companied by a reduced mobility of the chain segments.

Concluding Remarks. Association of globular proteins has been studied by nonradiative energy transfer between labels which were either covalently attached or adsorbed to specific binding sites.[12] Because of the well-defined geometry of the interacting molecules, the experimental results permit a precise interpretation, particularly if the labels are known to be situated at specific sites of the proteins. In fact, Fairclough and Cantor report[13,14] the reconstruction of the geometry of the relative positioning of *six* protein subunits of a ribosome from fluorescence data.

By contrast, the changes produced by the association of flexible-chain molecules are much more complex. Such association may change the extension of the chain, lead to a varying degree of interpenetration of the molecular coils, and reduce the micro-Brownian motion of the chain segments. Clearly, the single parameter obtained from energy-transfer data does not allow us to draw conclusions as to the extent of complexation or the nature of the complex.

Acknowledgment. We are obliged to the National Institutes of Health for supporting this investigation through Grant GM 50811.

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Triplet Luminescence Properties of Poly(1-vinylnaphthalene) Solid Films

R. D. Burkhart,* R. G. Avilés, and K. Magrini

Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557.
Received June 20, 1980

ABSTRACT: Both spectroscopic and kinetic studies of poly(1-vinylnaphthalene) (P1VN) in the solid film state have been carried out over the temperature range between 77 and 260 K. Luminescence decays with a chopper frequency of 30 Hz are nonexponential but with a frequency of 0.5 Hz two rather long-lived exponential components having lifetimes which are temperature invariant between 77 and 260 K have been observed. The phosphorescence emission is broad and red shifted compared with that of naphthalene itself or P1VN in rigid solution. With rising temperature the low-wavelength side of the emission preferentially loses intensity up to 180 K. Above this temperature a single emission band centered at 590 nm remains and is invariant in position to 260 K. The delayed-fluorescence emission retains essentially the same band shape and position from 77 to 260 K. The results suggest the existence of excimer-like triplet traps in these films which are populated by mobile triplet excitons. It is proposed that the delayed fluorescence arises primarily by interaction between mobile triplet excitons and trapped triplets.

Introduction

The photophysical properties of vinyl aromatic polymers have proved to be difficult to interpret in terms of simple mechanisms, and for many polymers only very general statements concerning the nature of the various luminescence processes may be made. Furthermore, mechanistic arguments applicable to dilute solutions of small molecules are often not at all appropriate for macromolecules where local high chromophore concentrations are found with varying degrees of conformational order. Thus, conventional interpretations of rate experiments are frequently not possible. A recent study of the lowest triplet properties of poly(2-vinylnaphthalene) (P2VN) in solution clearly points out the distinctive features associated with polymeric materials.[1]

Among the early investigations of poly(1-vinylnaphthalene) was a fluorescence study carried out by Vala and co-workers[2] in which it was shown that neighboring chromophore units of the chain form excimers. Triplet migration in this polymer was demonstrated by Cozzens and Fox,[3] who also showed that in rigid solutions at 77 K delayed fluorescence occurred by triplet–triplet annihilation. Both P1VN and P2VN, in rigid solutions, have delayed-emission spectra which are essentially identical with

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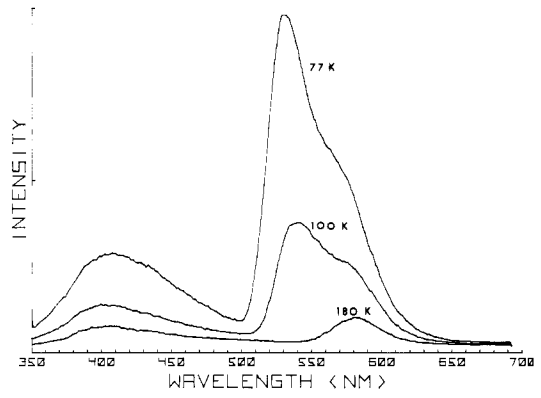

Figure 1. Delayed-luminescence spectra of P1VN solid films at various temperatures, using a 4-ms delay between excitation and emission.

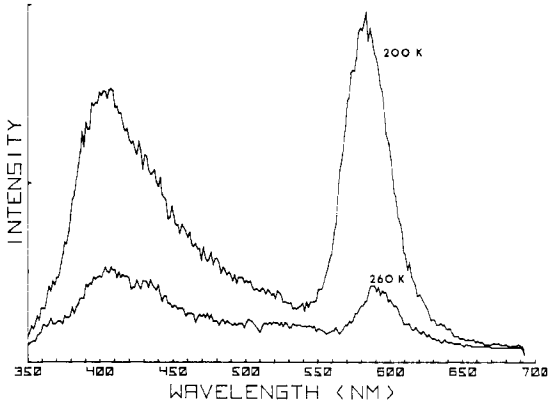

Figure 2. Delayed-luminescence spectra of P1VN solid films at 200 and 260 K.

those of the corresponding monomeric compounds[3,4] with the exception that relative delayed-fluorescence intensities are greatly enhanced in the polymeric compounds. Presumably, triplet–triplet annihilation events are more rapid in the polymeric material due to spatially nonhomogeneous chromophore distributions compared with homogeneously distributed chromophores in solutions of small molecules.

In the current investigation we decided to examine triplet processes in solid films of P1VN. The decision to study the pure solid was prompted by several considerations. First of all, applications of doped polymer films as antennae for solar energy collection has been suggested.[5] Therefore the kinetics of exciton migration at both the singlet and triplet level may have a certain technological importance. In addition, no previous studies of the photophysical properties of P1VN in the solid film state have been reported and, furthermore, it was our intent to focus attention upon the temperature dependence of triplet processes. Such studies are conveniently carried out on solid films rather than solutions, where fluidity variations must be accounted for. Finally, this work complements our earlier studies on solid films of poly(*N*-vinylcarbazole) at various temperatures,[6-8] comparisons with which will help in arriving at reasonable conclusions concerning mechanisms.

Experimental Section

The P1VN used in this work was a commercial polymer purchased from Scientific Polymer Products Inc. It has a molecular weight of 1.09×10^4, as determined by solution viscosity measurements using viscosity–molecular weight parameters determined by Utracki and co-workers,[9] and was purified by multiple reprecipitations, using benzene as solvent and methanol as nonsolvent. Methanol and benzene purification and sample preparation have been described before.[6] Some film samples were made from polymer purified as above but which, in addition, had been treated three times with boiling methanol to remove traces of monomer. No differences in decay times or spectra were noted in these specially treated samples.

The phosphorimeter was built in the laboratory and has been described previously.[7] It should be noted, however, that excitation and emission pulses with this instrument are controlled by choppers driven with synchronous motors. Chopper speeds between 1 and 1800 rpm were used. Attempts to observe triplet–triplet absorption spectra were made by using the same phosphorimeter but with an excitation chopper providing alternate excitation and analyzing pulses. The analysis lamp was a tungsten source taken from a Beckman DU spectrophotometer. It was positioned so that the analyzing pulses were reflected from front-surface mirrors mounted on the chopper. Proper operation of this instrument was verified by obtaining a triplet–triplet absorption spectrum of 1,2-benzanthracene in a polystyrene film, which agreed with published spectra for this compound. The excitation beam was unfiltered in all of these experiments, but the chopper geometry and optical alignment prevent interference from stray light in all but the very weakest emission signals.

Results

In Figure 1 are shown delayed-emission spectra taken at 77, 100, and 180 K of P1VN solid films. A broad, delayed-fluorescence band centered at 410 nm and, at 77 K, a phosphorescence emission with a peak at 530 nm are the prominent spectral features. Using neutral-density filters inserted in the excitation beam, we confirmed that the delayed-fluorescence intensity depends upon the square of the excitation intensity whereas the phosphorescence intensity exhibits a first-order dependence. This is in agreement with earlier reports of Cozzens and Fox.[3]

Several interesting changes in these spectra occur as the temperature rises. The most obvious is a shift in the center of gravity of the phosphorescence band to higher wavelengths. The emission component at 590 nm which appears as a shoulder at 77 K is the only phosphorescent band remaining at 230 K. Evidently some of the species responsible for phosphorescent emission are thermally depopulated. Figure 2 shows delayed-emission spectra of P1VN at 200 and 260 K. It will be noted that the center of both phosphorescence and delayed-fluorescence bands are the same at these two temperatures; however, the intensity of both bands decreases monotonically with increasing temperature. It is also important to note that the ratio I_{DF}/I_P increases as the temperature rises.

The spectra shown in Figure 1 were taken with a 4-ms dark period between excitation and emission. When this dark period was increased to 2 s, there was no appreciable change in the shape of the emission bands, but the relative intensity of delayed fluorescence increased. It is gratifying to note that the excimer-like phosphorescence emission found here for P1VN is essentially identical with that reported for di(1-naphthyl)alkanes as well as P2VN solid films prepared by AIBN-initiated radical polymerization.[10] Although we were not able to investigate effects of polymer molecular weight on emission spectra, it is noteworthy that the relative intensity of the phosphorescence emission at 590 nm of P2VN grows with increasing molecular weight in much the same way that this same component grows in P1VN spectra with increasing temperature.

The kinetics of phosphorescence and delayed-fluorescence decay have been investigated from 77 to 260 K. Naphthalene itself has a triplet lifetime at 77 K in rigid media of about 2.3 s,[11] and it might be supposed that the triplet processes in P1VN would be on the same time scale. In fact, it has been found that decay processes with characteristic lifetimes from 1 ms to greater than 1 s are present. The very fastest components cannot be well resolved into individual exponential decays. It was found,

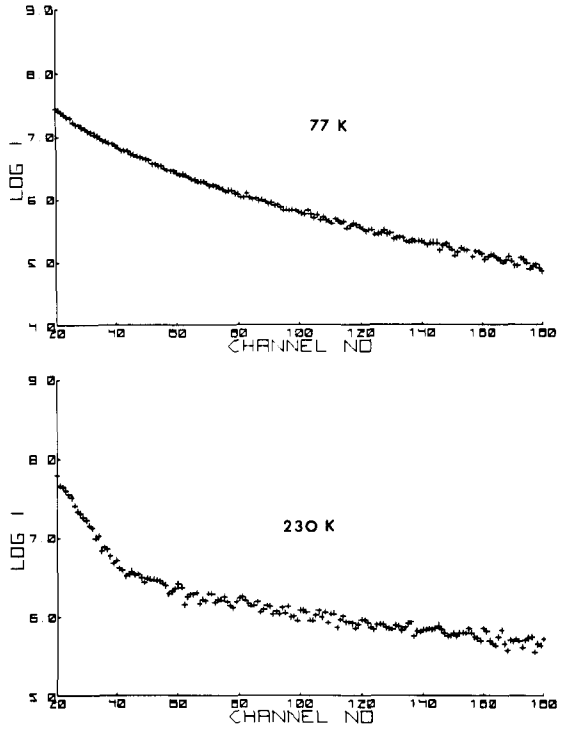

Figure 3. Graphs of the natural logarithm of the delayed-fluorescence intensity of P1VN vs. channel number, where each channel represents 0.02 s.

Table I
Lifetimes of Two Long-Lived Decay Components for both Phosphorescence and Delayed Fluorescence of P1VN at Various Temperatures

	DF lifetimes, s		phosphorescence lifetimes, s	
temp, K	τ_s	τ_l	τ_s	τ_l
77	0.27	1.29	0.30	1.28
100	0.31	1.48	0.28	1.37
150	0.31	1.40	0.22	1.02
180	0.27	1.72	0.24	1.37
200	0.26	1.49	0.22	1.08
230	0.28	1.42	0.41	
260	0.39	1.41	0.27	1.33
	0.31 ± 0.03[a]	1.46 ± 0.09[a]	0.26 ± 0.03[a]	1.24 ± 0.13[a]

[a] Average value.

however, that by using relatively slow chopping frequencies (6-rpm motors) it was possible to identify two fairly long-lived components which decay exponentially. The quality of the resolution depends upon the temperature as is shown in Figure 3, where the logarithm of the delayed-fluorescence intensity is plotted vs. time. At 77 K one sees a smooth transition from the fast to the slow component whereas the data at 260 K show a distinctly two-component curve. Phosphorescence decays monitored at 580 nm show the same type of behavior.

Computer programs which carry out the resolution into two components have been described previously[6-8] and the results of our analyses are summarized in Table I.

Both delayed-fluorescence and phosphorescence lifetimes are seen to be remarkably resistant to changes in temperature and, even more surprising, τ_s(DF) = τ_s(P) and τ_l(DF) = τ_l(P) within experimental error.

It was thought that additional valuable information on the kinetics of these triplet processes could be extracted from triplet–triplet absorption spectra. Using the phosphorimeter, modified as described above, we found no indication of triplet–triplet absorption over the temperature range from 77 to 150 K.

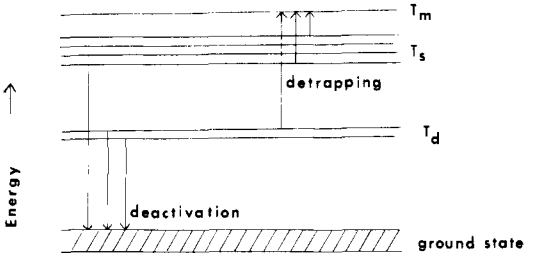

Figure 4. Proposed model for the triplet states of P1VN solid films showing mobile triplets (T_m), shallow triplets (T_s), and deep triplets (T_d).

Discussion

The shifting center of gravity of both delayed-fluorescence and phosphorescence emission bands to longer wavelength with rising temperature is a clear indication that trapped species are involved. The detrapping of shallow traps has been invoked to explain similar observations in other vinyl aromatic polymers[6-8] and is the probable source of the present spectral shifts. If the formation of triplet traps occurs mainly by interaction of mobile triplets (T_m) with trap sites ($^1N^0$), then the process is expected to be reversible for at least some of the trapped species. That is

$$T_m + {}^1N^0 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T_n + {}^1M^0 \qquad (1)$$

where T_n is the nth trapped triplet and $^1M^0$ is a ground-state chromophore not associated with a trap site.

In connection with this observation of temperature-induced spectral shifts is the fact that at sufficiently high temperatures no further shifts are observed. Above 180 K, λ_{max} for both phosphorescence and delayed fluorescence remain constant; however, the intensity of these emissions continues to decrease with rising temperature. In Figure 4 is a model of the various triplet states thought to be present in this system. A distinction is made between the mobile triplet, T_m, the shallow triplets T_s, and the deep triplets T_d.

Using this model it is possible to rationalize the red shift of the phosphorescence band as being due to detrapping of shallow triplets T_s. If the detrapping process occurs as is suggested by the reverse of eq 1, then not only would triplet populations at the top of the shallow trap band be depleted but also one would expect an increase in the steady-state concentration of mobile triplets. The consequences of this will be discussed in more detail below.

When sufficiently high temperatures are reached, the shallow trap sites are no longer effective as traps for mobile excitons. This leaves only the deep trap sites which have been designated T_d in Figure 4. That there are at least two such traps seems clear from the observation of two temperature-independent phosphorescence lifetime components. There may, however, be others which have escaped our detection. No spectral resolution of these trapped species has been possible, and so they presumably lie at very nearly the same energy levels.

Reversible trap formation as depicted in eq 1 could account for the increased ratio of delayed-fluorescence to phosphorescence intensity as the temperature is raised. The greater the temperature, the less effective are the shallow traps as quenchers of T_m and so an increase in the effective T_m population occurs at elevated temperatures. An increase in the steady-state T_m population would have

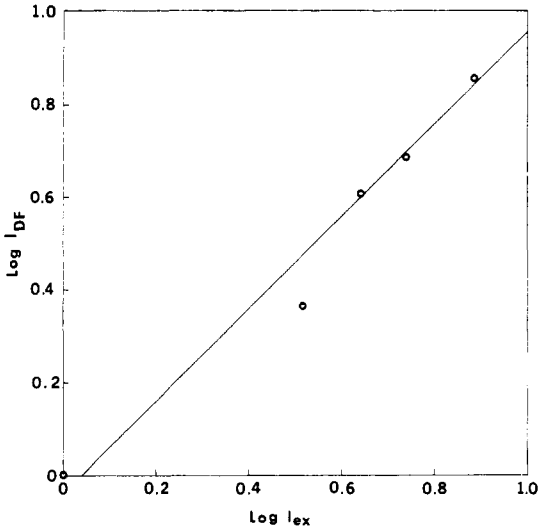

Figure 5. Plot of the logarithm of the delayed-fluorescence intensity vs. the excitation intensity (each normalized to unity for the smallest value used) for P1VN solid films at 230 K.

the effect of increasing the rate of $T_m + T_m$ homofusion as well as heterofusion processes involving T_m and a trapped species.

An effective way to investigate this possibility further is to determine the dependence of the delayed-fluorescence intensity on excitation intensity at elevated temperatures. It has already been shown that the tail of the delayed-fluorescence and phosphorescence decays can be well resolved into exponentially decaying components at temperatures above about 200 K. Thus, at long times (i.e., 600 ms) following the excitation pulse, first-order processes for triplet removal are much more important that second-order ones. With fast modulation speeds, however (i.e., 4-ms delay between the end of an excitation pulse and the beginning of an emission pulse), the delayed-fluorescence decay is found to be distinctly nonexponential at 230 K. Furthermore, when the effect of changing excitation intensity on the delayed-fluorescence intensity was investigated, the result shown in Figure 5 was obtained; that is, the delayed-fluorescence intensity depends on the first power of the excitation intensity. This, of course, is the expected result if second-order processes for triplet removal were the dominant process in this time and temperature regime. The possibility of thermal population of the excited singlet state from vibrationally excited triplets was considered as a possible explanation for this result. This is the well-known mechanism for E-type delayed fluorescence,[12] but it seems very unlikely here due to the wide energy gap between the singlet and triplet states involved.

Perhaps the most interesting aspect of the kinetic investigations is the occurrence of relatively long-lived phosphorescence and delayed-fluorescence components, which are two in number and which have the same lifetimes. The distinction between these two components is not particularly clear at 77 K but, as Figure 3 shows, above about 180 K the twofold nature of the decay process is unmistakable. For a delayed-fluorescence process having its origin in triplet–triplet encounters, the reciprocal of the delayed-fluorescence lifetime of the ith component is $1/\tau_{DF,i} = 1/\tau_m + 1/\tau_i$, where τ_m and τ_i are the lifetimes of the species involved in the encounter, τ_m being the lifetime of the mobile triplet.

Again, these results are understandable if one assumes that the singlet state (or states) responsible for the delayed fluorescence are populated from vibrationally excited triplets (i.e., E-type delayed fluorescence). As mentioned above, the energy gap between relevant singlet and triplet states seems too large to make this a viable explanation. Instead, it is proposed that $\tau_M \gg \tau_i$, where τ_i represents lifetimes of the trapped triplets responsible for the phosphorescence. In this way $\tau_{DF,i} = \tau_i$, in agreement with observations.

This conclusion is also in accord with the fact that no extremes are observed when the delayed-fluorescence intensity is graphed as a function of temperature. For solid films of PVCA two such extremes were observed between 77 K and room temperature, and this behavior has been shown to be compatible with a trapping–detrapping mechanism originally proposed by Siebrand.[13] Such a mechanism requires, however, that the mobile triplet have an intrinsic lifetime which is much shorter than that of the trapped triplets. Apparently this condition exists for PVCA but not for P1VN.

Since the long-lived delayed-fluorescence and phosphorescence lifetimes show exponential behavior, there has been a tendency in this work to place little emphasis on the shorter-lived species which actually account for a major fraction of the total emitted energy. Using various modulation frequencies for the excitation and emission beams, we have observed $1/e$ values between 1.1 and 128 ms for delayed fluorescence and phosphorescence. It was originally thought that these shorter-lived components were associated with emission from shallow trap sites; however, $1/e$ values of 4 ms have been observed even at 230 K, where the shallow traps are no longer effective. The most reasonable origin for this fast decay is that it is due to bimolecular homofusion and heterofusion processes involving mobile triplets; that is, if one considers

$$T_m + T_m \rightarrow {}^1M^* + {}^1M^0 \quad (2)$$

$$T_m + T_{1,d} \text{ (or } T_{2,d}) \rightarrow {}^1M^0 + {}^1D^* \quad (3)$$

and

$$T_{1,d} \text{ (or } T_{2,d}) \rightarrow {}^1N^0 + \text{heat (or } h\nu) \quad (4)$$

in conjunction with eq 1, then fast nonexponential decays would be expected as long as the rates of steps 2 and 3 are fast compared with that of (4).

Conclusions

Phosphorescence from solid films of P1VN originates from trapped triplets which have the character of excimers in that the emission signal is broad and red shifted from that of isolated naphthalene groups. The traps may be broadly categorized as "shallow" and "deep", the former being responsible for the high-energy phosphorescent emission centered at about 520 nm and 77 K. The deep traps are responsible for the 590-nm phosphorescence band which survives at temperatures above 180 K. The delayed fluorescence arises from triplet–triplet annihilation. Long-lived delayed-fluorescence and phosphorescence lifetimes are the same because the intrinsic lifetimes of mobile triplets are longer than that of the trapped triplets with which they interact.

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Photocycloaddition in Solid Poly(vinyl cinnamate). The Photoreactive Polymer Matrix as an Ensemble of Chromophore Sites

P. L. Egerton, E. Pitts, and A. Reiser*

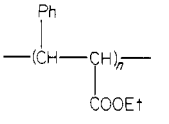
Research Division, Kodak Limited, Headstone Drive, Harrow, Middlesex HA1 4TY, England. *Received June 25, 1980*

ABSTRACT: The nature of photogenerated cross-links in solid poly(vinyl cinnamate) is investigated. Hydrolysis of irradiated films and subsequent chromatography of the hydrolysis products show that the principal matrix reaction is cycloaddition between polymer-bound cinnamoyl groups. The overall quantum yield of the cross-linking reaction decreases during irradiation and the reaction virtually stops while half of the potentially reactive chromophores are still intact. Since all cinnamoyl groups are identical in structure, the lack of reactivity of some must be attributed to their environment. This suggests a description of the matrix in terms of chromophore sites, where the reactive groups are considered together with their immediate surroundings. Sites are characterized by their reaction probability and by geometry. The distribution of site reactivities in the ensemble may be derived from the dependence of the quantum yield of the photoreaction on chromophore conversion. The distribution of chromophore configurations at the sites is inferred from the distribution of cyclic isomers in the final products. Product analysis after cycloaddition may thus be used as a probe into the micromorphology of the polymer matrix.

Poly(vinyl cinnamate) is the earliest synthetic photopolymer.[1] Its design, a polyvinyl backbone with cinnamoyl side chains, was conceived in the hope that photocycloaddition between polymer-bound cinnamoyl groups[2,3] would cross-link adjacent macromolecules. The practical aims of the inventors have been realized and a whole range of successful photopolymers has developed from the original idea,[4-6] but the actual mechanism of cross-link formation in these systems is still uncertain. Attempts to identify cyclobutane derivatives in irradiated films of poly(vinyl cinnamate) have repeatedly failed[7] and only in the very early stages of irradiation could Sonntag and Srinivasan[8] detect traces of α-truxillic acid in the hydrolyzed material. The very possibility of cycloaddition in amorphous polymer matrices was seriously questioned by Schmidt,[9] because of the stringent steric requirements of the cyclization process, and several further observations seemed to support this view: Krönert[10] had found only traces of cyclic products in the photolysis of neat liquid ethyl cinnamate, and Nakamura and Kikuchi[11] had detected the ESR signals of well-defined radicals in irradiated films of poly(vinyl cinnamate), suggesting a radical-based mechanism for the cross-linking process.

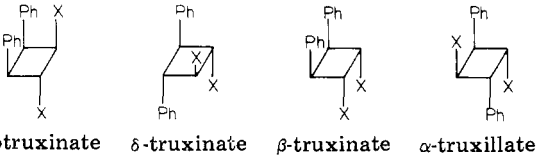
The aim of this paper is to establish the nature of the photogenerated cross-links and to investigate the effect of the solid matrix on the cross-linking process. Direct proof for or against the occurrence of cycloaddition may be obtained by hydrolyzing the cross-linked films and searching for cyclobutane derivatives in the hydrolysate. Sonntag and Srinivasan[8] have used this method on very lightly irradiated poly(vinyl cinnamate). We have now found that with the use of phase-transfer agents it is possible to hydrolyze even heavily cross-linked materials, in conditions which leave the cyclobutane rings intact and preserve their stereochemistry (see Table II).

The principal outcome of these experiments is the finding that in poly(vinyl cinnamate) at least 65% of the photoproducts are cyclodimers. The remaining part of the photoproducts are oligomers which have not been fully characterized. Their elemental analysis and their NMR and IR spectra are compatible with the general structure



This material, which is less abundant in low-temperature photolysis (see the last column in Table I), may have been formed by a radical polymerization mechanism, in agreement with early suggestions by Schmidt.[12] Such a mechanism would also explain the presence of side-chain and main-chain radicals observed by Nakamura and Kikuchi.[11]

The product distribution of the more important dimer fraction is indicated in the chromatogram of Figure 1. Four of the eleven stereoisomers, which in principle may be formed from two cinnamoyl groups, are observed. The identity of the chromatographic peaks was established by calibration with authentic materials (see the Experimental Section and ref 13). They correspond, in order of retention time, to the structures shown below.



neotruxinate δ-truxinate β-truxinate α-truxillate

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