye–dye interaction, there is a great tendency for dye aggregation during the film formation. However, for DIP films coated at a high spin-coating speed, as a result of the fast air circulation on the top of the coating film and as a result of the ultra-thin film prepared at these high coating speeds, the evaporation of the coating solvent is almost instantaneous. This produces a 'quenching' effect on the aggregation of I inside the polymer matrix. The dye molecules do not have enough time to distribute themselves according to that required by thermodynamics. Consequently, identical aggregation of I is obtained and less (or smaller) aggregates of I are formed in these films.

As the spin-coating speed becomes slower, owing to the thicker resulting film prepared under these conditions and to the slower air circulation above the top of the spinning film during the coating, the evaporation of the coating solvent becomes much slower. The solvent molecules thus plasticize the coating film for a relatively long period of time during the film formation. Consequently, I will have more time to diffuse within the plasticized film to form more (or higher) aggregates. Since the extent of the dye aggregation should increase as the rate of solvent evaporation decreases, the size or the number of the aggregates of I therefore increases as the spin-coating speed decreases.

The observation of a kinetically controlled aggregation of I for DIP films coated at high spin-coating speeds is not surprising. Similar quenching effect is also observed in other small molecule–polymer systems[23] and polymer–polymer blends[24]. Moreover, the above interpretation is further supported by the following two experiments. Firstly, at dye concentrations above the saturated concentration, the film quality of a cast DIP film can be improved or become optically clear when it is cast and dried at a very fast rate (by vacuum, simulation of high spin-coating speed conditions). Secondly, when an optically clear spin-coated DIP film of dye concentration above the saturated concentration is heated above the T_g for $\gtrsim 24$ h, the dye molecules crystallize out of the polymer matrix. On the other hand, no change could be detected when a spin-coated DIP film of dye concentration below the saturated concentration is subjected to the same treatment. These two experiments further illustrate our conclusion that, below the dye saturated concentration, the aggregation of I is thermodynamically controlled and is insensitive to various coating conditions; above the dye saturated concentration, the aggregation of I will be kinetically controlled and the exact degree of aggregation of I will be sensitive to various coating conditions, e.g. rate of solvent evaporation.

CONCLUSIONS

We have combined absorption, fluorescence emission and fluorescence excitation spectroscopic techniques, and differential scanning calorimetry to examine the aggregation of dye I in four different polymer matrices of varying dye–polymer compatibility under a wide range of spin-coating conditions. As the dye concentration increases, the dye reaches a saturated concentration. This saturated concentration depends on the dye–polymer compatibility: the saturated concentration increases as the dye–polymer compatibility increases. At dye concentrations below the saturated concentration, the dye–polymer system forms solid solution; the aggregation of the dye in the polymer matrix is thermodynamically controlled and is independent of the spin-coating condition. At dye concentrations above the saturated concentration, the aggregation of the dye in the polymer matrix becomes kinetically controlled. The film retains the same, kinetically controlled, aggregated form when it is spin-coated at high speeds (8000–2500 rpm) and becomes spin-speed dependent at low spin-coating speeds ($\lesssim 2500$ rpm): more (or higher) aggregates of I are formed as the spin-coating speed decreases.

Because of the technological importance of dye aggregation in some industrial applications[12], the present work may have impact on solvent coating technology of small molecule/polymer systems in general. For instance, we shall expect that, for a thermodynamically favourable system (compatible dye–polymer system), the aggregation of the small molecule will not be sensitive to various coating conditions. However, depending upon the structure of the small molecule and the structural relationship between the small molecule and the polymer, a small molecule/polymer system can deliberately be designed to be semi-compatible in a variety of ways. For such a system, fundamental understanding on the effects of various coating parameters on the aggregation of the small molecules may allow us to engineer various aggregated forms of small molecules inside the polymer matrix by just choosing an appropriate coating condition.

Finally, the present d.s.c. results clearly show no correlation between the T_g of the DIP system and the dye concentration. Although similar phenomenon have previously been reported in the literature[22], a complementary (spectroscopic) technique is presently used to provide direct evidence that this is due to the great tendency of dye aggregation of I inside the polymer matrix.

ACKNOWLEDGEMENTS

The author thanks Dr L. Alexandru and Mr P. Odell for the use of the d.s.c.

REFERENCES

1 O'Hagan, P. and Daughton, W. J. Proceeding of the Kodak Microelectronics Seminar, Monterray, California, 1977
2 Harris, R. A. Industrial Polymers: Characterization by Molecular Weight, Proceeding of Meeting, Teddington, England, 1973
3 Comstock, R. L., Moore, E. B. and Nepela, D. A. *IEEE Trans. on Magnetics*, 1970, **Mag-6**, 558
4 O'Hagan, H., Daughton, W. J. *Circuits Manufacturing*, 1978, **18**, 71
5 Givens, F. L. and Daughton, W. J. *J. Electrochem. Soc. Solid-State Sci. Technol.* 1979, **126**, 269
6 Washo, B. D. *IBM J. Res. Develop.* 1977, **21**, 190
7 (a) Law, K. Y. *et al. Appl. Phys. Lett.* 1980, **36**, 884;
(b) Law, K. Y., Vincett, P. S. and Johnson, G. E. *Appl. Phys. Lett.* 1981, **39**, 718
8 Howe, D. G. and Wrobel, J. J. *J. Vac. Soc. Technol.* 1981, **18**, 92
9 Loutfy, R. O. and Law, K. Y. *J. Phys. Chem.* 1980, **84**, 2803
10 Law, K. Y. *Chem. Phys. Lett.* 1980, **75**, 545
11 Law, K. Y. and Loutfy, R. O. *Macromolecules* 1981, **14**, 587

12 Dulmage, W. J., Light, W. A., Marino, S. J., Salzberg, C. D., Smith, D. L. and Standenmayer, W. J. *J. Appl. Phys.* 1978, **49**, 5543; and Borsenberger, P. M., Chowdry, A., Hoesterey, D. C. and Mey, M. *J. Appl. Phys.* 1978, **49**, 5555

13 Loutfy, R. O. and Sharp, J. H. *J. Chem. Phys.* 1979, **71**, 1211

14 Law, K. Y. and Loutfy, R. O. manuscript in preparation

15 Daughton, W. J., O'Hagan, P. and Givens, F. L. Proceedings of the Kodak Microelectronics Seminar, San Diego, California, 1978

16 Kelly, R. Proceedings of the Kodak Seminar on Microminiaturization, Kodak Park, Rochester, N.Y., 1965

17 The uncertainty of our Tallystep instrument is ~50 Å; film thickness measurements become inaccurate for films <200 Å

18 All d.s.c. measurements were scanned from −120° to 200°C

19 Curtis, A. J. *Progress in Dielectrics* 1960, **2**, 29 and references cited therein

20 Pochan, J. M. and Pochan, D. F. *Macromolecules* 1980, **13**, 1577

21 Pochan, J. M., Gibson, H. W., Froix, M. F. and Hinman, D. F. *Macromolecules* 1978, **11**, 165

22 see Wurstlin, F. *Kolloid Z.* 1953, **134**, 135; Thurn, H. and Wurstlin, F. *Kolloid Z.* 1958, **156**, 21; Luther, H. and Weisel, G. *Kolloid Z.* 1957, **154**, 15; Broens, O. and Müller, F. H. *Kolloid Z.* 1955, **141**, 20

23 Onu, A., Legras, R. and Mercier, J. P. *J. Polym. Sci. Polym. Phys. Edn.* 1976, **14**, 1187

24 Shultz, A. R. and Young, A. L. *Macromolecules* 1980, **13**, 663