



PHOTOPHYSICAL STUDIES OF SPIN-CAST POLYMER FILMS

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ABSTRACT

Previous research on spin cast films has centered on macroscopic variables such as film thickness and uniformity. This work has focused on the microscopic properties of polymer chains that compose these films, using materials and processing conditions that are similar to those used in lithographic applications. It is believed the process of spin casting causes the polymer chains to exist in oriented, non-equilibrium chain conformations. Orientation of the polymer chains will increase the Trans conformational segments as found by Jasse and Koenig [1], which slightly increases the concentration of intramolecular EFS. However, this increase is insufficient to account for the observed 200% increase in I_e/I_m caused by the spinning process. An increase in Intermolecular EFS and/or the rate of energy migration must be included. After long annealing times near the T_g the short chain stress can be relaxed by secondary relaxation phenomena, as measured by I_e/I_m value. Long chain stress, however, still remains in the film. Consequently, significant residual stress may still remain in resist films after the prebaking process commonly used in the industry. The spin cast films of novolac polymers in solution with a small molecule dye indicate that aggregation may occur for pyrene concentrations as low as 6 mol %. This is well below the concentration of sensitizer in many commercially used positive resist systems, indicating that the resist films may be inhomogeneous.

Keywords: photo physical studies, spin casting, polymer films, excimer fluorescence, molecule dye.

1. INTRODUCTION

Spin casting is a commonly used technique for producing thin, uniform polymer films, especially for semi-conductor fabrication. There has been little attention given to the response of the polymers at the molecular level, however. We have reviewed previous literature on the spin casting process, as well as pertinent aspects of solvent cast and oriented polymers. Our experimental work has focused on the use of excimer fluorescence to elucidate polymer chain conformation and fluorescent probe environment. The effects of spin speed and polymer molecular weight on spin cast polystyrene films and subsequent annealing behavior has been studied. In addition, the aggregation of a small molecule dye (pyrene) in novolac films was investigated.

The U.S. - Australia Symposium on Radiation Effects on Polymeric Materials contained research presentations on fundamental radiation chemistry and physics as well as on technological applications of polymer irradiation. This paper reports a hybrid contribution of these two areas, examining a field of extensive technological importance. Spin casting of radiation sensitive polymer resists for microelectronic fabrication was photo physical techniques that are sensitive to the fundamental radiation response in ultraviolet range.

Thin, uniform polymer films can be formed by casting a polymer solution onto a rotating disc. Investigations of spin casting have, to date, focused on the process at a macroscopic level of primary concern has been the ability to predicate the final film thickness and any radial dependence of the thickness induced by spinning. Various models have been derived to relate the spinning and solution characteristics to film thickness and uniformity. These parameters are of very practical importance in the present applications of spin casting, especially for resists. The intent of our investigations is to

study the effects of spincasting on polymers at a molecular level. The polymers may be radiation sensitive materials such as poly (methyl methacrylate) (PMMA), polysulfones, or polystyrene derivatives, or radiation insensitive materials such as novolac or pure polystyrene. In all cases; photo physical techniques will be used to interrogate the polymer structure and film homogeneity (for the films which are mixtures of a radiation insensitive polymer and a radiation sensitive material). There has been little effort given to understanding the effects of spin casting on configuration of polymer chains up until now. Indeed, for circuit geometries above the sub-micron regime, it is less important because any small inconsistencies or inhomogeneities in the resist film are within the allowable tolerances, But as image dimensions creep down into the 0.5 μm range, and tolerances are reduced into the realm of polymer dimensions, the behavior of the film on the molecular level may play an important role in enhancing resist control and reproducibility.

Spin casting applies radial stress to the polymer film as the solvent evaporates. As a result, it is likely that the polymer chains will be frozen into stretched, non-equilibrium configurations. Radial orientation and stress in the polymer backbone could slightly change the response of the polymer to radiation or solvent developers. Release of the stress may appear in the form of micro-cracking (1) of the film, or loss of adhesion with the substrate [2]. Resist films generally receive a post spinning bake at a temperature which may be above or below the glass transition temperature (T_g) of the polymer, depending on the resist. Many resists, such as most positive diazoquinone resists are too thermally sensitive to be baked above the T_g of the polymer. The bake is intended to remove any remaining trapped solvent and to relax stresses induced by spinning, but there has been no



thorough study of the effectiveness of commonly used baking conditions. Aggregation of individual components of the resist during spinning could change the development characteristics of the resist, the effect of which would be dependent on the size of the aggregated domains. In particular, some roughening of the image sidewalls or overall dimensional variation would be expected. Intrinsic and extrinsic fluorescence can be used as very sensitive probes of the polymer environment and configuration. A particular example is excimer fluorescence, which can occur when two aromatic groups interact in a coplanar structure. The rings must be within three to four angstroms to produce a suitable excimer forming site, so the excimer fluorescence yields, information on the local concentration of these properly oriented aromatic chromophores. Excimer formation may be intermolecular if the two aromatic rings are on different polymer chains, or intramolecular if they are on repeat units of the same polymer chain. Changes in the ratio of excimer to monomer fluorescence intensity (I_e/I_m) of aromatic polymers such as polystyrene have been used to measure the level of orientation in a uniaxially stretched film [3]. This technique can be applied to the radial orientation caused by spin casting. The fluorescence of probes such as pyrene* can also yield a variety of insights into the effects of spin casting. Probes that are chemically attached to the polymer chain can yield configurational information on otherwise non-fluorescent polymers. Aggregation of free fluorescent probes can be monitored and used as a model system for polymer/dye type positive resist systems. We will present the initial results obtained using these fluorescent techniques to evaluate the extent of orientation and dye aggregation induced by spin casting and the effectiveness of annealing to remove orientation and stress in polymer systems.

2. PREVIOUS RESEARCHES

Background on Spin Casting, As early as 1958; Emslie, *et al.*, [4] proposed a theoretical treatment of spin casting for nonvolatile Newtonian fluids. This theory predicted that films on a flat rotating disc would have radial thickness uniformity. They predicted that the final film thickness would depend on spin speed (ω) and viscosity (η) as well as other variables such as liquid density and initial film-thickness. The dependence of thickness on ω and η was also recognized by many of the other authors reviewed in this paper, and their proposed relationships are compared in Table-1. Acrivos, *et al.* [5] extended the Emslie treatment to the general case of non-Newtonian fluids, a category into which most polymers fall. Acrivos predicted that non-Newtonian fluids would yield films with non-uniform radial thickness. Meyerhofer [6] included the effects of solvent

evaporation during spinning in his model, which he found to be in good agreement with experimental results for Photoresist films. Chen [7] also recognized the importance of solvent evaporation on final film thickness. Chen pointed out that as the solvent evaporates, it will cool the solution, causing an increase in viscosity. He claimed that the film thickness should be related to the physical parameters of the solvent such that the same thickness film could be attained with a low viscosity solution of a highly volatile a solvent or with a high viscosity solution of a low-volatility solvent. Weill [8] noted that the viscosity of a polymer solution is dependent on both the polymer concentration and molecular weight (MW.). Weill found that the thickness of films cast from several solutions with the same viscosity but varying MW increased with MW, although no exact relation between MW and final thickness was derived.

Jenekhe [9, 10] also incorporated the changing rheological properties of the drying film into his thickness model. He defined an experimentally determined parameter (α) that measures the time dependent change in viscosity due to-solvent evaporation during casting, with $\alpha=0$ for nonvolatile fluids. A range of $\alpha=0.44-3.00$ was found to account for previous empirical results for spin cast films. Jenekhe found that many polymer solutions, including those of interest to the microelectronics industry, can be described by the Carreau non-Newtonian viscosity equation, which was shown to predict radially uniform films at sufficiently long spinning times. Flack, *et al.* [11] took the changing rheological properties into account by allowing viscosity to vary with concentration and shear rate during spinning. They determined that convective radial flow dominated the calculated thickness during the early stages, and that solvent evaporation became more important in the later stages of the spinning process. They also indicated that radial thickness dependence should be expected if a ramp of the spin speed were used. Born side, *et al.* [12] also attempt to separate the spinning process into deposition, spin up, spin off, and evaporation stages, and to model these stages using fewer of the simplifying assumptions employed by previous authors. The model promises to be very complex.

Several authors have tried to determine empirical relations that will accurately predict the dependence of final film thickness on ω , η and other parameters. The relationships obtained by [13], Daughton and Givens [14], and Malangone and Needham [15] are included in Table-1 for comparison with the predictions of the theoretical models.

**Table-1.** The predicted dependence of film thickness (h) on ω and η according to $h \propto \omega^n \eta^m$.

Reference	n	M	Other variables
Emslie [4] Damon [13]	-1 -0.5	0.5 -	density, spinning time, initial thickness initial concentration
Meyerhofer [6]	-0.67	0.33	evaporation rate, initial concentration
Daughton [14]	-0.5-0.8	0.29	spinning time, initial concentration
Malangone [15]	-0.5	0.33	initial concentration
Chen [7]	-0.5	0.36	evaporation rate, heat capacity, latent heat of evaporation
Jenekhe [9]	-2/(2+00)	1/(2+a)	spinning time, initial thickness, index of viscosity change (a)

It is obvious from the previous discussion and Table-1 that there has been no general agreement on the effect of ω and η thickness, and even less agreement on what other variables are significant in determining final film thickness. While the exponent for viscosity tends to be about 0.3 in most of the models, the empirical exponent of spin speed varies from -0.5 to -0.8. The various models also give different relative weighting to the two parameters: The variety of other variables that were included in the models indicates that there is still a great deal of disagreement as to what the critical parameters for spin casting are. The macroscopic properties of spin cast films are difficult to predict from first principles, and do not lend themselves to empirical analysis either Daughton and Givens [14] found different empirical relations to apply for different polymer systems. These simple models are giving way to much more complicated, multi-step models, but there is obviously still much that is not understood about the "simple" macroscopic aspects of spin casting.

Resist systems may be more complicated than just a single polymer in a single solvent. They may be composed of polymer, polymer/dye, or polymer/polymer combinations (where the small molecule dye or additional polymer increases the radiation sensitivity of the resist film) with one or more solvents. The more complicated polymer/dye or polymer/polymer systems have the added possibilities of phase separation or aggregation during the non-equilibrium casting process. Law [16] investigated the effects of spin casting small molecule dye in solution with polymers. He found a slight increase in the aggregation of the dye at high dye concentration (>40%) and low spin speed. Law suggested that spinning conditions could affect the kinetically controlled aggregation of polymer/dye systems with poor compatibility.

Even at their best, the models are able to predict only macroscopic properties of the films, yielding no information on microscopic parameters that may affect resist performance. It is highly probable that spin casting induces some structure or preferential chain orientation into the films, or causes secondary effects such as the aggregation observed by Law. These effects are barely addressed in the currently available literature. However,

some earlier works [3, 17-19] on solvent (static) cast films have investigated the molecular orientation of polymer chains as well as chain relaxation due to thermal annealing.

Prest and Luca [17] found that the solvent-casting process preferentially aligned polymeric chains in the plane of the film, as measured by the optical anisotropy of the films. Cohen and Reich [18] reported that films cast from monodisperse low molecular weight (< 30, 000) polystyrene exhibit high ordering close to the substrate, but this ordering decays within 1 μm from the substrate. Films cast from monodisperse, high molecular weight polystyrene (> 30, 000), on the other hand, exhibit a much smaller, but very long-range (-10 μm) degree of order. Croll [19] studied the formation of stresses in solvent cast films as the solvent evaporates. The thickness of the film will decrease, but the area is constrained by adhesion to the substrate. Because of this constraint, internal stress arises in the plane of the coating. He further concluded that the residual internal stress is independent of dried coating thickness and initial solution concentration. Polymer orientation has also been studied with stretched polymer films. Jasse and Koenig [1] studied uniaxially oriented polystyrene films using fourier transform infrared spectroscopy and concluded that the orientation process produces alignment of the chains as well as an increase in the amount of trans conformational segments. We believe that the photophysical approach described in this paper will allow us to investigate similar microscopic properties of spin cast films.

3. EXPERIMENTAL

3.1. Materials

Polystyrene samples of molecular weights 10, 000, 50, 000, 300, 000 and 600, 000 were obtained from Polyscience Inc.; they all have narrow molecular weight distributions, with $M_w/M_n < 1.1$. They were purified by three precipitations from tetrahydrofuran (THF) into methanol. The novolac sample was provided by Kodak, and was synthesized from pure meta-cresol and formaldehyde. The material was quite polydisperse with $M_w - 13, 000$ and $M_w/M_n = 8.5$, as measured by gel permeation chromatography (GPC. with polystyrene



standards. The material was purified by three precipitations from (THF then into hexane: The pyrene and pyrene butyric acid (PBA) were recrystallized from toluene prior to use. The dried by refluxing and distilling over sodium and benzophenone. Spectral grade dioxane (Aldrich), THF (Alltech), 2-methoxyethyl ether (Aldrich), and reagent grade methanol (Aldrich) were used.

3.2. Pyrene tagging

The tagged novolac materials were prepared by the reaction of pyrene butyric acid chloride (PBA-C1) with the polymer. This reaction covalently bonds the pyrene butyric acid to the novolac by forming an ester linkage through the phenolic group on the novolac. The PBA-C1 was synthesized by reacting pyrene butyric acid (3.42 g, 11.8 mmol) with chloride (17.5 ml, 20.0 mmol) in dichloromethane (75 ml) at room temperature and stirred overnight.

The solvent and excess oxalyl chloride was pulled off under vacuum. The crude product was dried under vacuum for two hours. To obtain the most highly tagged sample, the crude PBA-C1 (2.0 g, -6.5 mmol) was dissolved in dry THF (15 ml) and added slowly to a stirred solution of novolac (2.1 g, 17.7 mmol monomer) and pyridine (10 ml), as a base, in dry THF (50 ml). The reaction was performed under nitrogen. The mixture was refluxed for three hours, and then stirred at room temperature overnight. The solution was washed twice with 10% aqueous ~ and twice with water. The organic layer was dried over $MgSO_4$. The polymer was precipitated three times from the/hexane, and the -product dried in vacuum for 24 hours. Four samples tagged with lower levels of pyrene were prepared in a similar manner using 1.2 g of novolac with 0.2, 0.12, 0.05, or 0.02 g of PBA-C1 and 0.5-1 ml of N, N-diisopropylethylamine, which is a better base than pyridine.

About 64-75% of the polymer was recovered after the reactions.

To ensure that the pyrene was attached to the polymer chain, a sample of the purified polymer was analyzed by-GPC with tandem UV and refractive index detectors. There was no detectable (<1%) free pyrene in the sample. The MW and dispersity of the novolac also appeared to be unchanged by the reaction. The concentration of pyrene tags was determined by UV absorption spectroscopy using solutions of methyl-1 pyrene butyrate for calibration. It was found that the polymers had 19.6, 5.03, 2.74, 1.18 and 0.43% of the monomer units.

Tagged with pyrene: Assuming a weight average molecular weight of 13,000, this would result in 21, 5, 3, 1.3 and 0.5 pyrene groups per chain, respectively. It is assumed that the pyrene is randomly attached along the polymer chain, although this has not been experimentally verified.

3.3. Samples for spectroscopic analysis

Solvent cast films of PS (10 μm thick) were prepared by casting from dioxane solution onto quartz

wafers at room temperature in a dry nitrogen ambient. Spin cast films of PS (0.1 - 1.0 μm thick) were prepared by flooding the water with a solution of PS in dioxane and spinning them in a dry nitrogen ambient at a given spin speed for 60 seconds using a Metron Systems LS-8000 spinner. The films were prepared under a dry-nitrogen ambient to reduce the uptake of moisture by the dioxane, which can lead to poor quality films. In order to determine the effect of residual solvent on fluorescence spectra, spectra of samples kept under vacuum at room temperature for eight hours were compared with spectra of samples which were not placed under vacuum. No differences were observed. Solutions of the novolac samples were prepared with 2-methoxyethyl ether (diglyme) and were cast onto glass discs using the LS-800 spinner. Fluorescence measurements of novolac solutions were made from solution prepared with diglyme. The solutions were prepared to be 1×10^{-6} M pyrene, with the concentration of polymer varying according to its tagging level.

3.4. Fluorescence instrumentation and measurements

Fluorescence spectra of the PS samples were obtained on a steady state spectrofluorometer of modular construction with a 1000 W xenon arc lamp and tandem quarter meter excitation monochromator and quarter meter analysis monochromator. The diffraction grating the excitation monochromators have blaze angles that allow maximum light transmission at a wavelength of 240 nm. Uncorrected spectra were taken under front-face illumination with exciting light at 260 nm. Monomer fluorescence was measured at 280 nm and excimer fluorescence was measured at 330 nm, where there is no overlap of excimer and monomer bands.

Fluorescence spectra of the novolac samples were measured on a Spex Fluorolog 212 spectrofluorometer with a 450 W xenon arc lamp and a Spex DM18 data station. Spectra were taken with front-face illumination using a 343 or 348 nm excitation wavelength for solutions or films, respectively, which are near the maximum transmission region of this spectrometer. Spectra were corrected using a rhodamine B reference. Monomer fluorescence was measured at 374 and 378 nm and excimer fluorescence was measured at 470 nm. Monomer and excimer peak heights were used in calculations of I_e/I_m . The I monomer peak of pyrene was used to reduce overlap with the excimer emission.

4. RESULTS

4.1. Fluorescence of polystyrene films

Films of various MW polystyrene were prepared at spin speeds from 1,000 to 8,000 rpm. The ratio of excimer to monomer emission intensity, I_e/I_m is plotted in Figure-1 as a function of ω (spin speed) the spin cast films always have higher I_e/I_m values than the solvent cast films. I_e/I_m increases with spin speed, with larger increases observed for the higher molecular weight samples. Because the thickness of spin cast film is proportional to (spin speed), Figure-1 can be also interpreted as e/I_m



increases as film thickness decreases. The highest I_e/I_m was obtained for the 600, 000 MW polystyrene sample spin cast at 8, 000 rpm; this amounts to a 200% increase in I_e/I_m compared with the solvent cast film, The relaxation behavior of that film in the region of the PS glass transition is plotted in Figure-2. As the annealing temperature increased, I_e/I_m dropped more rapidly and attained lower final values after long annealing times. It is interesting to note that even after annealing for 24 hours the values were still larger than those for solvent cast films.

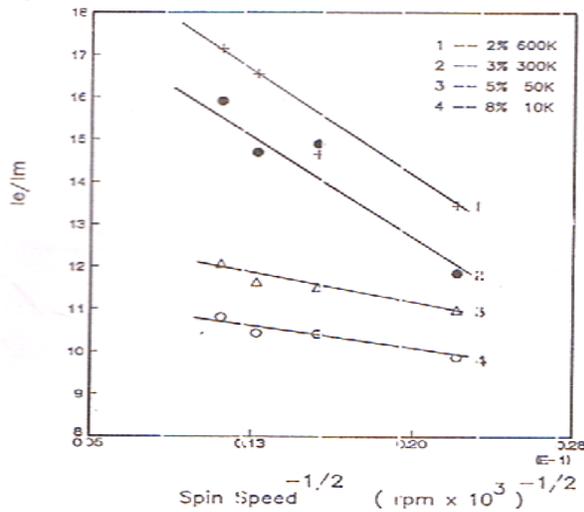


Figure-1. Ratio of excimer (I_e) to monomer (I_m) fluorescence intensities of spin cast polystyrene films as a function of (spin speed).

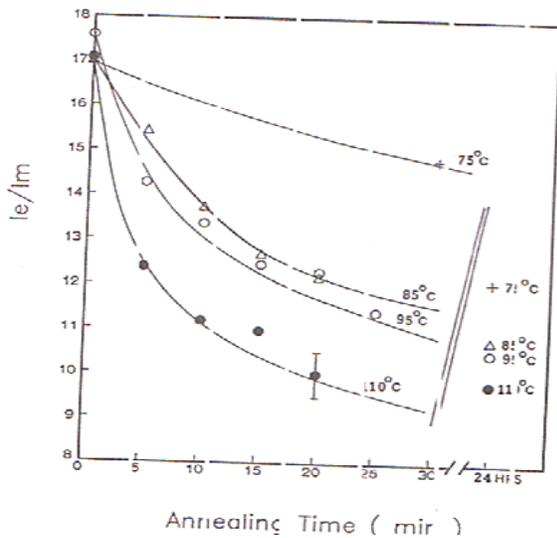


Figure-2. Time dependence for 600K MW poly styrene films spin cast at 8,000 rpm and annealed at different temperatures.

For a given annealing temperature the extent to which the spin cast film has relaxed can be measured by the difference between I_e/I_m for a given annealing time and after 24 hours annealing. This difference, calculated from Figure-2, is plotted as a function of annealing time in Figure-3. A semilogarithmic relationship between this difference in I_e/I_m and annealing time was observed. Thus, it is possible to calculate a relaxation rate constant for annealing from the best fitted straight line. We found that films annealed at higher annealing temperatures had a larger relaxation rate constant. An Arrhenius plot of the relaxation rate constant vs the reciprocal of the annealing temperature is shown in Figure-4. An activation energy of 16.9 kcal/mol for the relaxation process was obtained.

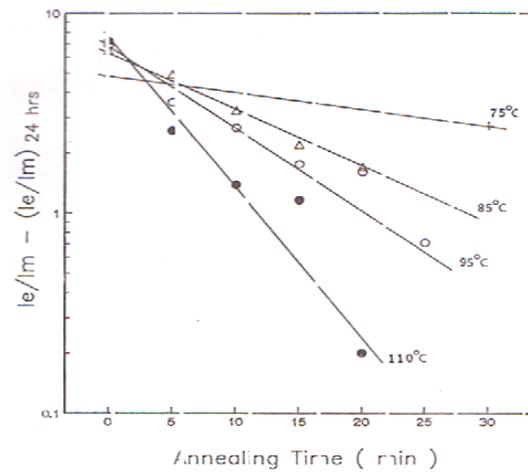


Figure-3. The reduction of I_e/I_m at different annealing temperatures as a function of annealing time.

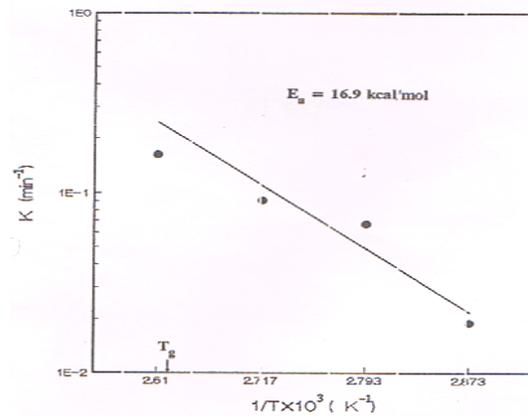


Figure-4. Arrhenius plot of rate constants determined for 600K MW polystyrene samples.

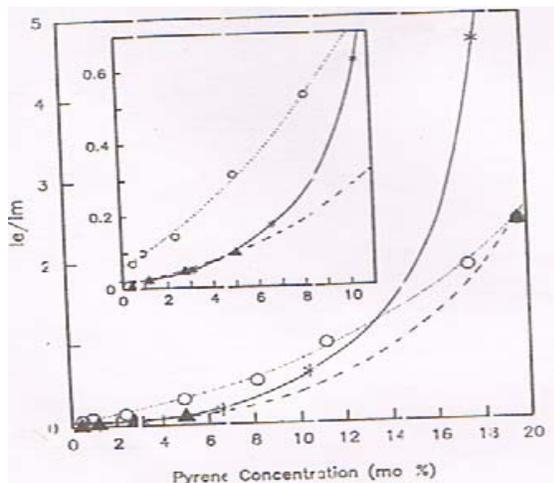


Figure-5. Comparison of excimer intensity for free and tagged pyrene in novolac films.

4.2. Film composition

Free pyrene in novolac; (Δ) pyrene tagged novolac; (o) 19.6 mol % pyrene tagged novolac mixed with untagged novolac. The inset is an expansion of the graph for low pyrene concentrations segments for films stretched by 300% [3]. This increase is insufficient to account for the 200% increase in I_e/I_m observed for the 300% stretched films by Gupta and Gupta [3], as well as for the differences between spin cast and solvent cast films observed in the present study. It seems more likely than higher I_e/I_m values of the spin cast films can be explained by two factors: (1) the spin cast films may have a higher concentration of intermolecular EFS; or (2) there may be a higher rate of energy migration in the spin cast films. As the film thickness decreases the polymer chain is more likely to be aligned in the plane of the substrate which will enhance those two factors.

The annealing experiments (in spin cast film) show drop in I_e/I_m , although after 24 hours of annealing I_e/I_m is still higher than for a solvent cast film than has undergone radial stress. This implies that non-equilibrium chain structures still exist in the spin cast films cast films even after long annealing times. Inter- or intramolecular excimer formation between two chromophores must result from rotation about methylene linkages; similar vibrational motion is not sufficient. Clearly, such rotation will be hindered in the glassy state. However, short chain segmental motion is possible below T_g even in the presence of chain entanglement, and it could certainly lead to a change in the EFS population. Helfand [20] has considered a number of fundamental comparative segmental motions that would produce the necessary Trans gauche rotation to modify the number of EFS. In addition Manner [21] has used various three bonds and four bonds jump models to simulate the dynamics of motion on a tetrahedral lattice. Typically, the apparent activation energy for this secondary relaxation process is relatively small, 10-20 kcal/mole [22], and only weakly dependent on side chain structure. As we have shown in this work, the apparent

activation energy obtained from the kinetic measurements of the annealing process is, also of this order. Thus, the experimental results are consistent with this being a possible mechanism.

4.3. Pyrene fluorescence spectra

Solutions of the tagged polymers in diglyme were prepared to have 1×10^{-4} M pyrene, based on the levels mentioned in the previous section. This resulted in polymer concentrations of 2.23×10^{-4} , 8.47×10^{-5} , 3.65×10^{-5} , 1.99×10^{-5} monomer for the 0.43, 1.2, 2.7, 5.0, and 19.6% tagged polymers, respectively. Emission spectra of the tagged polymers were measured and compared to the spectra of pure PBA. The emission spectra are plotted in Figure-5, normalized to the intensity of the emission at 398 nm. I_e/I_m of the tagged polymers increases with increasing tagging level and it is insensitive to dilution (inset, Figure-5), indicating that excimer formation in solution is intramolecular.

Solutions of the tagged novolacs in diglyme were spin cast into films and this spectrum of these films were measured. I_e/I_m of the films was reduced significantly over that in solution (inset, Figure-5), which is expected due to the extremely limited mobility of the chromophores in the solid phase. Films were also prepared in which the tagged polymer was "diluted" with untagged material. This allowed the same overall concentration of pyrene to be achieved with a different distribution in the film. The 19.6% tagged material was combined with pure novolac to obtain films with concentrations between 0.47 and 19.6 mol % pyrene. Films with various concentrations of free pyrene were also prepared. This allows the comparison of three systems: (1) the pyrene is forced to be randomly distributed in the systems for which all novolac chains are tagged with pyrene; (2) the pyrene is forced to be localized onto specific chains in the blends of the 19.6 mole% pyrene tagged novolac mixed with untagged novolac; and (3) the pyrene is free of direct constraints by the polymer in novolac films containing free pyrene. I_e/I_m for the three systems are plotted in Figure-6. At pyrene concentrations less than 6 mol%, I_e/I_m is equivalent. For the sample: with free or uniformly tagged pyrene (inset, Figure-6).

The films that are mixtures of tagged and untagged novolac have a much higher ratio of excimer fluorescence at these low pyrene concentrations. At higher pyrene concentration, however, I_e/I_m of the films with free pyrene far exceeds that of the tagged pyrene.

5. DISCUSSIONS

5.1. Spin cast polystyrene films

I_e/I_m has previously been used to gain information about chain conformation. Gupta and Gupta [3] studied the fluorescence of uniaxially stretched polystyrene films, and reported that 300% stretched polystyrene films have a 200% higher ratio of excimer to monomer emission intensity. They suggested that this was due to orientation effects which either increased the rotational mobility of the pendant groups, or promoted the



formation of excimer traps. However, in the glassy state the probability of rotational mobility of the pendant groups is very low so that their first explanation of the increase in I_e/I_m is unlikely. It is known that the orientation process in uniaxially stretched polystyrene films produces alignment of the chains as well as an increase in the

concentration of Tran's conformational segments [1]. This could be expected to increase the number of intramolecular excimer forming sites (EFS) formed between adjacent repeat units. However, that increase amounted to only about 5% of the total Trans conformational.

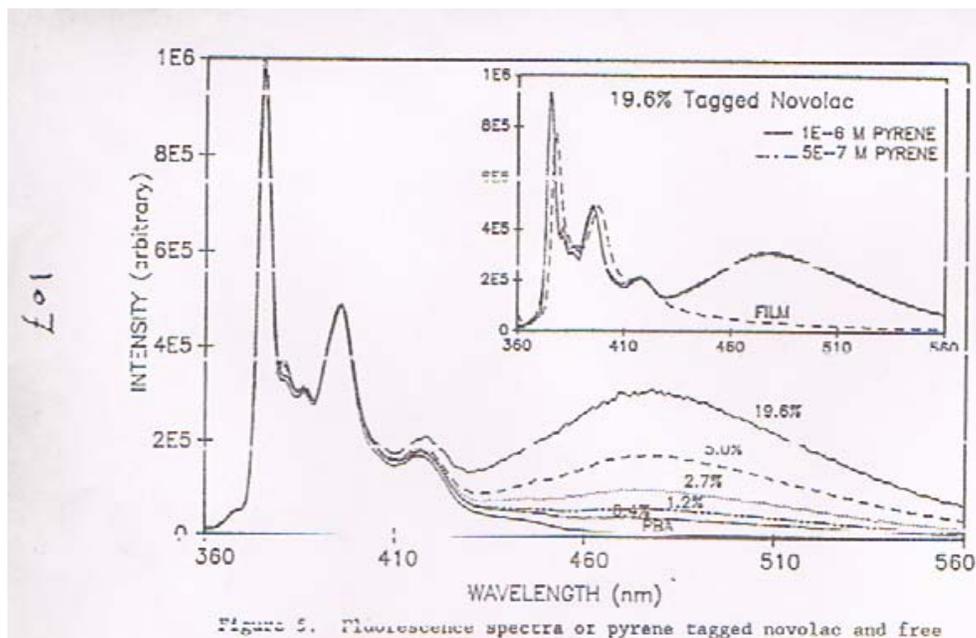


Figure-6. Fluorescence spectra of pyrene tagged novolac and free pyrene butyric acid (PBA) in diglyme. Spectra are labeled with percent of monomer units tagged. The pyrene concentration in solution is 1×10^{-6} M, except in the inset where different pyrene concentration compared along with the spectra of the film containing the tagged polymer.

5.2. Pyrene / novolac films

Changes in I_e/I_m can be used as a measure of the local concentration of pyrene. In solution, excimers can be formed by diffusion together) and existed and an unexcited molecule during the lifetime of the excited state. At very low concentrations, little or no excimer formation is expected, as is the case for the solution of pure PBA. If the pyrene is indeed tagged onto the polymer chains, the local concentration of pyrene will be higher in the vicinity of the chain: for dilute solutions, and should result in higher I_e/I_m . The increase in excimer emission with higher levels of tagging, but equivalent overall pyrene concentration (Figure-5), verifies that the pyrene is bound to the novolac.

In a film, however, molecular mobility is severely limited, so that excimer fluorescence must arise mainly from pairs or groups of pyrene molecules that were approximately in the excimer configuration when the film was cast. Thus, the intensity of the excimer emission is also an indication of the local concentration of pyrene in the cast film. If the pyrene aggregates, we expect that the excimer fluorescence would increase with aggregation. This system can be used to look at the aggregation of very low concentrations of a small molecule dye in a polymer film, and potentially detect macular aggregation before: it would be observable by other techniques such

as turbidity. In this case, the randomly tagged polymers are used as standards for molecularly dispersed pyrene. It was found that the I_e/I_m was nearly identical for free and tagged pyrene at low dye concentration (<6 mol%, or 10 wt%), but that the excimer intensity increased rapidly for the free dye above that concentration, as shown in Figure-6 indicating aggregation of the free dye. The novolac/pyrene system is similar to many positive photoresists that have a small molecule dye (a diazoquinone) as UV-sensitizer: dispersed in a novolac matrix. The dye/polymer compatibility may reach a "saturated" level, as proposed by Law [16], above which increased aggregation of the dye occurs. The concentration at which this starts to occur for pyrene is well below the level of sensitizer loading for many of the positive resist systems currently in industry. Such resists may contain as much as 15 to 50% sensitizer by weight [23, 24].

Mixtures of the 19.6% tagged novolac with untagged novolac higher I_e/I_m , at low overall pyrene concentrations, than the corresponding free or pure randomly tagged pyrene films - indicating that intramolecular excimer formation is occurring for the 19.6% tagged material. The differences in I_e/I_m decrease with increasing pyrene concentration; however, until the I_e/I_m for the free pyrene surpasses that of the highly tagged material, indicating that the free pyrene has



aggregated to create local concentrations that are higher than those enforced by the highly tagged material.

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