Table IX
Activation Energies (E_a), Preexponentials (A), and Rate Constants of Excimer Formation (k_{DM}) of *meso*-D1PP and *meso*-B1PEE

	meso-D1PP	*meso*-B1PEE
E_{a_1}, kJ mol^{-1}	11.7	8.3
A_1	1.6×10^{10}	6.5×10^{10}
E_{a_2}, kJ mol^{-1}	20.8	18.7
A_2	1.5×10^{12}	3.3×10^{12}
k_{DM_1}(298 K), s^{-1}	2.9×10^{8}	1.5×10^{9}
k_{DM_2}(298 K), s^{-1}	4.8×10^{8}	1.8×10^{9}

there is some indication that the pyrene group in the G position is lying in the same plane as the ether chain.[20] If this is so, the number of conformational possibilities is diminished to two. Only the T_1G_1 and the T_2G_1 conformation should be present. The kinetic data in Table IX could then be adequately explained with these two conformations. The lower activation energy is caused by the partial rotation necessary to form the staggered excimer from the T_2G_1 rotamer. The higher activation energy could be explained by the rotation to form the eclipsed excimer from the T_1G_1 rotamer. However, if the T_1G_2 rotamer is also present, the high activation energy could be related to the kinetically similar T_1G_1 and T_1G_2 rotamers. Since, in the case of *meso*-D1PP no obvious reason can be found why either the T_1G_2 or the T_2G_1 rotamer is more stable, the second explanation is presently favored.

Conclusion

The compounds investigated here are a model for the isotactic and heterotactic diads of poly(1-vinylpyrene). The already complex kinetic behavior of these fairly simple molecules suggests a highly complex kinetic behavior of the corresponding atactic polymer. The spectral and kinetic differences between *meso*-B1PEE and *meso*-D1PP indicate that B1PEE should not be considered as an appropriate model for poly(1-vinylpyrene).

A conformational study of bichromophoric compounds is a necessity whenever intramolecular excimer formation is investigated. Conformational data are useful to explain the sometimes complex excited-state behavior of these compounds. If the chromophores investigated are not symmetrically substituted, the existence of several rotamers should be taken into account. This also includes the possibility of having more than one excimer species.

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Inverse Gas Chromatography. 2. The Role of "Inert" Support†

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ABSTRACT: Retention volumes of nonpolar *n*-hexane, moderately polar ethyl acetate, and strongly polar ethanol were measured on chromatographic columns of Chromosorb W-Aw-DMCS treated, uncoated by any polymer, and on columns coated with polyisobutylene and poly(methyl acrylate), respectively. For each column and probe, the dependence on the amount injected was studied. The DMCS treatment seemed to produce some poly(dimethylsiloxane) attached to the uncoated support; this led to (linear) retention of all probes. In addition, the remaining strongly polar groups on the surface of the support interacted with polar probes extensively and in a strongly nonlinear way. To obtain meaningful data for the retention of the probes, the retention volumes measured on the uncoated column had to be subtracted from the data for coated columns. For polyisobutylene, the new procedure yielded specific retention volumes V_g that were independent of the injected amount, flow rate, and polymer loading of the column for all probes.

Introduction

In recent years, inverse gas chromatography (IGC) has become an almost routine method for obtaining thermodynamic data on polymeric systems.[1-31] The method is termed "inverse" because, unlike standard gas chromatography, it is the stationary phase (polymer or polymer blend) which is of interest. Despite broad usage, the method remains complicated by experimental and theoretical factors that are not completely understood. Some

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of these factors were recognized by previous researchers.[32-39] Based on those results, a consensus has developed among workers in the field, which recognized the main complicating factors to be (1) concentration effects associated with larger probe injections, (2) slow diffusion of the probe through the polymer layer, and (3) adsorption of the probe on the surface of the polymer. The following steps were deemed satisfactory to obtain meaningful values for the specific retention volume, V_g: (1) The data were either extrapolated to vanishing amounts of injected probe or measured by using injection amounts arbitrarily defined as vanishingly small. (2) The data were extrapolated to infinite loading by polymer to eliminate the effect of the adsorption of the probe on the surface of the polymer. The retention by the support was never considered explicitly. (3) The data were extrapolated to zero flow rate of the carrier gas to compensate for slow establishment of phase equilibrium. (We note that this procedure could have been very harmful if the flow rate was measured incorrectly.[40])

In our effect to better understand all aspects of inverse gas chromatography, we have studied the dependence of retention volumes on the amount of injected probe. In some cases we found very significant dependence that could not be explained by traditional approaches. These discrepancies were eventually traced to the interaction of the probes with the so-called inert chromatographic support. It has been long known that Chromosorb type support shows strong retention of polar probes. While the treatment with trimethylchlorosilane or hexamethyldisilazane reduces this retention, it does not eliminate it completely.[41,42]

In this paper we reinvestigate the retention of both polar and nonpolar probes on chromatographic columns using Chromosorb W treated with dichlorodimethylsilane as support. Columns coated by either a nonpolar polymer (polyisobutylene) or more polar poly(methyl acrylate) were employed as well as columns uncoated by any polymer. A simple model of interaction was developed which allowed elimination of the effect of support on IGC data.

Experimental Section

Apparatus and Procedures. Measurements were made on a modified Varian Aerograph Model 2100-40 gas chromatograph equipped with a flame ionization detector (FID). The modifications made to this instrument and the method of coating the polymer onto the support have been reported previously.[43] For comparison we have also prepared one column coated by polyisobutylene using the traditional method of coating: suspending the support in the solution of the polymer and evaporating the solvent in a vacuum rotary evaporator. We further modified the instrument and redesigned the plumbing system by reducing the dead volume at the injection port and the detector to obtain the most symmetrical peaks possible. We have achieved reasonable symmetry for the peaks of alkane. The most pronounced tailing observed for polar probes is therefore not an instrumental artifact, but results from interaction of these probes with the chromatographic column.

Dried helium was used as a carrier gas. The flow rate F_f (10 mL/min at 25 °C) was controlled by a thermostated precision needle valve and soap bubble flowmeter. We have found that helium, as a carrier gas, diffuses through the soap bubble, causing an apparent reduction of the retention volumes by almost 10% at the lowest flow rate (4 mL/min). A correction has been applied to compensate for this reduction. (We have reported the analysis of the erroneous flow rate measurements elsewhere.[40])

A 1-μL Hamilton syringe was used to inject the probes. The smallest injections (a few nanograms) of probe were achieved by using the so-called "spitting injection", wherein the syringe was emptied 3 times and only the amount remaining in the needle was injected. Sometimes we injected the needle into a hot false injection port to evaporate most of the probe and then injected the remaining amount into the real port. The relative areas of the chromatographic peaks were measured by using a Varian CDS III integrator in conjunction with a Hewlett-Packard dual-channel strip chart recorder. The peak maxima obtained by the recorder were then compared with those obtained by the integrator; usually these agreed within 0.02 min. The retention time was measured at the peak maximum.

Table I
Description of the Chromatographic Columns

column	length, ft	wt of support, g	wt of PIB, g	loading,[a] %
I	5	8.0040	0	0
II	5	7.9760	0.2294	3
III	5	7.7980	0.5139	7
IV	5	7.8087	1.0084	12
V	5	7.5098	0.4533[b]	7

[a] Approximate. [b] PMA.

Materials. We selected polyisobutylene (PIB) as a model to perform our studies. The PIB sample had intrinsic viscosity in cyclohexane at 20 °C $[\eta]$ = 195 mL/g corresponding to M_V = 379000. We also studied poly(methyl acrylate) (PMA), which had intrinsic viscosity in butanone at 20 °C $[\eta]$ = 116 mL/g corresponding to M_V = 381000.

Five columns were prepared by using Chromosorb W, acid washed and treated with dimethyldichlorosilane, as a solid support: one column with no polymer coating, three columns with different loadings of PIB, and one with 7% PMA. Table I shows the description of these columns. The coated support was packed under vacuum into $^1/_4$ in. o.d. copper tubing that had been previously washed with methanol and then annealed. These columns were conditioned for 24 h above 80 °C prior to use.

Computation. The retention volume V_r and the specific retention volume V_g were calculated by using the relationships

$$V_r = t_m F_f f(P)(T_c/T_f) \quad (1)$$

$$V_g = V_r/w \quad (2)$$

where t_m is the net retention time of the probe after subtracting the retention time of the marker (in minutes), F_f is the flow rate (in mL/min) measured at T_f, and T_c and T_f are the column temperature and the flowmeter temperature, respectively. V_g is the specific retention volume (in mL/g), and w is the mass of the polymer (in grams). The pressure correction factor $f(P)$ was calculated as[42]

$$f(P) = \frac{3}{2}\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \quad (3)$$

where P_i and P_o are the pressures at column inlet and outlet, respectively.

Results and Discussion

In the first series of experiments, we measured the probe retention by the support itself, uncoated with any polymer. The retention was found to be significant for all probes tested. Moreover, the elution curves and retention volumes depended strongly on the injected amount of the probe. The type of dependence varied with the nature of the probe (Figure 1a–c). Nonpolar probes, represented by hexane, exhibited only small dependence of retention volume on injected amount (Figure 1a, bottom line). The elution curves were more or less Gaussian for all injected volumes. For moderately polar ethyl acetate at very small injections, we observed very asymmetric peaks with a sharp onset and pronounced tailing. Retention volumes were rather high. At higher injections, peaks became more Gaussian and retention volumes leveled off at a lower value (Figure 1b, bottom line). The strongly polar ethanol exhibited this behavior to an even higher degree (Figure 1c, bottom line). It should be noted that for very small injections the desired volumes are delivered by the syringe

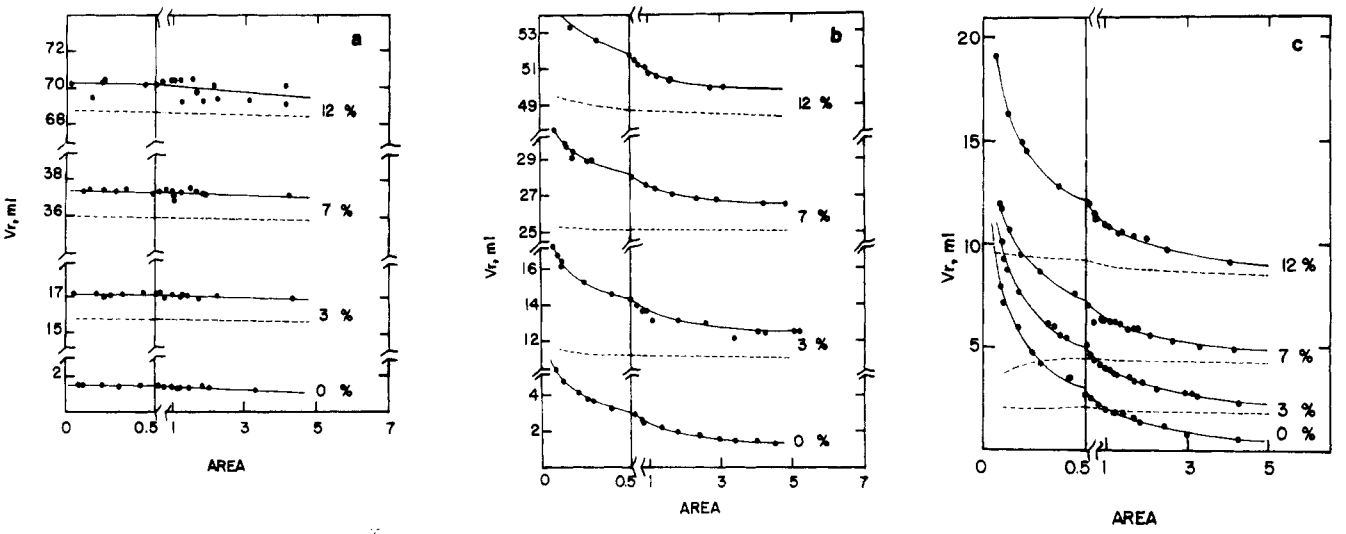

Figure 1. Dependence of retention volume on injected amount of probe at 0%, 3%, 7%, and 12% PIB loading at 60 °C and 10 mL/min flow rate: (—) before correction, (- - -) after correction, for (a) hexane, (b) ethyl acetate, (c) ethanol. Note the change of scale on the injected amount axis and broken scale on the V_r axis.

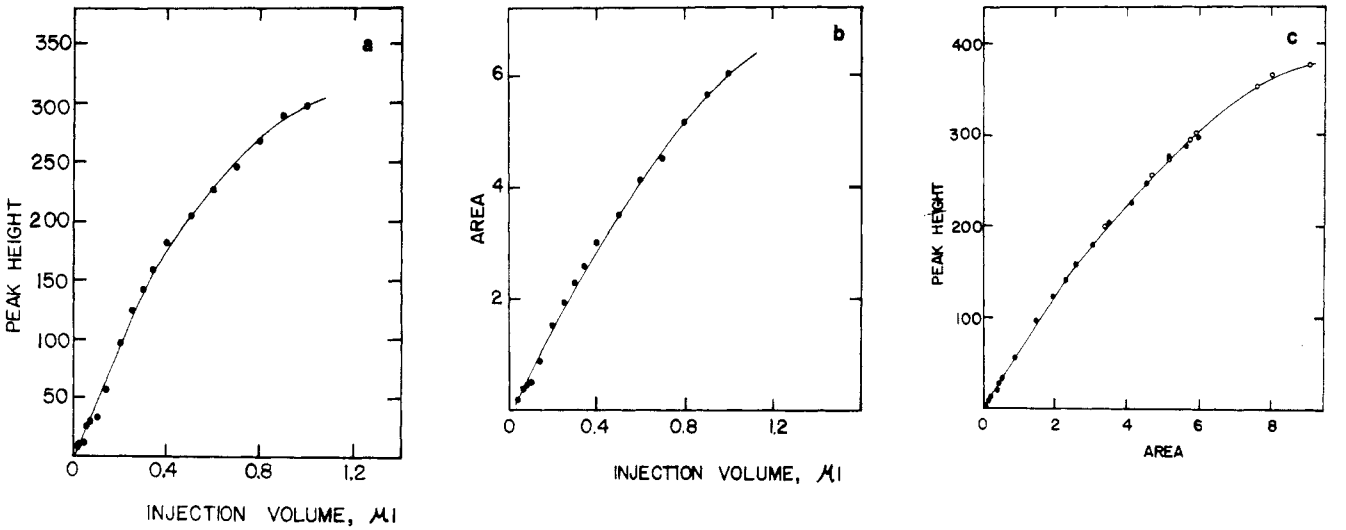

Figure 2. Uncoated column, using pentane as a probe, at 60 °C: (a) dependence of peak height on injected amount of probe, (b) dependence of peak area on injected amount of probe, (c) dependence of peak height on peak area of probe; (○) large syringe, 10 μL, (●) small syringe 1 μL.

with poor reproducibility. Therefore, we are using the areas of the chromatographic peaks in arbitrary units as a measure of the injected amount. On this scale, 0.1-μL injection corresponds to approximately 0.9 for hexane, 0.5 for ethyl acetate, and 0.5 for ethanol. The observed results clearly are the result of sorption of the probe onto the support material. In our opinion, two mechanisms of sorption are present. The retention of hexane at all injections and the retention of the polar probes at high injections are similar to the retention caused by the presence of a small amount of polymer on the column. We believe this polymer to be poly(dimethylsiloxane) which was deposited on and attached to the support during its dimethyldichlorosilane treatment. Indeed, the elemental analysis of the Chromosorb (performed by Galbraith Laboratories, Inc.) revealed the presence of about 0.2% of the hydrocarbon residues (presumably methyl groups). This amount was fully compatible with the measured retention volumes of alkanes. The strong retention of polar probes injected in miniscule amounts seems to be an adsorption effect of the hydroxyl groups on the surface of the support (essentially a silicate) which were not protected by the dimethyldichlorosilane treatment. Indeed, in experiments with untreated Chromosorb the adsorption effects were so strong as to prevent meaningful measurement altogether. On the other hand, attempts to remove the interacting groups by further treatment with trimethylchlorosilane were not successful: the adsorption behavior was not changed. The postulate of the presence of a small number of strongly interacting groups on the surface of the support is fully compatible with the observed distortion of the peaks at small injections (nonlinear Langmuir-type isotherm) and with the steep decrease of retention volume at large injections (saturation of adsorption sites).

It should be noted that the shape of the chromatographic peaks at larger injection volumes is strongly influenced by the nonlinear response and saturation of the detector. According to our observation, the dependence of apparent peak height on the injected amount starts to deviate significantly from linearity when the peak height reaches about 20–30% of the saturated value. For our experimental conditions and for probes retained on the column only slightly, this deviation point was reached with injections of about 0.1–0.2 μL. The FID response depends upon the number of probe molecules reaching the detector in unit time; consequently, the higher is the flow rate, the earlier the deviation point is reached (assuming a constant concentration of probe in the carrier gas).

Table II
Specific Retention Volume (V_g) at 60 °C of Three Probes at Different Loadings of PIB, before and after Correction

probe	loading, %	V_g(uncor), mL/g 0.01 μL[a]	V_g(uncor), mL/g 0.1 μL[a]	V_g(cor), mL/g
n-hexane	3	74.5	74.4	68.7
n-hexane	7	72.7	72.5	70.0
n-hexane	12	69.5	69.3	68.1
ethyl acetate	3	72.2	61.7	50.4
ethyl acetate	7	59.0	54.6	48.8
ethyl acetate	12	53.9	51.3	48.6
ethanol	3	40.6	21.8	8.5
ethanol	7	22.2	14.3	8.1
ethanol	12	16.8	12.3	9.4

[a] Interpolated for injection volume as noted.

Above the deviation point, the dependence of both peak height (Figure 2a) and peak area (Figure 2b) on injected amount becomes nonlinear, as does the dependence of peak height on the area (Figure 2c). The latter dependence is not influenced by the poor reproducibility of the injected amount: it can be measured quite precisely and consequently serves as the most useful criterion of detector nonlinearity.

At superficial inspection, the apparent shape of the peaks, the height of which exceeds the deviation point, is not much different from the undistorted peaks. Specifically, the position of the maximum is still recorded correctly. However, the detailed shape of the peak can no longer be analyzed, since the apparent width at half-height $w_{1/2}$ increases significantly.

Saturation at the top of the peak (flat top) also occurs when a large amount of a high-boiling probe is injected at too low a temperature. In this case, the phenomenon is caused by condensation of the probe in the column entrance. Such peaks are very difficult to interpret quantitatively.

In the next series of experiments, three supports were coated by 3%, 7%, and 12% polyisobutylene, respectively. For each probe (hexane, ethyl acetate, and ethanol), a series of experiments was performed in which injection volume was varied between 0 and 1 μL. The dependence of the retention volumes on the amount of the probe injected exhibited the same characteristics for the polymer-coated columns as for the uncoated columns. The results are plotted in Figure 1a–c, together with the values for the uncoated support. The parallel curves in these figures suggest that the support and the polymer retain the probe more or less independently. If this is true, subtracting the values for the uncoated support from the values for the coated columns should yield the retention volume for the polymer itself. The broken lines plotted in Figure 1a–c show the results obtained when the values for the uncoated support (solid lines) were subtracted from the values of the coated ones (solid lines). For small injections, uncorrected values of V_r vary by as much as 5 mL for ethyl acetate and 7 mL for ethanol. In contrast, corrected values for all probes at all column loadings over the entire experimental region varied at most by ±0.4 mL, well within our experimental error.

Specific retention volume V_g was calculated from both the uncorrected and corrected values of V_r (Table II). The difference was found to be small but still significant for hexane. The uncorrected data show a clear decrease of V_g with increasing loading, while the corrected data were constant within the range of experimental error. For ethyl acetate the difference between the corrected and uncorrected data was very large; for ethanol, it was dramatic. In both cases the corrected values of V_g were virtually independent of polymer loading.

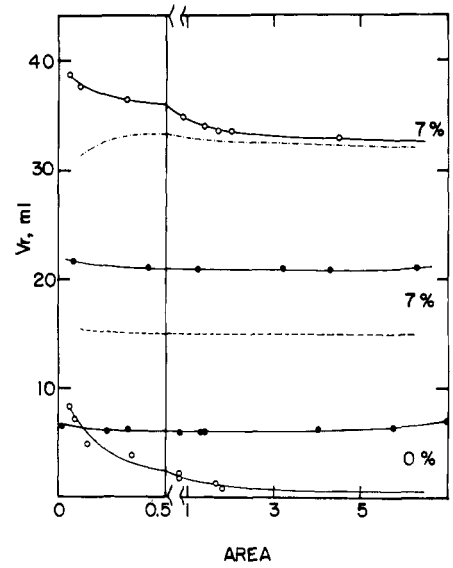

Figure 3. Dependence of retention volume on injected amount of probe at 7% PMA loading at 60 °C: (●) octane, (○) methyl acetate; (---) octane after correction; (---) methyl acetate after correction. Note the change of scale on the injected amount axis.

The fact that the dependence of corrected specific retention volume on injected amount was virtually constant in the region of low injections is a strong argument for our model of parallel retention. The steep variation for polar probes would be difficult to explain by probe–polymer interactions alone. Another support for the parallel model is the fact that V_g values were independent of polymer loading. In some preliminary experiments using several alkanes, we found V_g values to be independent of flow rate. Since we expect V_g values to be dependent on both the polymer loading and flow rate (due to slow diffusion of the probe into the bulk polymer) and this dependence is not eliminated by accounting for the probe–support interaction, we must therefore conclude that in our experimental system (polyisobutylene at 60 °C, using relatively small probes), the apparent independence of V_g from flow rate was caused by fast diffusion. For other polymers and/or other experimental conditions, V_g values could still depend upon both flow rate and polymer loading.

To test the validity of our procedures for other systems, we measured the retention of octane and methyl acetate on a column coated with poly(methyl acrylate) (Figure 3). The results were quite analogous to those obtained on PIB. However, because of the small retention of alkanes by PMA, the correction for retention by the support becomes very significant, even for octane.

To test the possibility that the observed chromatographic behavior is a result of the new soaking method for coating the support, we repeated the measurements using a column coated by polyisobutylene in the traditional way. The chromatographic behavior of this column was fully comparable to that of other columns.

Another aspect of the problem merits attention. It seems to be significant that the strong adsorption of polar probes is not modified even by heavy loading of the polymer. Perhaps the common assumption that the whole surface of the support is more or less uniformly coated by the polymer should be abandoned in favor of a model in which pools of polymer accumulate in some pores while most of the support surface remains uncoated.

Conclusions

Chromosorb W, acid washed and treated with dimethyldichlorosilane, is a material used as an "inert"

support in most studies in inverse gas chromatography. This material seems to contain small amounts of polymeric materials, most probably poly(dimethylsiloxane) (PDMS), which interacts with most chromatographic probes. In addition, the support has a small number of highly polar surface groups (probably hydroxyls) which interact strongly with polar groups. PDMS retains most probes, making a constant contribution to retention volume. The polar groups retain only the polar probes, making a very large contribution to the retention volume at very small injections, and having a smaller effect at large injections. The retention characteristics of the support are preserved even when columns are coated with polymers. To obtain meaningful data for the retention volume V_g of various probes on polymer (and for the thermodynamic quantities derived from them), it is necessary to subtract the contribution to V_g that is caused by the support from the overall retention volume. Using this procedure for polyisobutylene and several polar and nonpolar probes, we obtained V_g values that were independent of the amount of probe injected, polymer loading, and flow rate. This method seems also to apply to the more polar polymer, poly(methyl acrylate). Using the correction procedure is particularly important for both polar probes and for polymer-probe pairs that interact only sparingly.

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Energy Migration in the Aromatic Vinyl Polymers. 4. Blends of Poly(2-vinylnaphthalene) with Poly(cyclohexyl methacrylate)

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ABSTRACT: A significant problem in the modeling of photostationary excimer fluorescence of blends of aryl vinyl polymers is the need for data on the various photophysical parameters for these models. One parameter of general importance is the ratio of the intrinsic quantum yields of the excimer to the monomer, Q_e/Q_m. In this work a photophysical model and experimental technique are developed that allow the determination of Q_e/Q_m. In order to apply this method, the host matrix must be miscible with the guest fluorescent polymer at low concentrations and a suitable small probe molecule must be available to model the polymer monomer signal. Solvent-cast films containing 0.1–1.0 wt % poly(2-vinylnaphthalene) (P2VN) and 0.0–2.0 wt % 2-ethylnaphthalene in poly(cyclohexyl methacrylate) (PCMA) were prepared and studied by using photostationary excimer fluorescence. Two major results were obtained from the application of the model to the data. First, Q_e/Q_m for P2VN dispersed in PCMA was found to be 0.44 ± 0.08. Second, the ratio of the rate of nearest-neighbor energy transport to the monomer decay rate was found to be 1 order of magnitude larger for P2VN than for polystyrene.

Introduction

In a recent series of papers, excimer fluorescence has been used as a molecular probe of the thermodynamics of polymer blends.[1-5] Despite the success of the rather phenomenological approach employed in the early work, a detailed understanding of the photophysics of these

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