Fourier Transform Infrared and High-Resolution Solid-State Carbon-13 NMR Spectroscopic Characterization of Cured Polystyrylpyridine Resins

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Synopsis

Interesting crosslinked materials possessing good mechanical and thermal properties are obtained by condensation of 2,4,6-trimethylpyridine (collidine) with terephthalic aldehyde in the presence of an acidic catalyst. Fourier transform infrared spectroscopy has been used to follow the kinetics of the chemical reactions involved in the formation of the tridimensional network using aldehyde and ethylene absorption bands. The first steps of the reaction consist in the addition of aldehyde groups on the methyl groups of collidine followed by a dehydration reaction which leads to the formation of ethylenic functions. Crosslinking is obtained by an addition reaction of the methyl groups of collidine on the double bonds created in the first processes. These reactions are strongly dependent on the reaction temperature. Cured resins prepared with different acidic catalysts have been studied by carbon-13 NMR. *p*-Toluene sulfonic acid leads to residual aldehyde groups in the cured resins whereas no residual aldehyde groups are observed after a relatively short curing time when sulfuric acid is used as the catalyst. The networks created in the two cases are not equivalent and present different mechanical properties.

INTRODUCTION

There exists an important need in the aerospace industry for thermosetting matrices of composite materials that are stable at high temperature. In the class of high-temperature-resistant polymers, polystyrylpyridines (PSP) represent a new kind of highly crosslinked products which possess a good mechanical behavior above 250°C.[1,2] As the mechanical properties depend on the details of the curing processes, it is interesting to obtain measurable parameters that uniquely describe the specific cure state of crosslinked polymers. Chemical characterization methods remain limited to the early stages of the reaction, i.e., to very low conversion rates where the prepolymers are still soluble. Spectroscopic methods, in particular Fourier transform infrared spectroscopy (FT-IR) and high-resolution solid-state NMR, appear as interesting tools to get a deeper insight into the chemical changes that occur during the curing process in the solid state. The present work deals with the FT-IR and carbon-13 NMR characterization of polystyrylpyridine resins as a function of the curing parameters.

BACKGROUND

PSP results from the reaction of terephthalic aldehyde (I) with 2,4,6-tri-methylpyridine (collidine) (II), in the presence of an acidic catalyst such as sulfuric acid or p-toluene sulfonic acid. A fundamental study of the chemical reactions involved in the synthesis of these compounds has been carried out by Clavreul et al.[3,4] on model molecules. Two chemical reactions have been shown to occur during the first steps. First, the addition of methyl groups from the collidine molecule to the aldehyde functions of terephthalic aldehyde is followed by the elimination of water leading to the formation of ethylenic bonds:
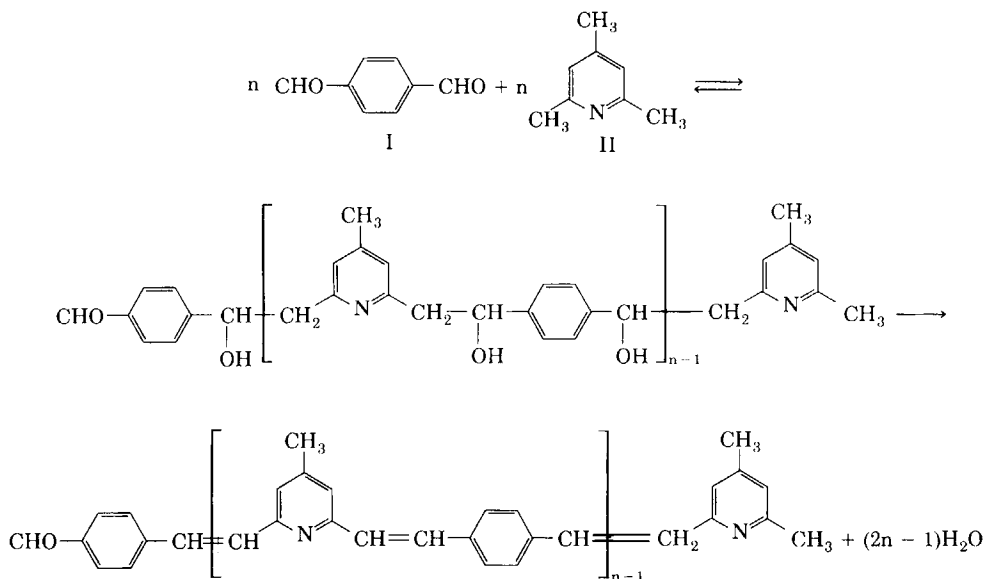
A secondary crosslinking reaction consists of the addition of a collidine methyl group to the double bonds formed in the first process:
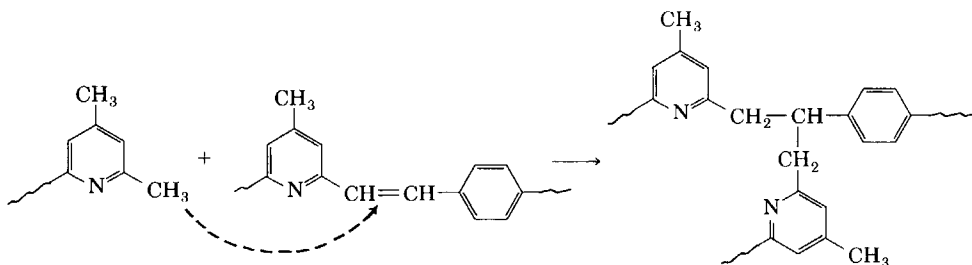
Though this addition mechanism is not the only reaction liable to occur, it appears to be the most favored one.[3] The problem then consists of establishing to what extent these two mechanisms, which were deduced from model

molecule reactions, account for the reactions occurring during the curing of the PSP resins. In a high-resolution solid state carbon-13 NMR study, Lauprêtre et al.[5] have shown that the chemistry of cured PSP can be interpreted quantitatively in terms of the two previous reaction steps. Furthermore, the methyl groups in para position on the collidine ring react only when most of the ortho-methyl functions have disappeared.

EXPERIMENTAL

The preparation of model compounds is described in Ref. 3. PSP samples, as well as prepolymers, were prepared in bulk from terephthalic aldehyde and collidine in equimolar proportions with p-toluene sulfonic acid or sulfuric acid as catalyst.[3]

The collidine used was either pure or "industrial," leading to pure or "industrial" PSP resins. The composition of industrial collidine is as follows: 2,4,6-trimethylpyridine 71.9%; 2,3,6-trimethylpyridine 21.7%; 2,6-dimethylpyridine + 2,5-dimethylpyridine 6.3%. The curing cycles used in the preparation of the different PSP samples are summarized in Table I.

Infrared spectra were recorded on a Nicolet 7199 Fourier transform infrared spectrometer. Thirty-two co-added interferograms were scanned at 2 cm^{-1} resolution. According to Griffiths,[6] absorbance values not greater than 0.7 have been used for quantitative measurements. The prepolymer films were obtained by casting a chloroform solution on KBr plates. The solvent was then removed, and a second plate added on the thin film obtained. The two plates were then put in a Mettler FP 82 heating cell directly located in the sample compartment of the spectrometer. The heating rate of the cell was chosen in order to reach the reaction temperature in about 12 min whatever this temperature was. The initial reaction time was chosen at the beginning of the isothermal heating which was monitored at $\pm 0.2°C$. Infrared spectra of solid samples for band assignment were obtained using KBr pellets.

Carbon-13 cross-polarization, proton dipolar decoupling, and magic-angle spinning NMR experiments were done at 25 MHz on a Bruker CXP-100 spectrometer, with quadrature detection and a single r.f. coil, which was double-tuned for both ^{13}C and ^{1}H. The matched spin-lock cross-polarization

TABLE I
Curing Treatments of the Different PSP Samples Characterized by Carbon-13 NMR

Sample	Curing treatment
Pure PSP	
PSP 1	3 h at 200°C
PSP 2	8 h at 200°C
PSP 3	8 h at 200°C + 2 h at 250°C
PSP 4	8 h at 200°C + 16 h at 250°C
PSP 5	8 h at 200°C + 48 h at 250°C
"Industrial" PSP	
PSP I1	None (prepolymer)
PSP I2	1 h at 200°C + 0.16 h at 250°C + 0.66 h at 275°C
PSP I3	PSP I2 + 8 h at 250°C
PSP I4	PSP I3 + 16 h at 250°C

transfers used ^{13}C and ^{1}H magnetic field strengths of 50 kHz. Spin–tempera-
ture inversion techniques were used to minimize baseline noise and roll.[7]
Flip-back[8] was also used to shorten the delay time between two successive
pulse sequences. Spinning experiments were done with boron nitride rotors at
spinning speeds of 3.5 kHz. Depending on the sample, 2000–10,000 scans were
needed to obtain a good signal-to-noise ratio.

RESULTS

Vibrational Analysis

Infrared spectra of different model molecules were run in order to warrant
band assignments. Collidine, terephthalic aldehyde, and compounds III–V
were used for this purpose:

III

IV   V
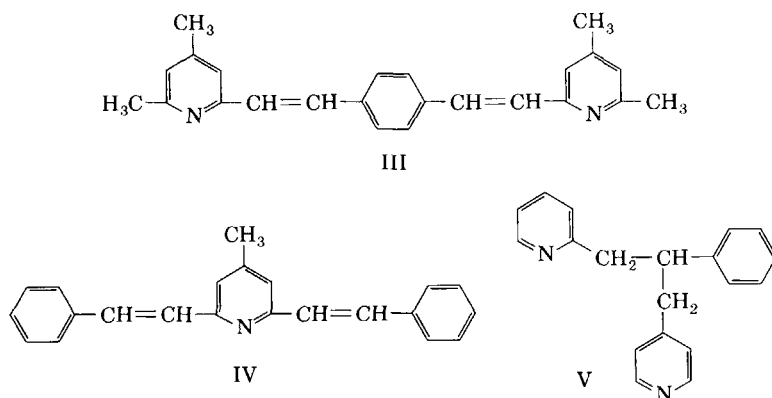
The compounds III and IV foreshadow the first step of the reaction, i.e., the
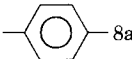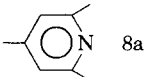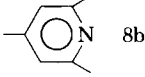creation of a linear polymer containing ethylenic double bonds. Compound V
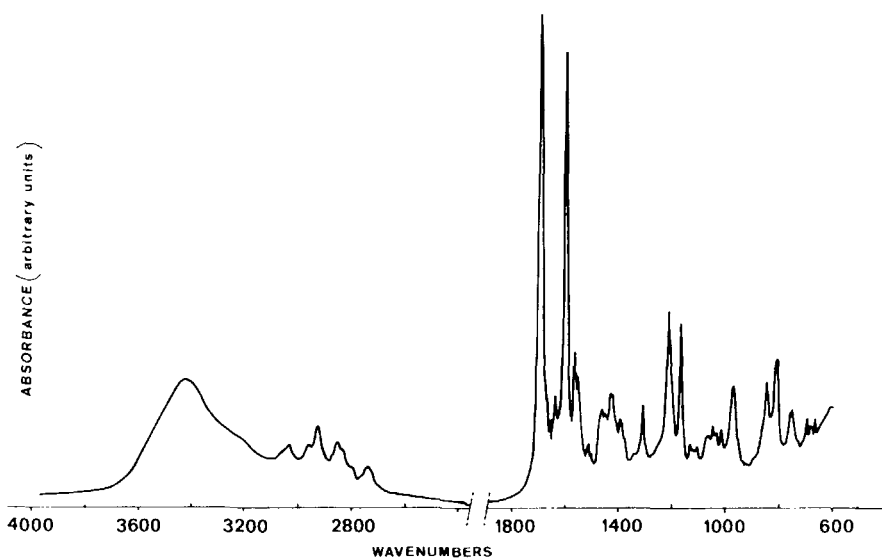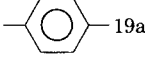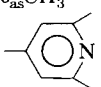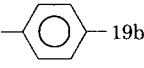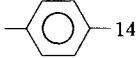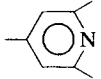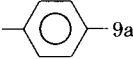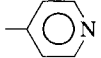
Fig. 1.   Infrared spectrum of the PSP prepolymer.

TABLE II
Tentative Assignment of Main Absorption Bands of PSP Prepolymer and Model Compound III[a]

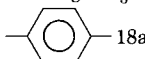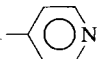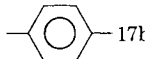| Compound III	Prepolymer	Tentative assignment
	3420 s	νO—H
3030 w	3040 w	ν=C—H
2970 w	2960 w	$\nu_{as}CH_3$
2920 w	2920 w	ν_sCH_3
	2850 w	νCH$_2$ (crosslinks)
	2740 w	ν—CHO
	1695 vs	ν—C=O
1630 m	1630 m	(phenyl ring) 8a
1600 vs	1600 vs	(pyridine ring N) 8a
1550 s	1560 m	(pyridine ring N) 8b
1510 m	1510 w	(phenyl ring) 19a
1450 m	1460 m	$\delta_{as}CH_3$
1420 m	1420 m	(pyridine ring N) + (phenyl ring) 19b
1400 w } 1370 m }	1390 m	$\delta_sCH_3 + \beta$CHO
1300 m	1300 m	(phenyl ring) 14
1210 m	1210 s	(pyridine ring N) 14 + (phenyl ring) 9a
1160 m	1170 s	(pyridine ring N) 18a
1035 m		Rocking CH$_3$
1010 w	1010 w	(phenyl ring) 18a
975 vs	970 m	γ-CH=CH $trans$
850 s	850 m	(pyridine ring N) 5
810 m	810 m	(phenyl ring) 17b
745 m	750 w	(phenyl ring) 1
670 m		γ-CH=CH cis

[a] vs = very strong; s = strong; m = medium; w = weak

is representative of the $-CH_2-CH-CH_2-$ group resulting from the crosslinking reaction.

Although we do not intend to give a complete vibrational assignment of these molecules, we are interested in the characterization of the main absorption bands of the prepolymer, the spectrum of which is shown in Figure 1. Benzene ring vibrational modes were assigned according to Varsanyi[9] whereas collidine vibrations were assigned from previous results on trimethyl-pyridines.[10] The results for the molecule III and the prepolymer are given in Table II.

Infrared Kinetic Study

The curing of a PSP prepolymer based on pure collidine and catalyzed by p-toluene sulfonic acid has been studied at different temperatures between 125 and 225°C. In order to obtain comparative results between the different sets of measurements, it is necessary to use an internal thickness band to normalize the spectra. Absorption bands of the pyridine ring are not usable because a slight loss of collidine occurs during the curing reaction as pointed out by Clavreul.[11] Fortunately, the 18a mode of the benzene ring of the terephthalic moiety at 1010 cm^{-1} is not affected by the curing process and can be used as an internal thickness band. From the results of the vibrational analysis given in Table II, one can follow the reaction of the terephthalic aldehyde group, i.e., the first step of the condensation reaction, by the change of absorbance of the $\nu C=O$ absorption band at 1695 cm^{-1}. This reaction creates secondary alcohol groups which are quickly transformed into ethylenic double bonds by the dehydration reaction. The concentration of the double bonds can be followed by using the 970 cm^{-1} absorption band which is assigned to the *trans* configuration. The absorption band corresponding to the *cis* configuration, which is observed at 670 cm^{-1} in model compound III is much too weak to be used in PSP samples.

As the ratio $C_0 = A_0/A_{ref}$ of the absorbance A_0 of a chemical group and of the absorbance A_{ref} of an internal thickness band can be considered as representative of the concentration of this chemical species in arbitrary units at time zero, the ratio $C = A_t/A_{ref}$, where A_t is the absorbance at time t, represents the concentration of the same chemical group after a reaction time t. The change in the amount of any chemical function as a function of reaction time t can then be expressed by the ratio $C/C_0 = f(t)$. Data obtained from the 1695 cm^{-1} ($\nu C=O$) and the 970 cm^{-1} (*trans*- $C=C$) absorption bands are given in Figures 2 and 3, respectively.

At a temperature of 125°C, the reaction is quite slow and only a small decrease in the amount of aldehyde functions is observed. Simultaneously the number of double bonds increases, suggesting that, at this temperature, the condensation reaction mainly takes place; it is likely that the crosslinking reaction is not yet involved.

When the reaction temperature is increased up to 225°C, the reaction rate of aldehyde functions rapidly increases and at 225°C the amount of aldehyde becomes constant after about 1 h. It is important to notice that, at this
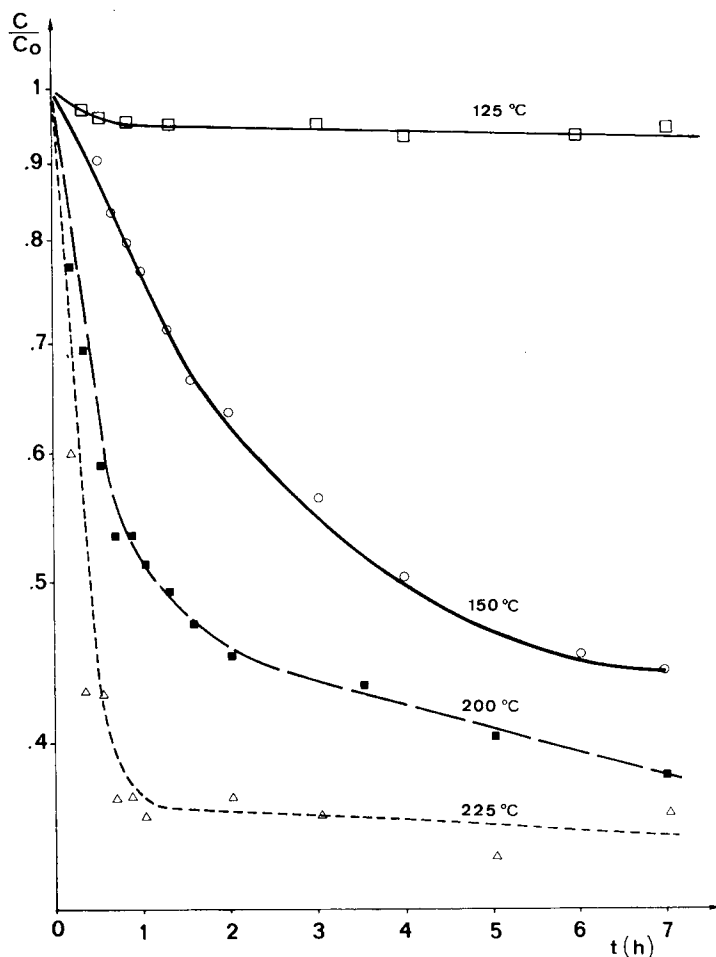
Fig. 2. Evolution of the relative intensity of the 1695 cm^{-1} aldehyde absorption band as a function of time and temperature of reaction.

temperature, aldehyde groups are still present in the polymer, even after 7 h of reaction.

Similarly the amount of double bonds decreases rapidly when the reaction temperature reaches 150°C. In fact, we observe an equilibrium between the creation of double bonds originating from the first steps of the reaction and the disappearance of double bonds due to the crosslinking reaction. At 150 and 200°C the amount of double bonds levels off with $C/C_0 = 0.65$. At 225°C the crosslinking process is dominant and is not completed even after 7 h of reaction.

The present infrared results are in good agreement with the reaction schemes proposed by Clavreul et al.[3,4] as well as with the conclusions of the high-resolution solid-state NMR study of cured PSP.[5] The whole set of data can be interpreted in terms of the two mechanisms, polycondensation and
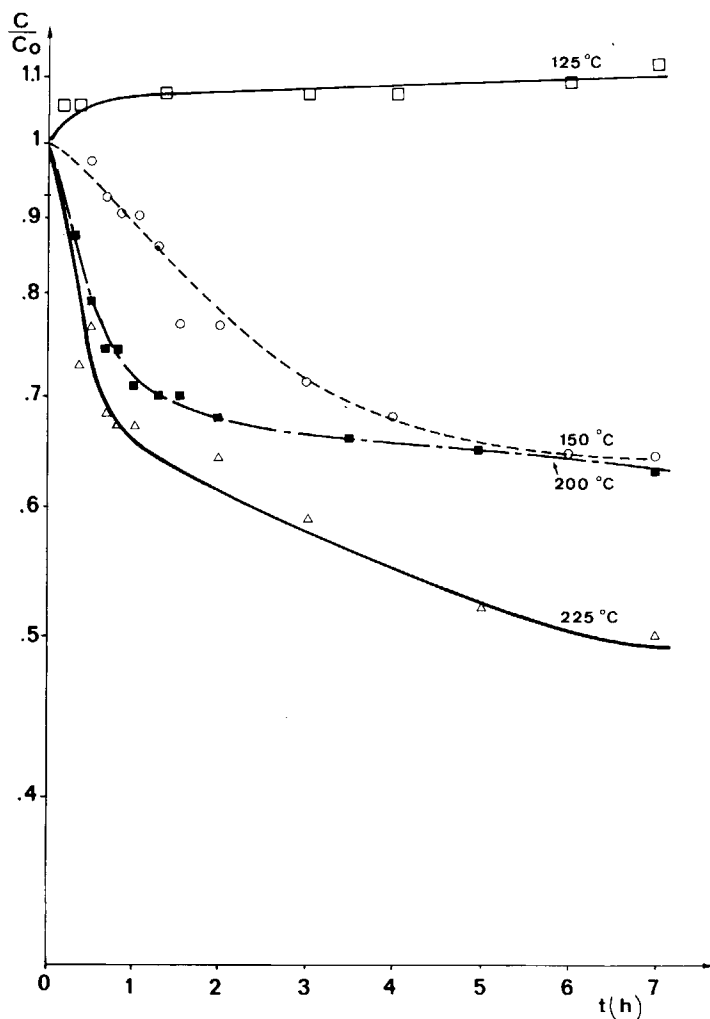
Fig. 3. Evolution of the relative intensity of the 975 cm^{-1} ethylenic double bond absorption band as a function of time and temperature of reaction.

crosslinking, schematized above and observed for the initial states of the synthesis.

CARBON-13 NMR STUDY OF CURED PSP

The high-resolution solid-state carbon-13 NMR spectrum of a series of cured PSP resins based on pure collidine are shown in Figure 4. Each spectrum consists of several lines assigned from right to left, in order of decreasing magnetic field, as a composite line due to the p- (20 ppm) and o- (24 ppm) collidine methyl carbons, a composite line (~ 45 ppm) corresponding to the CH and CH_2 carbons of the crosslinking points, an envelope of resonances (115–160 ppm), from the aromatic and ethylene carbons, and a line (190 ppm) from the aldehyde carbons. The polycondensation reaction can be studied using the aldehyde peak and the crosslinking reaction using the line
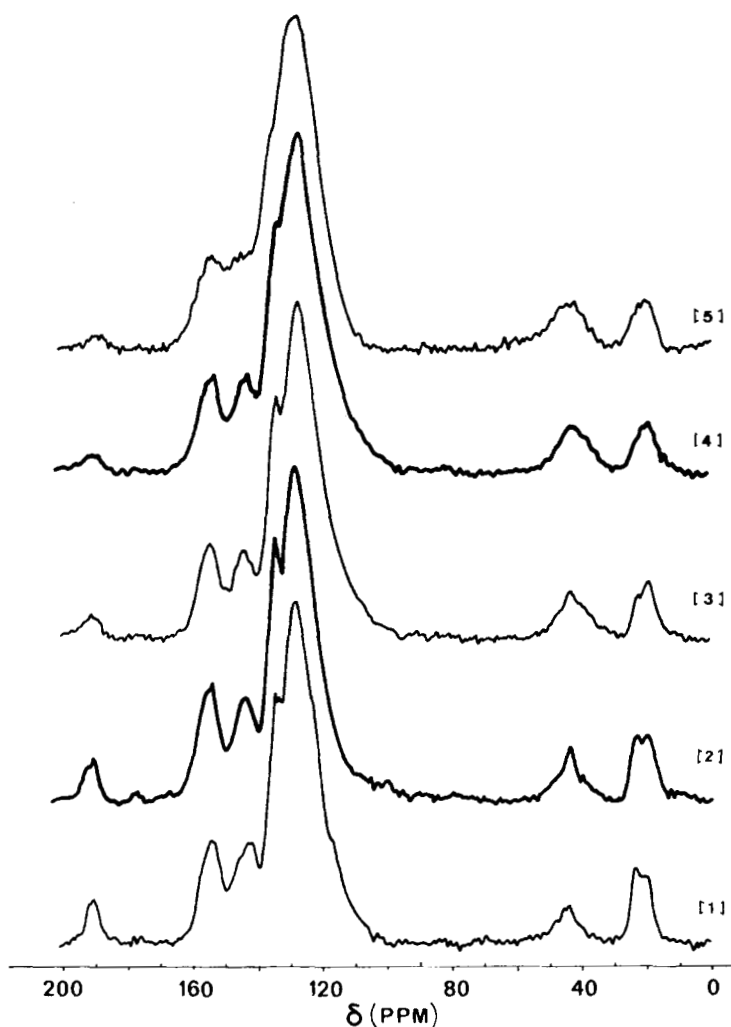
Fig. 4. Magic-angle spinning cross-polarization proton–dipolar decoupled 25 MHz ^{13}C-NMR spectra of pure PSP samples as a function of the curing parameters (contact time 1 ms): (1) PSP 1; (2) PSP 2; (3) PSP 3; (4) PSP 4; (5) PSP 5.

for the aliphatic CH and CH_2 carbons. As observed in the FT-IR spectra and supported by the quantitative analysis carried out in Ref. 5, there exist residual aldehyde groups in these PSP resins based on pure collidine and catalyzed with p-toluene sulfonic acid.

Carbon-13 NMR spectra of industrial PSP resins based on industrial collidine and catalyzed by sulfuric acid are shown on Figure 5 as a function of the curing process. As regards the number and chemical shifts of the carbon-13 lines, they are very similar to the spectra of the pure samples and can be interpreted in the same terms of the two reactional mechanisms schematized above. However, in contrast to the results obtained in Figure 4, the aldehyde peak disappears after a relatively short curing time. This result is independent of the nature of the curing cycle. It is also observed for the industrial resins
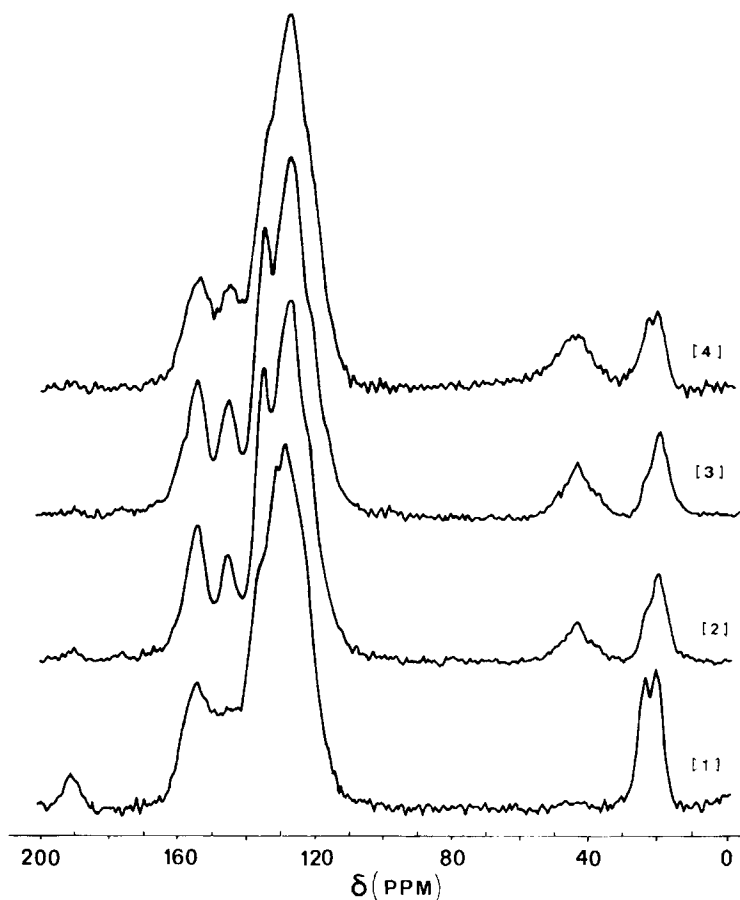
Fig. 5. Magic-angle spinning cross-polarization proton–dipolar decoupled 25 MHz ^{13}C-NMR spectra of industrial PSP samples as a function of the curing parameters (contact time 1 ms): (1) PSP I1; (2) PSP I2; (3) PSP I3; (4) PSP I4.

cured with the same temperature and duration conditions as the PSP based on pure collidine.

In order to investigate the influence of the catalyst on the chemical composition of the resins, we have prepared two resins from pure collidine, using the same curing cycle, the first one being catalyzed by p-toluene sulfonic acid, the latter being catalyzed by sulfuric acid. The spectra of these resins are plotted in Figure 6. They show that the resin prepared with sulfuric acid as a catalyst does not contain residual aldehyde functions, whereas there are residual aldehyde functions when p-toluene sulfonic acid is used. In the first case the condensation reaction is more complete and leads to longer chains than in the second case. Furthermore, the number of CH and CH_2 groups created by the crosslinking reaction with respect to the remaining CH_3 groups is more important in the case of the p-toluene sulfonic acid catalysis. This result implies that the crosslinking density is larger in that case. Summarizing, p-toluene sulfonic acid catalysis leads to relatively short chains which are highly crosslinked whereas the use of sulfuric acid yields longer polymer
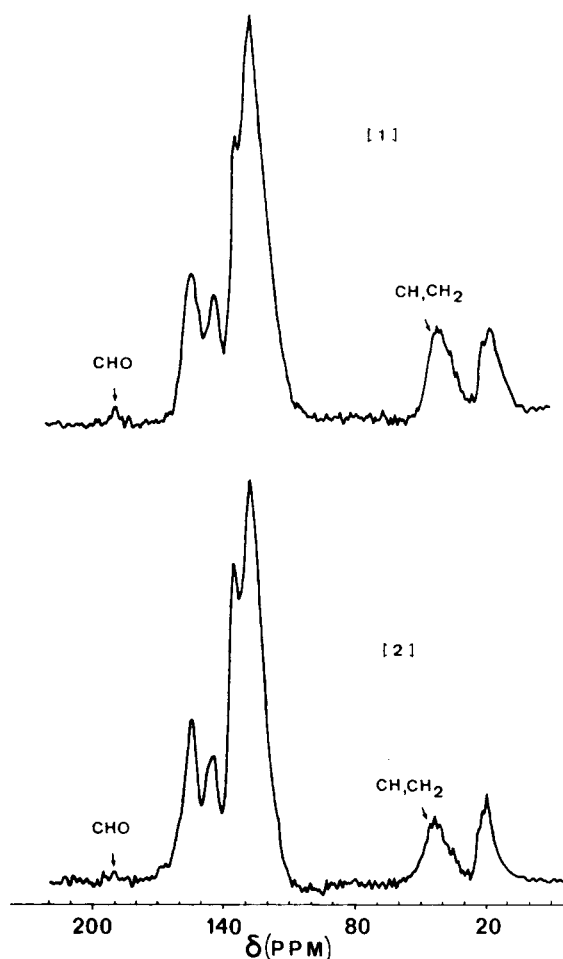
Fig. 6. Magic-angle spinning cross-polarization proton–dipolar decoupled 25 MHz ^{13}C-NMR spectra of pure PSP samples as a function of the catalyst: (1) *p*-toluene sulfonic acid; (2) sulfuric acid.

chains which are less crosslinked. The two networks are not equivalent, and their mechanical properties should be different. As a matter of fact, the resin prepared with *p*-toluene sulfonic acid as the catalyst is more brittle than the resin prepared using sulfuric acid.[12]

References

1. B. Bloch and M. Ropars, *Natl. SAMPE Symp. Exhibit. (Proc.)*, **23**, 836 (1978).

2. M. Ropars, B. Bloch, and B. Malassiné, in *5th European Conference on Plastics and Rubbers D-24*, Paris, June 1978.

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3. R. Clavreul, B. Bloch, M. Brigodiot, and E. Marechal, *Makromol. Chem.*, **188**, 47 (1987).

4. R. Clavreul, B. Bloch, M. Brigodiot, and E. Marechal, *Makromol. Chem.*, **188**, 67 (1987).

5. F. Lauprêtre, L. Monnerie, and B. Bloch, *Anal. Chim. Acta*, **189**, 117 (1986).

6. P. R. Griffiths, *Appl. Spectrosc.*, **31**, 497 (1977).

7. E. D. Stejskal and J. Schaefer, *J. Magn. Reson.*, **18**, 560 (1975).

8. J. Tegenfeldt, U. Haeberlen, and J. S. Waugh, *J. Magn. Reson.*, **36**, 453 (1979).

9. G. Varsanyi, *Vibrational Spectra of Benzene Derivatives*, Academic, New York, 1969; *Assignments for Vibrational Spectra of 700 Benzene Derivatives*, Adam Hilger, London, 1974.

10. J. H. S. Green and D. J. Harrison, *Spectrochim. Acta*, **29A**, 293 (1973).

11. R. Clavreul, thesis, Paris, 1984.

12. O.N.E.R.A. Technical Report No. 4/3521 M, 1983.