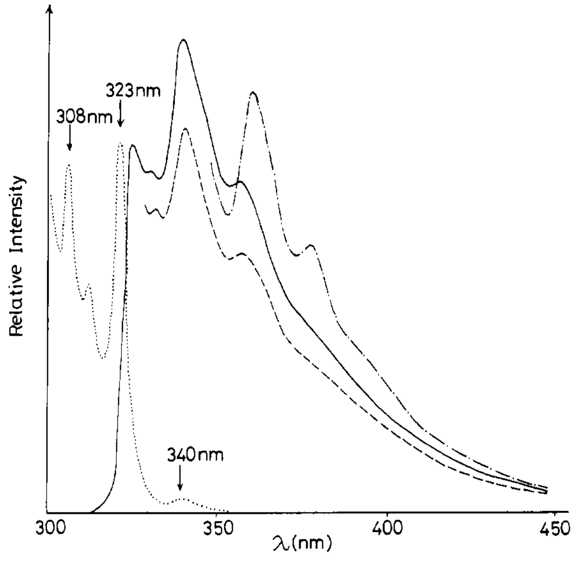


Figure 3. Fluorescence spectra of PtBVN in ethyl acetate (5 × 10^{-5} mol/L in chromophore concentration) at room temperature: (—) λ_{ex} = 308 nm; (---) λ_{ex} = 323 nm; (-·-) λ_{ex} = 340 nm; (···) absorption spectrum of PtBVN in ethyl acetate.

neglected the possibility of second-excimer-like traps giving the emission. For example, while Frank and Gashgari were examining polymer blend compatibility, they observed emission, nearly identical with observed here, from PVN in the thermodynamically good host matrix poly(isopropyl methacrylate).[8] Similar emissions were also observed from a film of an alternating copolymer of 2-vinylnaphthalene and methyl methacrylate[9] and from a film prepared from the polymer of general structure $-[CH(C_6H_5)CH_2CH_2CH(C_6H_5)(CH_2)_n]-$.[10] Irie et al. also reported similar emission from poly(1-vinylnaphthalene) in a thermodynamically poor solvent, i.e., cyclohexane.[11] They attributed the emission to that from "dimer" formed by the increased chromophore interaction and conformational rigidity in the poor solvent. Our preliminary study on poly[(2-naphthyl)alkyl methacrylate] films also revealed that a second-excimer-like fluorescence identical with that observed here is emitted by poly[1-(2-naphthyl)ethyl methacrylate], which has methyl groups, unfavorable for excimer-forming interaction, that are located near the naphthalene chromophores. The films of other polymers with linear alkyl chains, e.g., poly[(2-naphthyl)methyl methacrylate] and poly[2-(2-naphthyl)ethyl methacrylate], afforded mostly excimer emission.[12]

Therefore, high-energy trap formation is quite general in polymers having pendant aromatic chromophores. The only requirement appears to be that chromophores be separated, by steric or other structural causes or by extensive host–guest polymer interpenetration, by distances longer than that for excimer-forming interaction and further that chromophores be fixed in place by decreased chain mobility as in a film or in a poor solvent. Since the stabilization due to charge resonance interaction, both in the excited state and in the ground state, appears to be rather small compared with that of excitation resonance in a low-energy excimer,[1] the above geometric requirement needs to be fulfilled before the high-energy trap can form and emit prior to dissociation to excited- and ground-state monomers or conversion to the more stable low-energy excimer. A more complete study including the temperature dependence of the high-energy trap emission is in progress and will be reported in a future publication.

References and Notes

(1) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(2) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 22.
(3) Hoyle, C. E.; Nemzek, T. L.; Mar, A.; Guillet, J. E. *Macromolecules* **1978**, *11*, 429.
(4) Tagawa, S.; Washio, M.; Tabata, Y. *Chem. Phys. Lett.* **1979**, *68*, 276.
(5) Keyanpour-Rad, M.; Ledwith, A.; Hallam, A.; North, A. M.; Breton, M.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1978**, *11*, 1114. Keyanpour-Rad, M.; Ledwith, A.; Johnson, G. E. *Ibid.* **1980**, *13*, 222.
(6) Nakahira, T.; Sakuma, T.; Iwabuchi, S.; Kojima, K. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 413.
(7) Harrah, L. A. *J. Chem. Phys.* **1972**, *36*, 385.
(8) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1979**, *12*, 163.
(9) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.
(10) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1974**, *10*, 1181.
(11) Irie, M.; Kamijo, T.; Akiwa, M.; Takemura, T.; Hayashi, K.; Baba, H. *J. Phys. Chem.* **1977**, *81*, 1571.
(12) Nakahira, T.; Ishizuka, S.; Iwabuchi, S.; Kojima, K., submitted for publication.

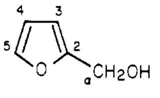
Takayuki Nakahira,* Satoshi Ishizuka, Susumu Iwabuchi, and Kuniharu Kojima

Department of Applied Chemistry
Faculty of Engineering, Chiba University
Yayoi-cho 1, Chiba 260, Japan

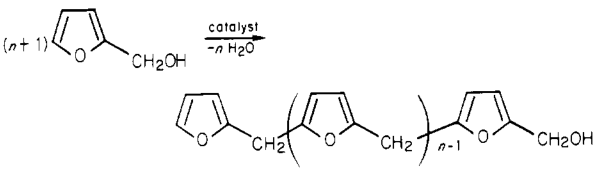
Received April 7, 1982

^{13}C NMR Study of Cured Furfuryl Alcohol Resins Using Cross Polarization and Magic-Angle Spinning

Resins prepared from furfuryl alcohol (I) are of considerable interest.[1-4] The formation process of uncured resins has been studied extensively and is relatively well understood in terms of the following reactions:[2,3]

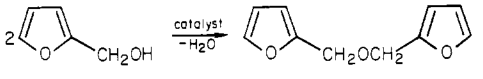


I



(1)

II



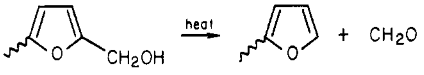
(2)

III

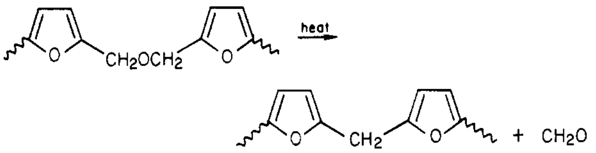
Knowledge of the curing process(es) of these resins by heating, with or without a catalyst, is less detailed.

0024-9297/82/2215-1218$01.25/0

Formaldehyde is evolved in the curing, presumably by processes of types (3) and (4).[1,5]

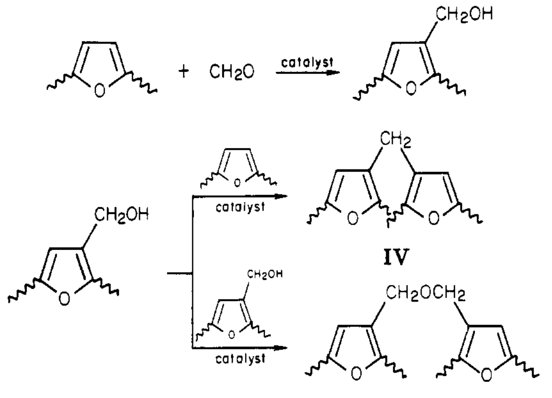


(3)



(4)

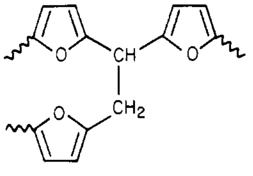
Wewerka[5] has suggested that in the curing process with strong catalysts or at higher temperatures, formaldehyde generated from reaction 3 or 4 reacts at the 3,4 positions of the furan rings of the resin to form methylene or oxydimethylene bridges as follows:



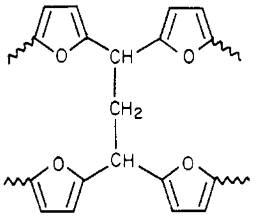
IV

V

In contrast, on the basis of evidence from IR spectroscopy, Conley and Metil[6] suggested that cross-linking reactions in the curing can occur via the coupling of methylol groups or formaldehyde with methylene linkages, forming species such as VI and VII. Because of the insoluble character of these resins, it has previously been difficult to address these kinds of considerations experimentally.



VI



VII

The recent emergence of solid-state ^{13}C NMR approaches employing cross polarization (CP)[7] and magic-angle spinning (MAS)[8] has opened new avenues for the characterization of synthetic and naturally occurring macromolecules.[9] This communication describes preliminary ^{13}C CP/MAS NMR studies of cured furfuryl alcohol (FA) resins. The spectra were obtained at 15 MHz on a JEOL FX 60QS spectrometer, using MAS speeds of about 2.3 kHz. A cross-polarization contact time of 1 ms and a repeat time of 1 s were used. Figure 1a shows the ^{13}C CP/MAS spectrum of a FA resin (from Quaker Oats) that has been cured at 65 °C with 2% H_3PO_4 for 22 h before neutralization. The fact that the peaks are relatively broad indicates that, as one might expect, there is a considerable degree of structural heterogeneity, including conformational variations, in this resin, the spectrum of which is typical of several cured FA resins we have studied. The intensity distribution in the spectrum of Figure 1a is relatively complex, including contributions from shoulders. An in-depth analysis of all of these features will require completion of a detailed relaxation study and investigations of model compounds, studies that are now in progress. Nevertheless, the main features of the spectrum are readily interpreted and prove to be illuminating.

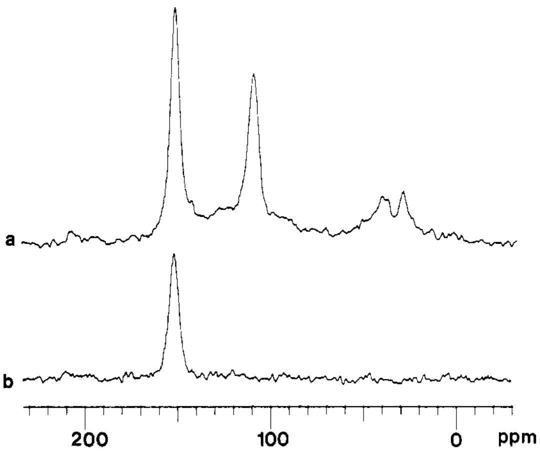


Figure 1. (a) 15-MHz ^{13}C CP/MAS spectrum of cured furfuryl alcohol resin. (b) ^{13}C spectrum of the same resin obtained with interrupted decoupling (100 μs).

The peak centered at about 29 ppm (to lower shielding than liquid tetramethylsilane (Me_4Si) reference) is assigned to the CH_2 linkage of the repeating unit in II, the peak at about 109 ppm to the 3,4 positions of II, and the peak at about 151 ppm to the 2,5 positions of II. The peak at about 38 ppm can be assigned to $>CH$ moieties attached to three carbon atoms, e.g., as in the bridging CH group in VI or VII; this assignment has been confirmed by a newly developed two-dimensional ^{13}C NMR technique that can determine the number of protons directly attached to carbon.[10]

There is no evidence in Figure 1a of oxydimethylene moieties of the type shown in III. The ^{13}C resonances of such carbons would be expected to occur at about 70 ppm. The absence of this linkage may mean either that reaction 2 is unimportant or that to the extent that reaction 2 occurs, this CH_2OCH_2 moiety is destroyed by formaldehyde elimination in process 4.

Further evidence on the nature of the cross-linking of the cure is obtained by an interrupted decoupling experiment.[11,12] In this approach the magnetization of ^{13}C nuclei to which one or more protons are directly attached is allowed to dephase during a period in which the ^1H decoupler is off. With 100 μs of decoupling interruption, only carbons without directly attached protons survive strongly in the ^{13}C CP/MAS spectrum. Figure 1b shows that only one peak, that at 151 ppm, survives the 100-μs interrupt time. Had significant substitution occurred at the 3,4 positions, according to the cross-linking hypothesis of Wewerka,[5] significant intensity would be expected at about 120 ppm in the interrupted decoupling experiment. Clearly, no such peak appears, so it must be concluded that 3,4-substituted furan rings cannot be present in substantial quantities in the cured FA resin.

In conclusion, the ^{13}C CP/MAS technique has shown great promise in the structural characterization of cured furfuryl alcohol resins. Equation 1 has been shown to account for most of the polymerization, and cross-linking via the methylene bridges, rather than substitution at C_3,C_4, is shown to be the main cross-linking mechanism.

Acknowledgment. We are grateful to the U.S. Department of Agriculture, Forest Products Laboratory, for partial support of this research and to Dr. Ad Bax and Dr. N. Szeverenyi for making the two-dimensional results available.

References and Notes

(1) Dunlop, A. P.; Peters, F. N. "The Furans"; Reinhold: New York, 1953.
(2) Schmitt, C. R. *Polym.-Plast. Technol. Eng.* **1974**, *3*, 121.
(3) Gandini, A. *Adv. Polym. Sci.* **1977**, *25*, 47.
(4) Milkovic, J.; Myers, G. E.; Young, R. A. *Cellul. Chem. Technol.* **1979**, *13*, 651.
(5) Wewerka, E. M. *J. Polym. Sci., Part A-1* **1971**, *9*, 1703.
(6) Conley, R. T.; Metil, I. *J. Appl. Polym. Sci.* **1963**, *7*, 37.
(7) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(8) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, Chapter 1.
(9) (a) Gould, R. F., Ed. "Carbon-13 NMR in Polymer Science"; American Chemical Society: Washington, D.C., 1979; ACS Symp. Ser., No. 103. (b) Woodward, A. E.; Bovey, F. A., Eds. "Polymer Characterization by ESR and NMR"; American Chemical Society: Washington, D.C., 1980; ACS Symp. Ser., No. 142.
(10) Bax, A.; Szeverenyi, N. M.; Maciel, G. E. *J. Magn. Reson.*, submitted.
(11) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(12) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5856.

Gary E. Maciel* and I-Ssuer Chuang
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

George E. Myers
Forest Products Laboratory
Madison, Wisconsin 53705

Received May 11, 1982