Molecular Weight Dependent Delayed Fluorescence in Solid Solutions of Poly(*N*-vinylcarbazole) in 2-Methyltetrahydrofuran[1]

W. Klöpffer,* D. Fischer, and G. Naundorf

Battelle-Institut e.V., D-6000 Frankfurt am Main, West Germany.

Received September 29, 1976

ABSTRACT: Dilute solutions of poly(*N*-vinylcarbazole) at 77 K show delayed fluorescence and phosphorescence. The intensity of delayed fluorescence increases and that of phosphorescence decreases with increasing molecular weight. This effect has been measured on samples fractionated by gel permeation chromatography in the range M = 2×10^4 to 5×10^6. At $M > 10^6$ both emissions become constant. The decay time of phosphorescence is three orders of magnitude longer than that of delayed fluorescence.

Delayed fluorescence in solid solutions of an aromatic polymer was first observed by Cozzens and Fox[2a] on poly(1-vinylnaphthalene) and interpreted as being due to intramolecular triplet–triplet annihilation. Subsequently this effect has been observed on polyriboadenylic acid,[2b] poly(*N*-vinylcarbazole) (PVCA),[3,4] and poly(naphthyl methacrylate).[5]

Furthermore, it has been recognized that in the case of PVCA the intensity ratio of delayed fluorescence to phosphorescence depends on the average molecular weight of the polymer[3] and that in the low-temperature total-emission spectrum the phosphorescence vanishes in high molecular weight samples.[6]

All these observations have been made on dilute solid solutions at 77 K when the macromolecules can be regarded as one-dimensional "crystals".[29]

The origin of the delayed fluorescence has generally been discussed as triplet–triplet annihilation although in the case of polyriboadenylic acid helices photoionization seems to be important.[7] The delayed fluorescence of poly(2-vinylnaphthalene) can be modulated by moderately strong magnetic fields[8] which appear to point to a triplet–triplet annihilation mechanism in this system.

Recently, delayed fluorescence has also been observed in solid films of PVCA[9,10] where triplet energy transfer is possible both intra- and intermolecularly.

In this paper we wish to report on measurements done with PVCA samples of different molecular weight including narrow molecular weight fractions obtained by gel permeation chromatography (GPC). It will be shown that delayed fluorescence strongly depends on the molecular weight of the polymer, high molecular weight favoring delayed fluorescence at the expense of phosphorescence. 2-Methyltetrahydrofuran (MTHF) was chosen for these experiments since it is a good solvent for PVCA and forms homogenous glasses at 77 K.

Experimental Section

The PVCA samples investigated have been described earlier.[3] They were prepared from purified monomer by cationic (PVCA-IV, $\overline{M}_n = 5.3 \times 10^5$; PVCA-VII, $\overline{M}_n = 1.2 \times 10^6$) and thermal (radical) polymerization (PVCA-V, $\overline{M}_n = 3.2 \times 10^4$; PVCA-VI, $\overline{M}_n = 3.6 \times 10^4$). The *N*-vinylcarbazole used for preparation of PVCA-VII was purified by careful zone melting,[11] keeping the temperature of the molten zones just above the melting point in order to prevent thermal polymerization. Small amounts of PVCA-(VI + VII) were fractionated in a GPC apparatus of Hupe and Busch (Karlsruhe) which is equipped with a series of analytical columns (50 cm) filled with Corning glass beads No. 10-2000, -1250, -700, -350, -240, and -125. The solvent used for elution was tetrahydrofuran. The columns were calibrated with a set of standard polystyrene fractions (Waters). It was checked by GPC that each fraction had a narrow molecular weight distribution.

After evaporation of the tetrahydrofuran, the fractions were dissolved in such an amount of MTHF that the concentration was 6×10^{-4} mol basic unit/L. The concentration was checked by UV absorption. The absorbance at 310 nm was 0.1/1 mm, the inner diameter of the phosphorescence tubes. Low-temperature fluorescence and phosphorescence spectra were recorded with a Hitachi Perkin-Elmer MPF 2A spectrofluorometer equipped with a phosphorescence accessory.

The solvent MTHF was purified by distillation until no impurity phosphorescence could be detected.

Results and Discussion

The low-temperature emission and excitation spectra of unfractionated PVCA-VII in MTHF are shown in Figure 1. The total and delayed fluorescence spectra are typical for *N*-alkylcarbazole derivatives. Although the 0–0 peak at 353 nm is somewhat decreased by reabsorption (in 10^{-5} M solution the 0–0 and 0–1 (373 nm) peaks have about equal intensities), the fluorescence is essentially of the monomer type. This is in contrast to the behavior of liquid solutions of PVCA[6] and of films[9,12] where this emission is due to (probably two different) excimers. We cannot, however, exclude that part of the initially created monomer singlet excitons trapped at excimer-forming sites, since the quantum efficiency of fluorescence in PVCA is somewhat smaller (about 20% in PVCA-VI) than that of *N*-isopropylcarbazole, i.e., the monomeric model compound, in MTHF at 77 K. This indicates a relative loss of singlet excitons which may be due to increased radiationless deactivation (intersystem crossing or, less probable, internal conversion) or by trapping. A small amount of excimers would be difficult to detect since ordinary excimer fluorescence is broad and has a small quantum efficiency of fluorescence[12] and since the emission of the second excimer (trap II)[3] almost coincides with the 0–1 peak of monomer fluorescence.[6]

The phosphorescence spectrum shows a strong delayed fluorescence component whose shape is identical with that of the prompt fluorescence (Figure 1); its intensity, however, is much smaller. The phosphorescence component, which can be seen better in Figures 2 and 3, is red shifted by 7 nm (0–0 peak) compared to the phosphorescence of *N*-isopropylcarbazole and less resolved.[3] It corresponds to a carbazole-type monomer phosphorescence which is somewhat modified by the neighboring side groups of the polymer. Again, a small amount of excimer phosphorescence[3,9] would be difficult to detect. The excitation spectra in Figure 1 correspond to the first two absorption bands in PVCA.[12]

The tremendous influence of the average molecular weight of the polymers on the ratio of delayed fluorescence-to-phosphorescence intensity is shown in Figure 2, where the phosphorescence spectra of PVCA-V (low molecular weight) and PVCA-IV (high molecular weight) are compared. The spectra have been recorded under identical experimental conditions. Figure 2 shows that delayed fluorescence is weak and phosphorescence strong in the low molecular weight

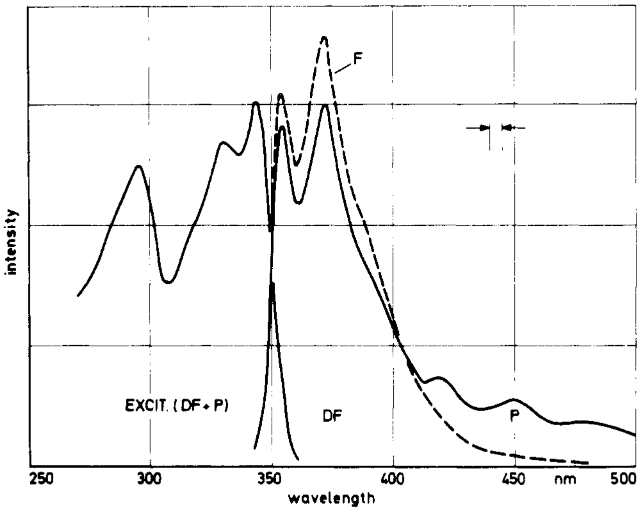

Figure 1. Fluorescence (F), phosphorescence (P), and delayed fluorescence (DF) emission and excitation spectra of PVCA-VII, 10^{-3} mol basic unit/L in MTHF glass at 77 K, not corrected for instrument response. The delayed fluorescence plus phosphorescence curve has a different intensity scale. The spectral slit width is indicated.

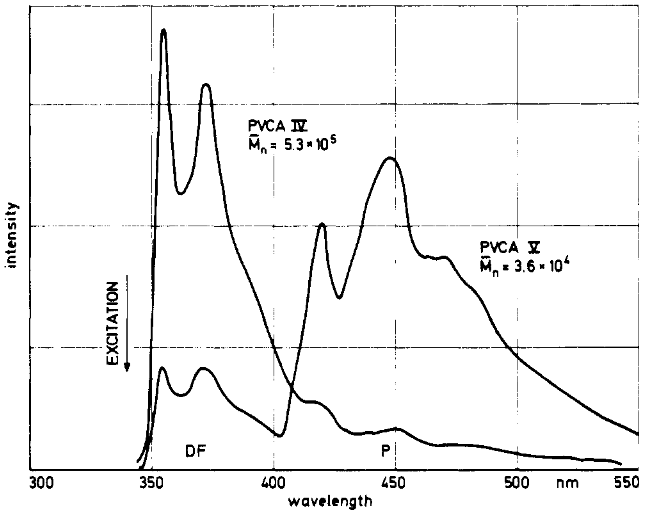

Figure 2. Phosphorescence spectra of two different PVCA samples, 10^{-3} M in MTHF at 77 K. Excitation wavelength 340 nm.

samples whereas the contrary is true for the high molecular weight sample. The molecular weight distribution being broad in both polymers ($\overline{M}_w/\overline{M}_n$ = 2–3),[3] this behavior had to be checked using fractionated PVCA samples with narrow molecular weight distribution; nine fractions could be used for spectroscopic investigation.

The phosphorescence spectra of three of these fractions showing widely different molecular weights are presented in Figure 3. As can be seen, the same qualitative behavior is found as in the case of unfractionated PVCA samples. The intensity of delayed fluorescence (I_{DF}) increases and that of phosphorescence (I_{P}) decreases with increasing molecular weight.

In Figure 4 the dependence of I_{DF} and I_{P} on the molecular weight (maximum of GPC distribution curves) of the nine fractions is shown. The intensity of both emissions becomes stationary at molecular weights higher than about 10^6. This may be due to an intramolecular saturation effect, i.e., the individual macromolecules may be considered as infinitely long in this range or, alternatively, the excitons can jump between the polymer coils.

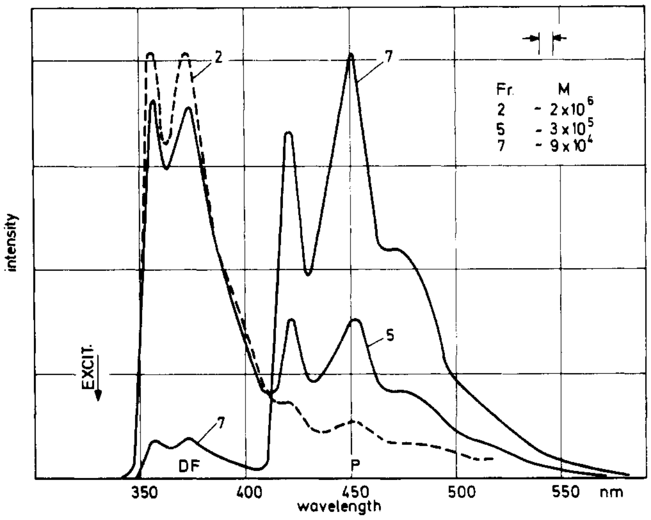

Figure 3. Phosphorescence spectra of three different PVCA fractions, 6×10^{-4} mol basic unit/L in MTHF at 77 K, recorded under identical experimental conditions. All spectra have the same intensity scale; they are not corrected for instrument response. Excitation wavelength 330 nm.

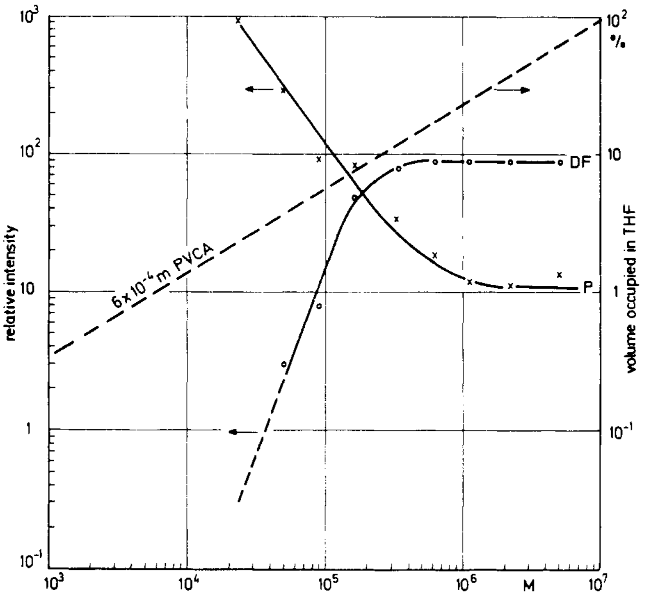

Figure 4. Dependence of delayed fluorescence and phosphorescence intensities (scale divisions at emission maximum) on molecular weight of PVCA fractions for identical excitation and recording conditions. The right-hand scale gives the volume occupied by PVCA coils in THF at room temperature.

Since the hydrodynamic parameters of PVCA in MTHF are not available, the total volume occupied by PVCA coils as a function of molecular weight has been calculated for THF as solvent[13] and included in Figure 4. The polymer coils have been assumed to form spheres.

Assuming that the low-temperature conformation is not very different from that observed at room temperature, it follows that in 6×10^{-4} mol basic unit/L solution of PVCA with $M = 10^6$, about 20% of the volume is occupied by PVCA coils.

Although MTHF might be a poorer solvent than THF and although the solvent filled coils consist only of a small percentage of polymer, we cannot be sure that intermolecular contact is excluded. For a quantitative study of delayed fluorescence as a function of molecular weight and excitation intensity, including the determination of quantum efficiencies and decay times, a poorer solvent has to be used in which the coils are smaller.

Toluene as the theta solvent at 37 °C[14] was chosen for such a study despite the poorer optical quality of glasses formed at 77 K. The results, which will be published elsewhere, show that the general spectroscopic behavior is rather similar in both solvents. Intramolecular triplet–triplet annihilation is therefore likely to be the cause of delayed fluorescence of PVCA in these solvents. The process is favored by the slow first-order triplet decay in carbazole derivatives. In 10^{-3} M solutions in MTHF at 77 K we measured $\tau_P = 8.2$ s (PVCA VI) and $\tau_P = 7.8$ s (*N*-isopropylcarbazole). Neglecting second-order decay, we roughly estimate that on the average we have one triplet/macromolecule if the molecular weight is 2×10^4. At higher molecular weights the chance to meet two or more triplets together at the same molecule increases and delayed fluorescence can occur (Figure 4), competing with phosphorescence. Delayed fluorescence decays much faster than phosphorescence ($\tau_{DF} \approx 3$–4 ms in toluene), which indicates that the triplets whose decay is observed in phosphorescence are not the mobile triplets causing delayed fluorescence.

Similar conclusions have been drawn by Yokoyama et al.[16] in a recent study of the phosphorescence of PVCA in which strong evidence from quenching experiments is presented for a trap (probably carbazole end groups) as origin of the phosphorescence.

Recently, delayed fluorescence due to photoionization and recombination has been observed in carbazole/ether at 77 K.[15] Using the monomeric model *N*-isopropylcarbazole in MTHF we did not detect any delayed fluorescence. In the case of the polymer, the molecular weight dependence seems to exclude photoionization as a major cause of delayed fluorescence. A final decision about the mechanism, however, can only be made after a kinetic analysis of the quantitative study now under way.

Acknowledgment. This work has been performed as part of the Battelle Institute program in physical sciences.

References and Notes

(1) Paper presented in part at the 3rd European Symposium on Polymer Spectroscopy in Uxbridge, London, April 1974.
(2) (a) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969); (b) C. Hélène and J. W. Longworth, *ibid.*, **57**, 389 (1972).
(3) W. Klöpffer and D. Fischer, *J. Polym. Sci., Polym. Symp.*, **No. 40**, 43 (1973).
(4) M. Yokoyama, T. Nakamo, T. Tamamura, and M. Mikawa, *Chem. Lett.*, 509 (1973).
(5) A. C. Somersall and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).
(6) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(7) M. Bazin, R. Santus, and C. Hélène, *Chem. Phys.*, **2**, 119 (1973).
(8) P. Avakian, R. P. Groff, A. Suna, and H. N. Cripps, *Chem. Phys. Lett.*, **32**, 466 (1975).
(9) W. Klöpffer and H. Bauser, *Z. Phys. Chem. (Frankfurt am Main)*, **100**, 25 (1976).
(10) R. D. Burkhart, *Macromolecules*, **9**, 234 (1976).
(11) D. Fischer, *J. Appl. Phys.*, **44**, 1977 (1973).
(12) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(13) G. Sitaramaiah and D. Jacobs, *Polymer*, **11**, 165 (1970).
(14) N. Kuwahara, S. Higashida, M. Nakata, and M. Kaneko, *J. Polym. Sci., Part A-2*, **7**, 285 (1969).
(15) D. Muller, M. Ewald, and G. Durocher, *Can. J. Chem.*, **52**, 3707 (1974).
(16) M. Yokoyama, T. Tamamura, T. Nakano, and H. Mikawa, *J. Chem. Phys.*, **65**, 272 (1976).

Temperature Dependence of Hydrogen Bonding in Toluene Diisocyanate Based Polyurethanes

C. S. Paik Sung*[1a] and N. S. Schneider[1b]

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Polymer and Chemistry Division, Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172. *Received October 7, 1976*

ABSTRACT: The temperature dependence of hydrogen bonding in 2,4-TDI and 2,6-TDI based polyurethanes was investigated using simple procedures to resolve hydrogen bonded and nonbonded NH and carbonyl. The fraction of hydrogen bonded carbonyl was used as a measure of the extent of interurethane hydrogen bonding. The onset temperature for dissociation of both hydrogen bonded NH and carbonyl in 2,6-TDI polymers occurs at 65 °C, independent of urethane content and well below the melting temperature of crystalline hard segment structure (130 to 170 °C). For 2,4-TDI polyurethanes the onset temperature for dissociation of hydrogen bonded NH occurs at 40 to 60 °C, close to the transition temperature for amorphous domain structure, but there is little change in hydrogen bonded carbonyl up to the highest temperature studied (150 °C). Heats of dissociation were about 4 kcal/mol in both series. The 2,4-TDI results demonstrate the preferential dissociation of urethane to soft segment bonding and, by contrast with the lower stability of interurethane bonding in 2,6-TDI samples, suggest that hydrogen bonding to the 4 position of the TDI ring is stronger than the 2 position. The structural implications of the 2,6-TDI and 2,4-TDI results are discussed. Overall, the behavior indicates that the cause of hydrogen bond dissociation bears little relation to the state of structural organization.

In previous work, two series of segmented polyurethanes, one based on 2,4-toluene diisocyanate (TDI), the second on 2,6-TDI, were investigated to determine the effect of asymmetric placement of the isocyanate groups on domain structure, microphase segregation, and polyurethane properties.[2a] Quantitative infrared analysis of the urethane NH and carbonyl bands was carried out as a means of assessing the degree of phase segregation,[2b] under the assumption that the fraction of NH involved in interurethane bonding was a direct measure of phase segregation. The infrared results showed that extensive mixing of hard and soft segment occurred in the 2,4-TDI polymers and provided a basis for explaining the rapid increase in the soft segment T_g which occurs with increasing urethane content in these samples.

In the present work, we have attempted to examine the relation between hydrogen bonding and the higher thermal transitions. The first such studies were carried out by Seymour and Cooper[3] to determine the relation between hydrogen bonding and domain morphology in MDI based polyurethanes. They showed that the transitions observed by DSC