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Observation of Relaxation Processes Near the Glass Transition by Means of Excimer Fluorescence[1]

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ABSTRACT: Excimer fluorescence of a guest aromatic vinyl polymer dissolved at low concentration in a polymer host matrix has been used to monitor relaxation processes near the glass transition region. Suitable intramolecular excimer forming sites in the guest result from specific chain conformational states. The concentration of these sites, while initially fixed by the temperature at which the film is cast, will change as a function of time due to molecular motion in the relaxation region of the host. The change in site distribution is reflected in the fluorescence, thus allowing the molecular rearrangement to be followed. Fluorescence results for 0.20% poly(2-vinylnaphthalene) in polystyrene are shown to correlate quite well with mechanical dilatometric data. Consideration is given to both kinetic and thermodynamic aspects of the process.

In a recent series of papers,[2,3] excimer formation has been examined in fluid and rigid solutions of poly(2-vinylnaphthalene) (P2VN), polystyrene (PS), and poly(4-vinylbiphenyl) (PVBP). An excimer is an electronically excited molecular complex formed between two aromatic chromophores in a coplanar sandwich arrangement. Excimer formation in aromatic vinyl polymers may result from both intermolecular and intramolecular interaction, particularly at high concentrations. However, the latter situation predominates in sufficiently dilute systems formed by placing the polymer under study in a suitable fluid solvent ($\sim 10^{-4}$ *M*) or in a rigid polymer matrix ($\sim$0.20 wt %), as used in this work. Furthermore, it has been shown that the intramolecular interaction in the vinyl polymers considered in this study is between adjacent chromophores.[2b]

Photophysical sampling of excimer sites consists of excitation of a pendent chromophore followed by random exciton migration along the chain until competitive trapping and fluorescence occurs from a suitable excimer chain conformation. In fluid solution interconversion of chain conformations proceeds rapidly with the lifetime of a particular conformation limited by collision with solvent molecules. As a result of free rotation, thermodynamic equilibrium of chain conformations will be maintained as the temperature is varied. However, the situation is quite different for rigid cast films. With the evaporation of the casting solvent below the glass transition temperature of the guest–host system, a chain conformation distribution will be frozen in which is characteristic of the casting temperature. To be sure, some molecular motion will be present on a limited scale below T_g, as evidenced by the various suborder transitions. However, the skeletal rotations necessary for excimer site formation will be severely restricted, thus fixing the site concentration.

It was shown previously that the distribution of excimer forming chain conformations which allow interaction of adjacent chromophores on the same polymer chain may be predicted by a simple statistical model.[2b] In this model, the rotational isomeric state approximation is used to enumerate nine possible chain conformations for a three-skeletal carbon dyad. The system is simplified by including only the ground and first excited conformations, the latter corresponding to excimer forming sites. This simplification is justified for certain vinyl polymers, such as P2VN which was used in this study. The equilibrium excimer site fraction $f_E^*(T)$ is then given by the Boltzman distribution

$$f_E^*(T) = \frac{N_E^*}{N_T} = \frac{W_E \exp(-\Delta E/RT)}{W_G + W_E \exp(-\Delta E/RT)} \qquad (1)$$

where N_E^* is the equilibrium number of excimer conformations, N_T is the total number of possible conformations, W_E and W_G are the degeneracies of the excimer and ground states, respectively, and ΔE is the excimer site conformation energy. ΔE is determined from a comparison of excimer and monomer fluorescence band intensities as a function of the casting temperature. Previous work with P2VN indicated a strong casting temperature dependence (ΔE = 2500 ± 300 cal) so that films prepared at elevated temperatures contain significantly more excimer sites than those cast at room temperature.[2b] f_E is related to the fraction of aromatic rings in excimer sites, f_R, by the relation $f_R = f_E P_E$, where P_E is a probability factor which is approximately 2.

Due to the freezing in of chain conformations in the casting process, the film will be in a metastable condition below T_g for any temperature other than that at which it was cast. Thus, a driving force exists for change in the chain conformational distribution; however, it will not be kinetically favored due to high potential barriers. This situation is altered in the region of the glass transition because molecular rearrangement is now possible. Since the relative guest excimer fluorescence may be directly related to the population of a specific conformational state in the guest, molecular rearrangement of those conformations will be reflected in changes of fluorescence. Thus, it may be possible to utilize the technique as a probe of relaxation in the guest–host system.

The method of dispersing a probe molecule in a polymer matrix for purposes of investigating solute–matrix interactions is not new. Previous workers have used dielectric or photochromic behavior of small solute molecules to elucidate internal modes of solute motion in the relaxation region of the host matrix.[4] However, the dielectric technique has the disadvantage of requiring high solute concentration and neither method provides a measure of specific chain conformational behavior, the object of this study.

It should be emphasized that the excimer probe is sensitive only to those guest–host–residual casting solvent interactions which affect the conformational mobility of the guest over a minimum of several skeletal segments; side chain torsional or vibrational motion will not be detected. It thus lends itself to the study of higher temperature relaxation processes, such as near the glass transition. Since the technique provides a measure only of the guest conformational changes, the amount of information obtained about the host matrix will depend upon the extent of guest–host coupling. This paper is intended to demonstrate the feasibility of such an approach for rigid films of 0.20% P2VN in PS. In the following, evidence for guest conformational rearrangement is presented, comparison is made with static mechanical measurements, and the kinetic and thermodynamic aspects of approach to conformational equilibrium are considered.

Experimental Procedures

(A) Sample Description. The majority of the work was done with rigid 0.20% P2VN–PS films (65 to 80 μ thick). A small amount of work was also done on neat P2VN and PS films (3 to 7 μ thick). Films were cast from Matheson Coleman and Bell spectroquality benzene or Fisher spectroquality chloroform on quartz or sapphire plates which were covered and placed in ovens immediately after solution deposition. The covers prevented convection patterns from being set up in the film and retarded solvent evaporation somewhat to allow for establishment of conformational equilibrium at the oven temperature. The use of two solvent systems enabled the effect of residual solvent plasticization to be qualitatively examined. The polystyrene host was similar for the two series. The benzene cast host had M_n and M_w values of 29,600 and 231,000 while the chloroform series had corresponding values of 25,500 and 217,000, as determined by gel permeation chromatography.

(B) Fluorescence Measurements. The basic spectrofluorimeter described previously[2b] was interfaced with a devoted PDP 8/S digital computer for these measurements. The computer had several functions: to generate control pulses for the wavelength drive stepper motor on the analyzing monochromator, to monitor the fluorescence intensity and thermocouple voltage which were supplied as analog signals to a 12 bit analog-to-digital converter, and to perform the data reduction. Overall experimental control was provided by a master program written in FOCAL language. The standard sequence was to step through three wavelengths, 3090 Å (for a scattering correction), 3300 Å (monomer intensity) and 3900 Å (excimer intensity), followed by a return to 3040 Å before resuming the cycle to allow for hysteresis in the wavelength drive. Intensity measurements were made at each wavelength with the values recorded being the averages of six readings. Furthermore, a wait cycle was entered after each wavelength advance and before the intensity measurements in order to allow the VTVM to settle.

Sample temperature was measured by a thermocouple attached to the clamp holding the film between two sapphire plates. Temperature readings were taken immediately before the monomer and after the excimer intensities and then averaged. Total cycle time was 29.4 sec with 18 sec between thermocouple readings. Linear heating and cooling profiles at 5°C/min were achieved by flow of preheated or cooled nitrogen over the sample. During relaxation measurements the temperature was held constant to within 0.5°.

(C) Mechanical Measurements. Dilatometric penetrometer measurements were made on a Perkin Elmer Thermomechanical Analyzer Model TMS-1 with temperature program control Model UU-1 at a heating rate of 5°C/min.

Results and Discussion

(A) Evidence of Conformational Change. The significant experimental parameter for examining excimer formation is the ratio R of the excimer intensity I_D to the monomer intensity I_M. Experimentally, R is calculated from intensities measured at positions of minimal overlap of monomer and excimer bands, not from band areas. However, this is a good approximation to the ratio of integrated intensities, within some constant factor, since the band widths do not change. A kinetic analysis presented previously indicated that for P2VN

$$R = \frac{I_D}{I_M} = \left[\frac{k_{FD}k_E}{k_{FM}k_D}\right]\left[\frac{f_R}{1 - f_R}\right] \qquad (2)$$

where k_{FD} and k_{FM} are excimer and monomer fluorescence decay constants, k_D is an overall excimer decay constant, k_E represents the excimer site sampling process, and f_R is the fraction of aromatic rings in excimer forming sites.[2b]

The temperature dependence of eq 2 may be conveniently divided into that of the collective rate constant ratio in the first bracket and that of f_R in the second. For temperatures appreciably less than the host T_g the fraction of rings in excimer forming sites for the guest will be constant and the temperature dependence is solely that of the rate constants. It has been shown that electronic destabilization of the P2VN excimer and subsequent decay by nonradiative processes is first measurable at about 200°K and becomes progressively more important as the temperature increases.[2b] The exact form of the temperature dependence of R is unimportant although it is primarily due to changes of

k_D and would be expected to decrease monotonically with temperature for constant f_R. The fraction of rings in excimer forming sites will remain fixed as long as the film temperature remains sufficiently below the glass transition region. Should that region be entered, however, molecular rearrangement can lead to a change in the excimer site concentration and, hence, of the excimer fluorescence.

This behavior is illustrated in Figure 1 which shows a heat–cool cycle for a 0.20% P2VN–PS film cast from chloroform at 51°. Here the experimentally determined R is plotted against reciprocal sample temperature on a semilog scale. The values as plotted do not include the spectral response correction since it is the relative change in R which is of interest. A complete heat–cool sequence through the glass transition region of the guest–host system is represented by circles for heating and triangles for cooling. As observed previously,[2b] R initially decreases due to electronic dissociation of the excited complex at fixed site distribution. At some temperature T_i', here approximately 83°, the data begin to deviate from the initial destabilization curve which is shown extrapolated over a modest range as a dashed line. Above this temperature there is a leveling followed by a rather rapid increase in R until a second leveling is observed above 106°. This high temperature "knee" may be characterized by a second temperature T_g', defined by the intersection of the two straight lines as shown. Although there is somewhat more scatter in the data, a similar knee can be defined for the cooling curve. In general, T_g'(heating) appears to be the same as T_g'(cooling) although more accurate data are needed to clarify the point. To be sure, both T_i' and T_g' are determined rather arbitrarily but they are useful for comparing the fluorescence with the mechanical results.

Upon cooldown there is a large hysteresis with the cooling segment parallel to the heating segment. If electronic destabilization of excimer sites were the sole process operating, one would expect the data to continue along the original curve as the temperature increases and then to retrace the path upon cooling. This situation does indeed apply if the relaxation region is not entered. That this is not the case for higher temperatures strongly suggests that some form of chain conformational rearrangement has taken place in the guest, i.e., an increase in the fraction of excimer forming sites.

Also shown in Figure 1 are data (squares) for a run in which the film was equilibrated at some intermediate temperature between T_i' and T_g'. During this equilibration period R was monitored as a function of time until no further increase was observed. This is represented by the vertical dashed arrow. The kinetic aspects will be considered later. For the moment, it is important to note that the equilibrated value of R is intermediate between the other two curves and that the cooling curve for this intermediate "anneal" is parallel to those of the complete heat–cool cycle through T_g. The first point is related to the effect of chain entanglement on the attainment of thermodynamic equilibrium and will be considered in more detail later. The second provides evidence that the temperature dependence of R below T_g is of electronic origin, i.e., independent of f_R.

Up to this point we have considered evidence for a change in excimer site distribution in the guest but no mention has been made of the type of molecular motion responsible for the rearrangement. Intramolecular excimer site formation between adjacent chromophores must result from rotation about methylene linkages. Simple vibrational motion is not sufficient. Clearly, such rotation will be hindered in the glassy state. However, one conformational motion which would lead to excimer sampling and which is possible below T_g for short chain segments even in the presence of chain entanglements is the so-called Schatzki crankshaft motion.[5] In this model, originally proposed to explain the suborder γ transition in polyethylene, an eight-carbon segment is selected which has the terminal carbon–carbon bonds colinear and the remaining carbon atoms on a diamond lattice. Rotation of the central four carbons about the terminal axis constitutes the group motion. The extensive review by Boyer on the effect of chemical structure on T_g deals at length with the relationship of crankshaft rotations to suborder transitions.[6] He indicates that rotation of three or two carbon units should also be possible if suitable seven- or six-carbon segments are present. The apparent activation energy for the process is relatively small, 10 to 20 kcal, and only weakly dependent on side chain structure. As will be shown, the apparent activation energies obtained from the kinetic measurements of this study are also of this order. Thus, the experimental results are at least consistent with this being one possible mechanism. Other mechanisms of similar energy which allow for rotational motion of small chain segments are also possible and cannot be distinguished. More difficult to assess, however, is the nature of the molecular coupling between the host and guest. Presumably, it is the segmental rotation of the interpenetrating PS which is responsible for driving the P2VN rearrangement but more definitive statements are not possible.

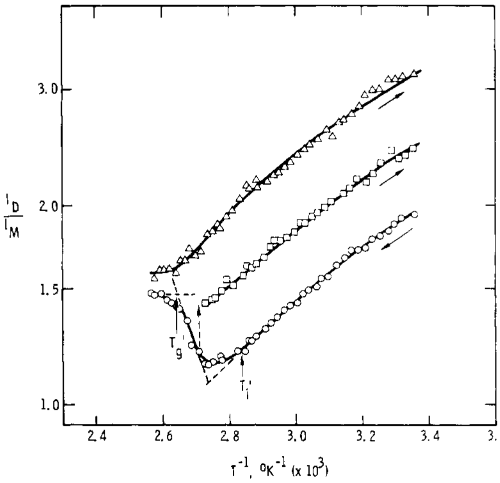

Figure 1. Heat–cool cycles for 0.20% P2VN–PS film cast from chloroform at 51°. A complete sequence through the glass transition is shown for heating (circles) and cooling (triangles) as well as an intermediate equilibration followed by cooling (squares). The fluorescence is characterized by the parameters T_g' and T_i' which are defined by the indicated arrows.

(B) Rearrangement in Neat Films. The use of the guest–host method to examine relaxation processes may seem to be an unnecessary complication for this particular system since polystyrene itself exhibits excimer fluorescence. Thus, both polymers conceivably could be examined separately in pure form. Although this situation would not apply in general, e.g., for a poly(methyl methacrylate) host, there are more basic objections. In the first place, use of neat films presents difficulties on a purely experimental basis due to self-absorption effects, necessitating the use of thin samples (3 to 5 μ) which are difficult to cast at elevated temperature. However, a much more significant objection involves the nature of the excimer sites which are being monitored. In the dilute system these are primarily intramolecular between adjacent naphthalene chromophores, whereas both intermolecular and intramolecular interactions are possible in neat films. In fact, based on ini-

Table I
Comparison of Fluorescence and Mechanical Results[a]

	Fluorescence			Mechanical		
T_{cast}	T_g'	T_i'	$T_g' - T_i'$	T_g	T_i	$T_g - T_i$
			A. Benzene Cast Films			
22	87 ± 3 (1)	71 ± 4 (3)	16	87 ± 0.1 (2)	72 ± 0.7 (2)	15
51	90 ± 3 (1)	77 ± 3 (1)	13	87 ± 1 (2)	74 ± 4 (2)	13
77	94 ± 3 (1)	82 ± 3 (1)	12	90 ± 1 (2)	80 ± 2 (2)	10
			B. Chloroform Cast Films			
51	104 ± 3 (2)	84 ± 2 (2)	20	102 ± 2 (4)	88 ± 5 (4)	14
77	109 ± 4 (2)	100 ± 2 (2)	9	108 ± 0.5 (4)	100 ± 0.6 (4)	8
100	108 ± 4 (2)	101 ± 5 (2)	7	106 ± 0.6 (4)	99 ± 2 (4)	7

[a] All temperatures in °C.

tial values of *R*, neat films of P2VN may have an order of magnitude more inter- than intramolecular sites. While there will certainly be an increase in intramolecular sites as molecular motion becomes possible, it is not clear that the distribution of intermolecular sites will be significantly altered.

To clarify this point, neat thin films of PS and P2VN were examined. In both cases, the initial behavior is for *R* to decrease steadily as a result of the electronic destabilization of the excimer. However, the fluorescence results in the relaxation regions were much less dramatic than for the dilute films. At about 95 ± 5° for PS and 133 ± 5° for P2VN there is a slight break in the curve and subsequently a small hysteresis effect upon cooling. The change for PS, which is smaller than that for P2VN, must be associated with its glass transition. Similarly, mechanical T_g measurements for P2VN yielded 130 ± 3°, in good agreement. Evidently, the excimer probe is indeed reflecting molecular motion characteristic of the glass transition in both pure polymers. However, the relatively small magnitude of departure from the expected electronic destabilization curve above the respective T_g's would seem to indicate that it is primarily the intramolecular excimer sites which are affected by thermal rearrangement. Inclusion of the much more numerous intermolecular interactions in the pure film simply reduces the size of the observed transition and hence the experimental accuracy.

In addition to the magnitude of the fluorescence change near T_g, the temperature at which the change is observed is important. From the dilute film data of Figure 1 it is clear that the P2VN conformational change occurs at temperatures much closer to that of pure PS than that of pure P2VN. This implies that the P2VN probe in the guest–host system is monitoring the relaxation of intimately associated PS chains. If P2VN were present as completely isolated microphases, no rearrangement would be observed until the higher temperatures characteristic of the neat P2VN; this is not the case. The relationship between the guest probe and the host matrix will be explored further in later sections.

(C) Correlation with Static Mechanical Results. By its very nature, the guest excimer probe is sensitive to relaxation on a molecular scale. It is of interest to compare these results with some bulk measure of relaxation. One of the simplest such mechanical dilatometric techniques is that of penetrometer deflection. These data, which were run at the same heating rate, may be characterized in terms of T_g, the glass transition temperature, determined at the "knee" of the deflection curve by the standard procedure and a second temperature T_i, where sample penetration is first observed. This second quantity is somewhat more variable but serves as a reasonably good indication of the initiation of the relaxation process on a bulk scale.

The results are tabulated in Table I along with T_i' and T_g' values from the fluorescence data. Standard deviations are listed along with the number of determinations in parentheses. For the moment, we consider only the mechanical results. The increase in T_g in going from the benzene to chloroform systems is as expected since it is known that benzene is difficult to remove from polystyrene, even with extensive pumping. The resulting additional solvent plasticization will tend to lower the T_g for the benzene series. As shown, the benzene and chloroform values bracket the generally accepted figure of 100° for polystyrene. Since, within experimental error, pure PS films cast from benzene gave the same results as for the dilute films shown in IA, it would appear that the presence of P2VN in such low concentration has little effect on the bulk T_g. This is to be expected from empirical formulas relating T_g to diluent concentration. The larger glass transition temperature for higher casting temperatures and the lower initiation temperature for films cast at lower temperature could result from more efficient removal of residual solvent at elevated temperature or some form of interrelationship of the T_g and the higher energy chain conformations which are favored for such films. The former is the more probable although the point is not significant for these results because we merely wish to demonstrate that molecular relaxation data from the excimer probe correlate with bulk mechanical data. As shown in the table, this correlation is indeed quite good. However, to some extent this may be the result of fortuitous definition of T_i', T_g', T_i, and T_g. Nevertheless, the agreement is consistent with the earlier neat film results which imply that the P2VN and PS are intimately related.

On the other hand, energy transfer measurements by Harrah on similar films have shown that exciton diffusion in the P2VN guest is three dimensional, requiring a random coiled configuration.[7] Furthermore, whereas the 0.20% films were transparent, attempts to prepare films from benzene with P2VN concentrations of 1% or greater invariably led to visible segregation. Both these points indicate that the P2VN–PS compatibility is only of limited extent. A consistent picture of the morphology of the dilute rigid solution thus requires existence of the P2VN in balled structures which are extensively interpenetrated by the host PS. These observations on guest–host interaction illustrate the possible application of such a method for compatibiltiy studies.

(D) Approach to Conformational Equilibrium. Having demonstrated that the P2VN probe serves as an adequate reflection of the PS host matrix relaxation behavior, we wish to consider the kinetic and thermodynamic aspects of the process. The approach to conformational equilibrium may be best understood with the aid of casting temperature data, as shown in Figure 2. Here the curves represent smoothed data for dilute films cast from chloroform at 51, 77, and 100°. There are several significant points. First, the initial curves for each of the casting temperatures are parallel, indicating that the temperature dependence below the relaxation region is strictly of electronic origin and independent of conformational structure, i.e., restricted to changes in rate constants in the first bracket of eq 2. Second, all samples, if heated sufficiently beyond their glass

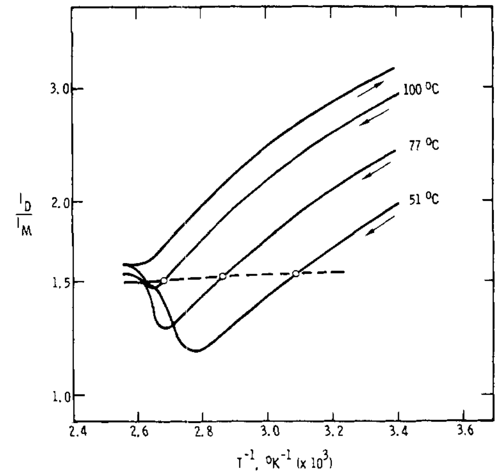

Figure 2. Composite curves showing the effect of casting temperature. The dashed line defines an equilibrium curve where the sample temperature is the same as the casting temperature. Molecular relaxation of the guest probe will take place toward this line.

transition region to allow for maximum rearrangement, will return along the same curve which represents the equilibrium frozen in at T_g. Also shown in the figure are points at which the sample temperature is the same as that at which the film was cast. A dashed line drawn connecting these points to the level portion above T_g represents the guest chain conformational thermodynamic equilibrium curve $R^*(T)$ for the guest–host system. Regions above and below this line represent nonequilibrium states; if sufficient molecular motion is possible, the system will relax toward the line. We must note, however, that this relaxation may be exceedingly slow. In the following sections we consider kinetic aspects of the approach to equilibrium both from below and above $R^*(T)$ and the extent to which equilibrium is achieved.

We first consider approach to equilibrium from below. Recall that this experiment consists of heating the film to a temperature between T_i' and T_g' and then holding at that temperature while the change in R is monitored. Typical results are shown in Figure 3 for a 0.20% P2VN–PS film cast from benzene at 22° and held at 73°. The significance of the solid curve will be considered shortly. It is clear that, within the time scale of the measurement, the data level off to a constant value. It should be recognized, however, that the possibility of long term relaxation still exists. We will come back to this point later.

One measure of the extent to which the sample is equilibrated at a given holding temperature over a short term is the fractional change $(R_f - R_i)/(R^* - R_i)$ where R_i is the initial I_D/I_M ratio at a given holding temperature and R_f is the final value after short term equilibration. Typical results are shown in Figure 4 for films cast from chloroform at 51°. Here the percent change in R is plotted against the difference between the mechanically measured T_g and the holding temperature. The errors are fairly large but two observations seem pertinent. First, it is interesting that conformational rearrangement is observed over such a large range below the glass transition temperature. Second, it is not surprising that an equilibrium distribution of excimer forming chain conformations is not achieved for rearrangement below T_g due to the presence of chain entanglements which restrict rotational motion. However, an exponential dependence would have seemed more reasonable than the approximately linear relationship which is observed. Further experiments are planned to clarify the point.

Limited measurements were also performed for approach to equilibrium from above. In one case a dilute film

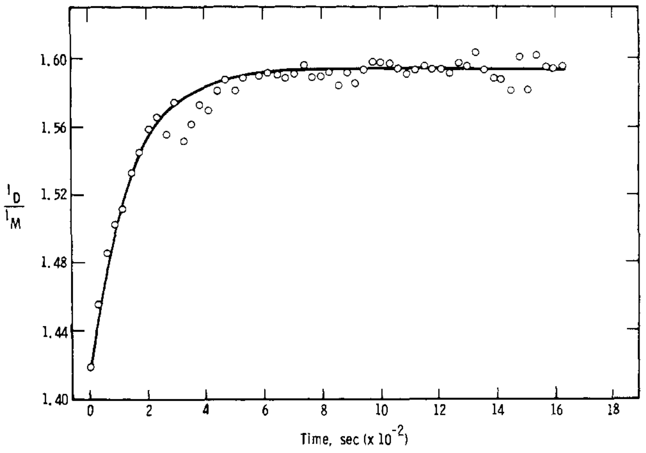

Figure 3. Time dependence for 0.20% P2VN–PS film cast from benzene at 22° and held at 73°. The solid line is a single exponential fit to the data.

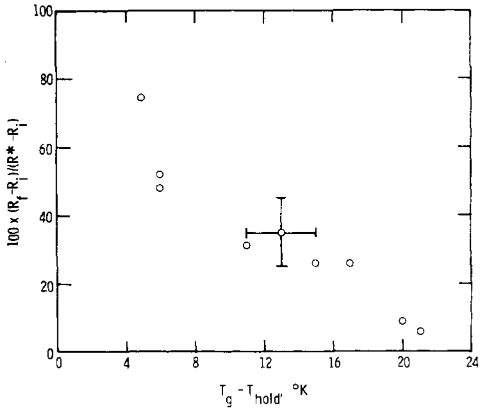

Figure 4. Approach to equilibrium for films cast from chloroform at 51°. The percent change in R is plotted as a function of separation from the glass transition.

cast from chloroform at 51° was heated past T_g and held at 125° for 15 min to allow for short term equilibration. It was then cooled to 101° and held at that temperature while R was monitored. The ratio did decrease toward the equilibrium curve as expected. However, it did so at a rate which was several times slower than that for approach from below. The experiment was repeated at a lower temperature and similar results were obtained. It is apparent that the large hysteresis shown in Figures 1 and 2 is a result of this reduced relaxation rate. The difference in rates may be due to differences in free volume as a result of the casting process and subsequent thermal history of the sample. Alternatively, it could simply result from further loss of residual solvent during the temperature cycle.

In one sense, the excimer probe technique may be viewed simply as a means of monitoring relaxation in the host matrix. On the other hand, the guest probe itself may be considered a model system for study of conformational rearrangement in that the probe molecular motion should be representative of motion near the glass transition in general. The advantages of isolating a particular conformational state in the guest–host method are apparent. With this in mind, we may analyze the kinetics of the relaxation process.

Numerous theories have been developed to explain the glass transition. No attempt will be made to present them even in outline form; rather, we refer to two recent reviews by Shen and Eisenberg.[8,9] These present experimental observations and representative theories which emphasize in turn free volume, kinetic or thermodynamic aspects, as well

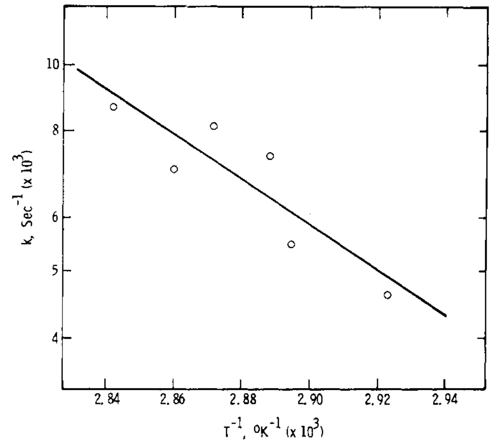

Figure 5. Arrhenius plot of rate constants determined for relaxation of 22° benzene cast samples.

as a unified treatment which relates both the relaxation and equilibrium behavior. Most pertinent to our results is the microscopic relaxation theory due to Wunderlich et al. in which a two-state system is assumed and transitions between states are treated by first-order kinetics.[10] It was shown earlier that such a two-state chain conformational model satisfactorily described excimer formation in P2VN.[2b] If N_E represents the actual number of excimer conformations at any temperature, the rate of approach to equilibrium, following Wunderlich, will be given by

$$dN_E/dt = (1/\tau)[N_E^*(T) - N_E] \qquad (3)$$

where τ is the relaxation time. Rewriting in terms of the fraction of rings in excimer sites f_R and integrating yields

$$\ln\left[\frac{f_R^*(T) - f_R(t)}{f_R^*(T) - f_R(0)}\right] = -\frac{t}{\tau} \qquad (4)$$

where $f_R(0)$ is the initial (nonequilibrium) concentration, $f_R(t)$ is the concentration at any time t, and $f_R^*(T)$ corresponds to the equilibrium distribution. Since f_R is of the order 10^{-2} for P2VN,[2b] it is apparent from eq 2 that changes in R should be directly proportional to changes in f_R at a given holding temperature where the photophysical rate constants are fixed. Thus, a plot of ln $[R^*(T) - R(t)]$ vs. t should be linear. In fact, this is not the case because this assumes that the equilibrium conformational distribution has arisen as a result of unrestricted chain rotation and translation. Due to chain entanglements, this condition is virtually unattainable for solid films which are initially in a nonequilibrium state at a temperature appreciably below T_g. Thus, the experimentally determined $R_f(T)$ is not equivalent to $R^*(T)$.

However, if $R_f(T)$ is used in place of $R^*(T)$ the relaxation data may be treated quite adequately by the proposed first-order mechanism. Such a single exponential fit is shown by the solid curve of Figure 3. Thus, it is possible to calculate a relaxation rate constant for a particular holding temperature. An Arrhenius plot of rate constants so calculated is shown in Figure 5 for films cast from benzene at 22°. A least-squares fit yields an activation energy of 15 ± 4 kcal. Films cast at 51 and 77° showed somewhat larger activation energies of 17 ± 5 and 21 ± 7 kcal, respectively. This may result from reduced solvent retained in the higher temperature cast films but the large errors preclude a definitive statement. Only limited data are available for the 77 and 100° cast chloroform films. However, more extensive rate results for the 51° chloroform films gave the same activation energy as for the corresponding benzene samples. Note that these energies are of the same magnitude as the crankshaft motion energies mentioned earlier.

Although the results are somewhat incomplete at this stage, the data presented for the approach to conformational equilibrium indicate that relaxation near the glass transition may be described in terms of two processes occurring at widely differing rates. The first consists of local short term relaxation of small segmental regions. It is this process which has been monitored in these experiments. In this process, skeletal rotation becomes possible in suitable regions for any one of several reasons such as local increases in free volume, solvent voids, or residual solvent plasticization. These regions are of limited size due to chain entanglements which effectively pin the coiled guest chains at random intervals. This has the effect of reducing the number of accessible chain conformations. In particular, the number of higher energy excimer conformations is reduced below that predicted by eq 1. It may prove possible to calculate this reduction in conformational states; this point is being pursued. The second process consists of long term extended segmental diffusion resulting from the gradual unpinning of chain entanglements. This differentiation is somewhat artificial and is more a question of degree than of kind since the cooperative nature of chain motion is expected to increase continuously as the temperature is raised to T_g. Nevertheless, it seems possible that the two processes may be separated over a long time scale for temperatures below T_g; this point is also being pursued.

Conclusion

It has been shown that use of the excimer probe technique with a suitable guest polymer dissolved at low concentration in the host readily senses rearrangement in the host matrix. It would appear that the method has significant implications for obtaining information about the host, the guest, and interactions between the two. In particular, the excimer probe provides a model system in which the dynamics of a specific chain conformational state may be studied. This should allow experimental verification of selected problems in chain conformational statistics.

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