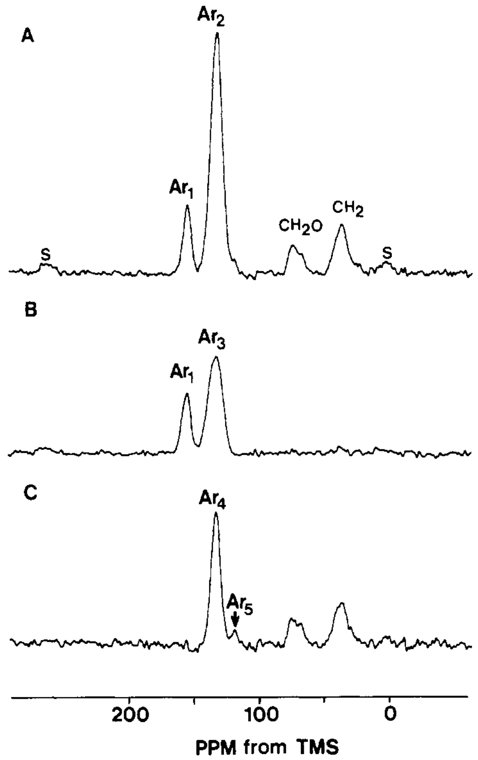

Figure 2. Solid-state ^{13}C NMR spectra of a solid rotor of a cured resol-type material similar to that used for Figure 1 obtained under the following experimental conditions: (A) magic angle spinning, 1-ms cross-polarization time, 2-s recycle time, 500 FID's (cf. Figure 1B); (B) conditions as in A except that during the 50-μs dwell before acquisition, the proton decoupler was gated off for the first 40 μs;[13] (C) result of subtracting 1.15 times spectrum B from spectrum A. The small peaks marked s denote spinning side bands.

larization/spin-locking step and the data acquisition during which time both carbon and proton radio-frequency fields are turned off. The magnetization of those carbons with directly bonded protons is rapidly destroyed due to the large proton–carbon dipolar interactions, while that of those carbons with no attached protons is relatively unaffected. The net result is that signals are observed for only the latter carbons.[13,14]

In the case of the solid phenolic resins, the experiment may be used to investigate the substitution pattern in the phenol ring. Figure 2 shows the results from such an experiment on a cured resol sample similar to that used to obtain the spectra shown in Figure 1. Figure 2A shows the normal cross-polarization spectrum, and Figure 2B the spectrum of only those carbons with no protons attached. The peaks are due to the aromatic carbon to which the OH is attached (Ar$_1$) and the ortho- and para-substituted ring carbons (Ar$_3$) as indicated in the figure. A comparison of the intensities of these two peaks gives the total substitution in the ring. Figure 2C is the difference between the upper two spectra and thus corresponds to those carbons with directly bonded protons. The largest peak at low field corresponds to the meta ring carbons where no substitution has taken place (Ar$_4$) and the small peak to unsubstituted ortho and para carbons (Ar$_5$), indicating a high overall degree of substitution. The two high-field peaks are due to methylol and methylene groups as before.

Similar measurements to those above made on a series of solid, cured resins of increasing degree of cure indicate qualitatively that the curing process involves the conversion of methylol residues to methylene bridges. Preliminary relaxation time measurements indicate that it should be possible to relate quantitatively the peak areas to the relative proportions of the different moieties present and to use these spectra in conjunction with IR both for quantitative analysis and also to quantify the energetics of the curing process.

Spectra of similar resolution to those described above are obtained for novolac-type resins and preliminary results indicate that other formaldehyde resins such as urea–formaldehyde and melamine–formaldehyde are also amenable to study by these techniques.[15]

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References and Notes

(1) (a) Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada. (b) Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.
(2) Gillis, J.; Oesper, R. E. *J. Chem. Educ.* **1964**, *41*, 224.
(3) Whitehouse, A. A. K.; Pritchett, E. G. K.; Barnett, G. "Phenolic Resins"; Iliffe: London, 1967.
(4) Sushko, N. I.; Makarevich, N. I.; Ivanov, A. I.; Glozova, T. I. *J. Appl. Spectrosc. USSR* (*Engl. Transl.*) **1973**, *18*, 495, 639.
(5) (a) Gibby, M. G.; Pines, A.; Waugh, J. S. *Chem. Phys. Lett.* **1972**, *16*, 296. (b) Pines, A.; Gibby, M. G.; Waugh, J. S. *Ibid.* **1972**, *15*, 273. (c) *J. Chem. Phys.* **1973**, *59*, 569.
(6) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *8*, 1.
(7) (a) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031. (b) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
(8) (a) Griffin, R. G. *Anal. Chem.* **1977**, *49*, 951A. (b) Andrew, E. R. *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two* **1976**, *4*, 173. (c) Mehring, M. "High Resolution NMR Spectroscopy in Solids"; Springer-Verlag: New York, 1976.
(9) (a) Fyfe, C. A.; Lyerla, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 1351. (b) Hill, H. D. W.; Zens, A. P.; Jacobus, J. *Ibid.* **1979**, *101*, 7090. (c) Lyerla, J. R.; Yannoni, C. S.; Bruck, D.; Fyfe, C. A. *Ibid.* **1979**, *101*, 4770. (d) Lippmaa, E. T.; Alla, M. A.; Pehk, T. J.; Englehardt, G. *Ibid.* **1978**, *100*, 1931.
(10) (a) Garroway, A. N.; Moniz, W. B.; Resing, H. A. *ACS Symp. Ser.* **1979**, *No. 103*, 67. (b) Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Schaefer, J. *Macromolecules* **1979**, *12*, 423. (c) Bartuska, V. J.; Macial, G. E.; Schaefer, J.; Stejskal, E. O. *Fuel* **1978**, *56*, 354.
(11) Fyfe, C. A.; Mossbruger, H.; Yannoni, C. S. *J. Magn. Reson.* **1979**, *36*, 61.
(12) Sojka, S. A.; Wolfe, R. A.; Dietz, E. A., Jr.; Dannels, B. F. *Macromolecules* **1979**, *12*, 767 and references therein.
(13) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(14) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5856.
(15) Fyfe, C. A.; Rudin, A.; Tchir, W., work in progress.

C. A. Fyfe,*[1a] A. Rudin,[1b] and W. Tchir[1b]
The Guelph-Waterloo Centre for
Graduate Work in Chemistry
Department of Chemistry, University of Guelph
Guelph, Ontario, Canada, N1G 2W1

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Role of the Triplet State in the Deactivation of Carbazole Exciplex Systems

By following the deactivation of the exciplex formed between several carbazole-containing polymers and dimethyl terephthalate (DMT) and comparing it to the same process in the monomeric *N*-isopropylcarbazole (NIPC)–DMT system, we have found that a major nonradiative decay route for exciplex deactivation involves a transition to the carbazole triplet state in the monomeric system but not in the poly(*N*-vinylcarbazole) (PVCz)–DMT system. Optically excited PVCz and NIPC interact with DMT and form an exciplex which is manifested by quenching of the PVCz or NIPC fluorescence and appearance of a new red-shifted emission band.[1-6] In a recent

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Table I
Exciplex Properties of Four Carbazole Systems

donor	acceptor	λ_{max},[a] nm	triplet absorp	triplet absorp in DMT-free soln
NIPC	DMT	450	+	+
BCP	DMT	510	−	+
PVCz(20)	DMT	510	−	+
PVCz	DMT	510	−	−
Cz-MMA	DMT	450	+	+

[a] Wavelength of maximum exciplex emission.

study[7] we measured the exciplex absorption spectrum of these systems in toluene solution and followed their decay kinetics by applying laser photolysis techniques. In both systems the exciplex absorption spectrum was similar to that of the sum of the corresponding $PVCz^{+\cdot}$ or $NIPC^{+\cdot}$ cations and the common $DMT^{-\cdot}$ anion. However, the $PVCz^{+\cdot}$ spectrum was markedly different from that of $NIPC^{+\cdot}$ and the difference was attributed to interaction and charge delocalization between the carbazole cation and neighboring carbazole chromophores along the PVCz chain.[8] Enhancement of NIPC triplet absorption was observed in the decay of the NIPC–DMT exciplex system compared to an NIPC (DMT free) system, and a time-dependent buildup of the triplet absorption corresponded to the exciplex emission decay. On the other hand, PVCz triplet absorption was not observed in either the PVCz–DMT exciplex system or a PVCz (DMT free) system.

This effect of the polymer environment on the exciplex decay mechanism may arise from a number of sources; it is possible that the triplet state is not formed in the polymer system, or, if it is formed, it may undergo rapid deactivation to the ground state by some nonradiative process.

In order to find out what role the triplet state has in the polymer system, we carried out a series of experiments with a number of carbazole derivatives. These were 1,3-bis(*N*-carbazolyl)propane (BCP),[9] a low molecular weight PVCz containing about 20 monomer units per chain [PVCz(20)], and a copolymer of vinylcarbazole and methyl methacrylate (Cz–MMA) containing about 5% carbazole units. The laser photolysis setup is described in ref 7. Measurements have been made with each compound (5×10^{-4} M) and DMT (0.07 M) in toluene solution. The solutions were flushed with nitrogen prior to and during the measurements.

Table I summarizes the exciplex properties of these systems. It is seen that the wavelength of maximum exciplex fluorescence is 450 nm with NIPC (monomer) and Cz–MMA (5% copolymer), and it is red shifted to 510 nm with BCP (dimer), PVCz(20), and PVCz (low and high molecular weight polymers). This shift indicates interaction between neighboring carbazole chromophores in the exciplex state which leads to lowering of its energy level. Transient triplet absorption in DMT-free solutions is observed with all these materials except PVCz; however, in solutions containing DMT, enhancement of triplet absorption is observed with the monomer and 5% copolymer but there is no triplet absorption with the dimer or either the low or high molecular weight polymers. From these measurements it is seen that once triplets are formed in the dimer BCP and low molecular weight polymer PVCz(20), they are relatively long-lived and can be observed and that, in the monomer NIPC and 5% copolymer Cz–MMA, DMT does not significantly quench the triplet state. Therefore, since triplets are not observed in the BCP–DMT and PVCz(20)–DMT systems, we conclude that the exciplex decay in them does not involve the triplet state.

The properties of these systems summarized in Table I are in accord with information reported in other studies. Intersystem crossing to the triplet state in PVCz was manifested by the appearance of phosphorescence in this system.[10–12] Both singlet[13,14] and triplet[10,11,15–17] exciton migration along the PVCz chain have been reported, so that under conditions of high-intensity excitation, exciton annihilation may compete with intersystem crossing to the triplet state and triplet–triplet annihilation may provide efficient nonradiative triplet deactivation. Each or both of these processes may be responsible for the lack of triplet absorption in PVCz solution when laser photolysis experiments are carried out. However, in each polymer chain at least one or two triplets (assuming trapping of excitation near the chain ends) will survive the annihilation process, so that at constant chromophore concentration the lower molecular weight polymer will yield more triplet states in the solution. This effect may well account for the appearance of triplet absorption in the low molecular weight PVCz(20) and its absence in the high molecular weight PVCz. Energy migration and annhilation were not observed in the Cz–MMA copolymer, where the distance between carbazole chromophores along the polymer chain is relatively large so that the probability for these processes is low, and the excited carbazole properties were similar to those of the monomer.

In the exciplex system triplet enhancement was observed in the NIPC–DMT system but triplets were not observed in the BCP–, PVCz(20)–, and PVCz–DMT systems. Since it is unlikely that the exciplex deactivation mechanism depends strongly on molecular weight, we conclude that the formation of triplet states is inhibited in both polymer systems. (It can be argued that in the polymer systems triplet energy migration can significantly increase the quenching cross section by DMT or any other impurity and thus account for the lack of observed triplets; however, this argument does not hold for the dimer exciplex system where there is no such migration and where no triplets are observed.) The 60-nm red shift in the polymer exciplex emission relative to the monomer exciplex and differences in the exciplex absorption spectra[7] indicate considerable interaction between carbazole groups within the chain. This additional stabilization of the cationic component of the exciplex results in lowering of its energy level and therefore an insufficient amount of energy available to form the triplet state. Similar behavior has been observed in the chemiluminescent oxidation of the fluoranthrene anion radical by the 10-methylphenothiazine cation radical.[18] In this system dimerization of the cation resulted in reduction of triplet yield.

The similarity of the results obtained with the Cz–MMA copolymer system to those for the NIPC monomer system verifies that all the polymer effects discussed above arise from chromophore interactions along the chain rather than from unusual conformational or solvation effects associated with the polymer chain.

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References and Notes

(1) M. Yamamoto, K. Tanaka, T. Omiti, M. Ooka, and T. Nishijima, First Symposium on Charge Transfer Complexes, Nagoya, Japan, June 1969, Preprints, p 105.
(2) K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2613 (1973).

(3) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976).
(4) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 22 (1977).
(5) C. E. Hoyle and J. E. Guillet, *Macromolecules*, **11**, 221 (1978).
(6) C. E. Hoyle and J. E. Guillet, *Macromolecules*, **12**, 956 (1979).
(7) U. Lachish, R. W. Anderson, and D. J. Williams, *Macromolecules*, **13**, 1143 (1980).
(8) U. Lachish, D. J. Williams, and R. W. Anderson, *Chem. Phys. Lett.*, **65**, 574 (1979).
(9) G. E. Johnson, *J. Chem. Phys.*, **61**, 3002 (1974).
(10) W. Klöpffer and D. Fischer, *J. Polym. Sci., Part C*, **40**, 43 (1973).
(11) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2037 (1976).
(12) R. D. Burkhart and R. G. Aviles, *J. Phys. Chem.*, **83**, 1897 (1979).
(13) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(14) F. Schneider, *Z. Naturforsch., A*, **24**, 863 (1969).
(15) R. D. Burkhart and R. G. Aviles, *Macromolecules*, **12**, 1073 (1979).
(16) W. Klöpffer, N. J. Turro, M. F. Chow, and Y. Noguchi, *Chem. Phys. Lett.*, **54**, 457 (1978).
(17) G. Rippen and W. Klöpffer, *Ber. Bunsenges. Phys. Chem.*, **83**, 437 (1979).
(18) D. J. Freed and Larry R. Faulkner, *J. Am. Chem. Soc.*, **94**, 4792 (1972).

Uri Lachish and David J. Williams*
Xerox Corporation
Webster Research Center
Webster, New York 14580

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CORRECTIONS

H. R. Allcock,* T. L. Evans, and D. B. Patterson: Reaction of Poly(difluorophosphazene) with Phenyllithium. Volume 13, Number 2, March–April 1980, page 203.

Three errors appear in Table I. The fourth column heading should read % PF_2, not % PR_2. The entries in the third and fourth columns of the last row should be interchanged.

G. A. Senich and W. J. MacKnight*: Fourier Transform Infrared Thermal Analysis of a Segmented Polyurethane. Volume 13, Number 1, January–February 1980, p 106.

The numerical values given in Table I (p 109) for the amount of hydrogen-bonded N–H and C=O are not percentages as indicated but fractions of the unit total and each is uncertain by a factor of 2% of the given value. A corrected version of Table I appears below.

Table I
Changes in the Degree of Hydrogen Bonding with Temperature

temp, °C	fraction bonded N—H[a]	fraction bonded C=O[a]
29	0.875	0.600
42	0.845	0.585
53	0.790	0.570
63	0.770	0.560
74	0.760	0.545
88	0.695	0.520
98	0.650	0.500
114	0.605	0.470
126	0.565	0.450
136	0.550	0.430
151	0.500	0.410

[a] Accurate to ±2%.