142. (c) McBrierty, V. J.; Douglass, D. C. *Macromol. Rev.* **1981**, *16*, 295. (d) Lyerla, J. R. *Methods Exp. Phys. Part A* **1980**, *16*, 241.
(25) (a) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854. (b) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5856.
(26) Slichter, C. P. "Principles of Magnetic Resonance"; Springer-Verlag: New York, 1978.
(27) (a) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw-Hill: New York, 1968; pp 300–301. (b) Cram, D. J.; Hammond, G. S. "Organic Chemistry"; McGraw-Hill: New York, 1964.
(28) Maciel, G. E.; Chuang, I-S., unpublished results.
(29) Conley, R. T.; Metil, I. *J. Appl. Polym. Sci.* **1963**, *7*, 37.
(30) Maciel, G. E.; Chuang, I-S.; Myers, G. E. *Macromolecules* **1982**, *15*, 1218.
(31) Reference 2, p 47.
(32) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(33) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

^{13}C NMR Study of Curing in Furfuryl Alcohol Resins

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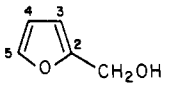
ABSTRACT: A ^{13}C CP/MAS NMR study of furfuryl alcohol resins is reported. A conformational rigidity is found for uncured or less cured resins. The contents of methylol groups and dimethylene ether linkages are found to be very small. It is postulated that cross-linking involves the breaking of methylene bridges in the curing process. Further confirmation is given that the major cross-linking processes that occur during curing involve linkages with bridging CH_2 groups, rather than substitution at the 3- and 4-positions of furan rings in the resins.

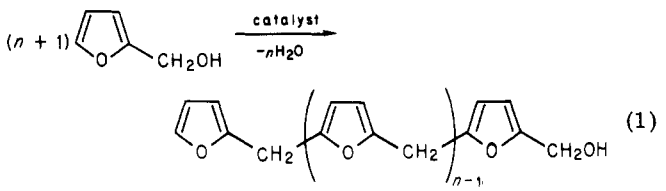
Introduction

General features of the initial process of formation of furfuryl alcohol resins from furfuryl alcohol (I) are well



I

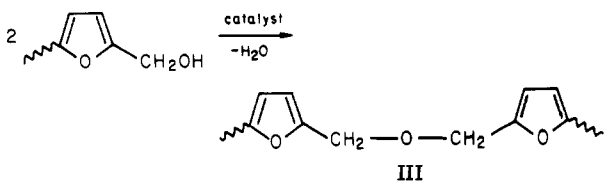
understood. It is accepted[1-3] that the methylol group of one furan ring condenses with the 5-position of another furan ring with dehydration to form a methylene linkage (II) or with the methylol group of another furan ring to form a dimethylene ether linkage (III):



(1)

II

or

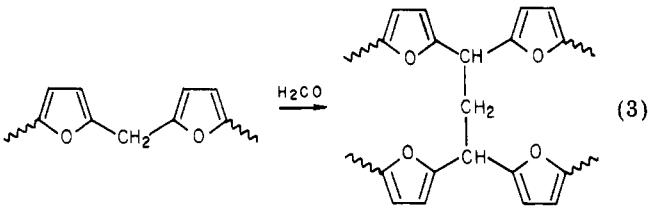


(2)

III

However, the curing process(es) of these resins initiated by heating, with or without a catalyst, is much less understood. The main reason for the difficulty in understanding the curing process(es) of furfuryl alcohol resins is the high molecular weights and low solubilities typical of the cured resins and the resulting difficulty of investigating them by ordinary analytic methods designed for liquid samples.

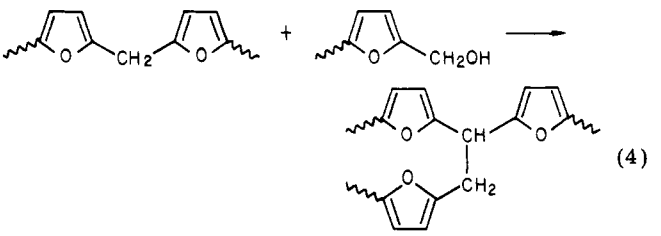
During the past decade, advances in high-resolution solid-state nuclear magnetic resonance (NMR) have been impressive. The combination of cross-polarization (CP)[4] and high-power proton decoupling with magic-angle spinning (MAS)[5] makes it possible to obtain high-resolution ^{13}C NMR spectra of complex molecules in a nondestructive way. This technique has recently been employed in the study of furfuryl alcohol resins,[6] a study which found evidence that some side reactions which appear to be unimportant in the early stages of resin formation occur during the curing process. This conclusion is perhaps not surprising in view of the more severe conditions employed for the curing of furfuryl alcohol resins in comparison to the early stages of formation of these resins. The main feature revealed by the previous study[6] is that the main curing process is the formation of cross-linking branches through the methylene linkage, as follows:[6,7]



(3)

IV

or



(4)

V

0024-9297/84/2217-1087$01.50/0

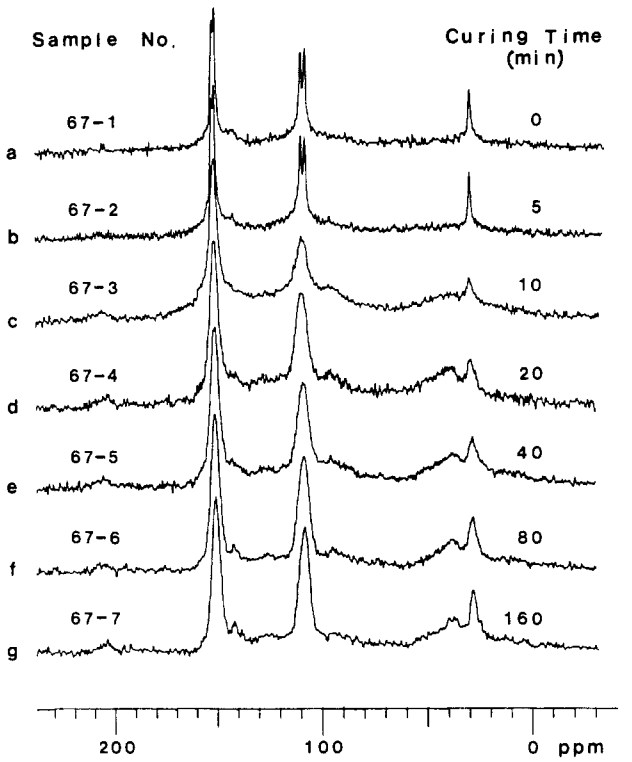


Figure 1. 15.0-MHz ^{13}C CP/MAS spectra of the seven furfuryl alcohol resins, with 1-ms CP contact time and 1-s repetition time (number of scans: 8000–77 000): (a) resin 67-1; (b) resin 67-2; (c) resin 67-3; (d) resin 67-4; (e) resin 67-5; (f) resin 67-6; (g) resin 67-7.

The evidence from the previous ^{13}C CP/MAS study shows that cross-linking through the 3- and 4-positions of the furan ring is not an important process at all. In the present paper we report a much more detailed ^{13}C NMR investigation of the curing processes of furfuryl alcohol resins, again based on CP/MAS experiments.

Experimental Section

The furfuryl alcohol resin was polymerized under nitrogen, using purified monomer. A 0.42% solution of H_3PO_4 in H_2O was used as the polymerization catalyst and was subsequently neutralized by addition of a 0.20% aqueous solution of NaOH. Samples were cured to varying extents by adding 3% BF_3-N-$H_2C_2H_5$ to the resin and heating under nitrogen at 100 °C for varying times.

The ^{13}C CP/MAS NMR experiments were conducted at 15.0 MHz on a JEOL FX-60QS spectrometer. The radio-frequency field strength of the proton channel was 12.5 G and the corresponding field strength for the Hartmann–Hahn match[8] of the ^{13}C channel was 50 G. The sample spinning rate was 2.3 kHz and the magic-angle setting was checked before and after each ^{13}C CP/MAS experiment by the ^{79}Br/KBr method.[9] The typical repetition time was 1 s and the cross-polarization time ranged from 0.06 to 10 ms. An interrupted-decoupling experiment[10] was attempted for each sample. 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 50–100 μs of decoupling interruption, magnetization of only carbons without directly attached protons (or with very mobile C–H vectors, as in a rapidly rotating CH_3 group) survives strongly in the ^{13}C CP/MAS NMR spectrum.

Results and Discussion

The ^{13}C CP/MAS NMR spectra of seven furfuryl alcohol resins are shown in Figures 1 and 2. These seven resins differ from each other in their curing times, ranging from 0 to 160 min. A detailed liquid-state ^{13}C NMR study of furfuryl alcohol resins of low molecular weight components in various solvents has been published recently,[11] and the relevant results are summarized in Table I for comparison.

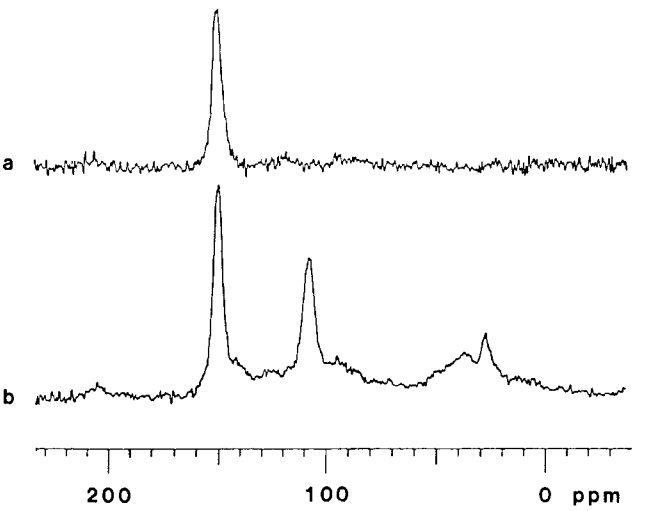
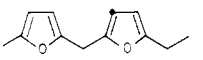
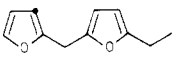
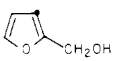
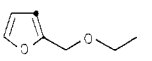
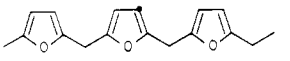
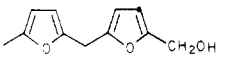
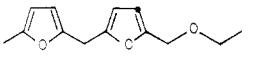
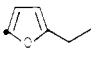
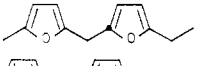
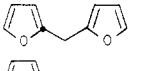
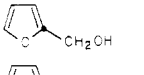
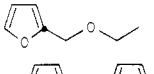
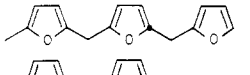
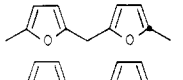
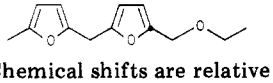


Figure 2. 15.0-MHz ^{13}C CP/MAS interrupted-decoupling spectra of resin 67-5, with 1-ms CP contact time and 1-s repetition time: (a) 100-μs interrupted decoupling, 40 560 scans; (b) usual CP/MAS spectrum, 21 560 scans.

Table I
^{13}C Chemical Shift Regions for Various Carbon Types Found for Furfuryl Alcohol Resins in Solution

structure	^{13}C chem shift,[a,b] ppm
	110.22–110.42
	107.23–107.43
	106.39–106.58
	107.03
	109.51
	107.23–107.30
	108.47–108.66
	110.58
	141.44–142.78
	150.43–151.75
	151.68–152.01
	154.42
	151.49
	150.45–150.82
	153.25–153.44
	150.53

[a] Chemical shifts are relative to liquid tetramethylsilane, larger numbers corresponding to lower shielding. Values refer to carbons indicated by dots. All spectra were reported at ambient temperature in $CDCl_3$. [b] Taken from ref 11.

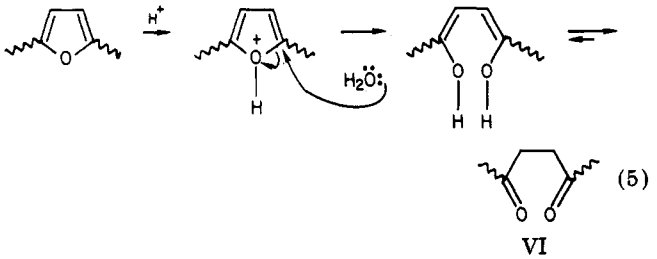
The ^{13}C CP/MAS NMR spectrum of resin 67-1 (no curing) shows two sets of doublets, one around 151 ppm

and the other around 108 ppm, and one single peak around 28 ppm. Resin 67-2 (short cure time, 5 min) shows evidence of a gradually changing NMR spectral pattern with increasing cure time; doublet peaks around 151 ppm start to show evidence of merging, and some signal intensity has developed around 142 and 90 ppm. There is little change in the doublet around 108 ppm or in the peak around 28 ppm. The spectrum of resin 67-3 (10-min cure time) continues the trend with increasing cure time; those two doublets around 151 ppm and around 108 ppm have merged. In addition to these changes, a broad peak appears around 36–44 ppm, together with a very weak peak around 204 ppm. Also, all peaks start to broaden, which reflects the increasing structural heterogeneity brought about by the cross-linking process. For resin 67-4 (20-min cure time) the broad peak around 36–44 ppm has grown somewhat. Resin 67-5 (40-min cure time) continues this trend; also two very weak ^{13}C NMR peaks appear around 177 and 125 ppm. The ^{13}C CP/MAS spectra of resins with the longest cure times, resins 67-6 and 67-7 (80 and 160 min, respectively), reveal no features that are qualitatively different from those of resin 67-5 (40-min cure).

From consulting Table I and ref 6, one can conclude that the peak around 151 ppm corresponds to the 2- and 5-positions of internal furan rings of the furfuryl alcohol resin or the 2-position of a terminal furan ring, and the peak around 108 ppm to the 3- and 4-positions of internal furan rings or the 3-position of a terminal furan ring. The 5-position of a terminal furan ring should appear around 142 ppm, for which NMR intensity is weak in the ^{13}C CP/MAS NMR spectra of resin 67-1.

The ^{13}C CP/MAS spectra of all the furfuryl alcohol resins we have investigated show no sign of existence of dimethylene ether linkage (III) or methylol groups directly attached to the furan ring (Fu), which should show some signal around 64 ppm (Fu–CH_2–O–CH_2Fu) and 57 ppm (Fu–CH_2OH), respectively. Also, there seems to be no sign of secondary amine groups attached[12] to the methylene linkages. The peak around 28 ppm can be assigned to the methylene linkage (II). The broad peak around 36–44 ppm, which starts to appear in the series of spectra for resin 67-3 and grows stronger for those resins with longer curing time, can be assigned to the >C–H moiety in the species, IV and V, which are formed by cross-linking through methylene linkages,[6] as shown in eq 3 and 4.

The peak around 204 ppm can be assigned to the γ-diketone species (VI)[7,13] or levulinic aid[2,13] ($CH_3COCH_2CH_2CO_2H$) (VII). The formation of species VI has been visualized as follows:[7]



(5)

VI

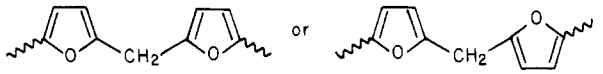
The weak peak that appears around 177 ppm in the spectra of resins 67-5, 67-6, and 67-7 obtained at longer contact times (not shown) can be assigned to the carbonyl carbon of amides formed by dehydration of levulinic acid and the curing agent, $BF_3{\cdot}NH_2CH_2CH_3$. The very weak peak around 125 ppm appearing in the spectra of resins 67-5, 67-6, and 67-7 can be assigned to the 3- and 4-positions of a furan ring that participates in cross-linking through the 3- and 4-positions. As far as can be detected by the ^{13}C CP/MAS NMR technique, cross-linking through the 3- and 4-positions is only a very minor occurrence in the curing of the furfuryl alcohol resins, even in the very late stages of curing.

In the spectra of resins 67-3 to 67-6 the peak around 90 ppm can be assigned to paraformaldehyde. The formation of paraformaldehyde during the curing of the furfuryl alcohol resin with $BF_3{\cdot}NH_2CH_2CH_3$ is discussed below.

The peak around 151 ppm seems to survive the interrupted-decoupling experiment much better than other peaks, as shown in Figure 2. This fact indicates that this peak belongs to carbon atoms without directly bonded hydrogens, a conclusion consistent with the above assignments.

From our ^{13}C CP/MAS NMR studies of furfuryl alcohol resins, there seems to be no doubt that the condensation process shown in eq 1 is a major route for the polymerization of furfuryl alcohol. Our results indicate that either the reaction shown in eq 2 is not an important process or the dimethylene ether linkage is destroyed by the elimination of formaldehyde[14] to form methylene linkages, even for the least cured resin, 67-1. The ^{13}C CP/MAS NMR spectra of resin 67-1 show evidence of the existence of terminal rings and no sign of the existence of methylol groups directly attached to furan rings; such structures should give rise to a peak around 142 ppm (weak signal observed) for the 5-position of a terminal furan ring and a peak around 58 ppm for methylol groups (no signal observed). The fact that only weak or no signals are observed in these two regions can be explained if either of the following two situations obtains: (a) the chain length of the resins is very long, such that the ratio of numbers of terminal rings to internal rings is very small (so the proportion of terminal can be neglected), or (b) the condensation of monomer units forms very large loops via methylene linkages.

The doublet patterns around 151 and 108 ppm can be explained in terms of the two different ring-to-ring conformations shown as structures VIII and IX. This kind



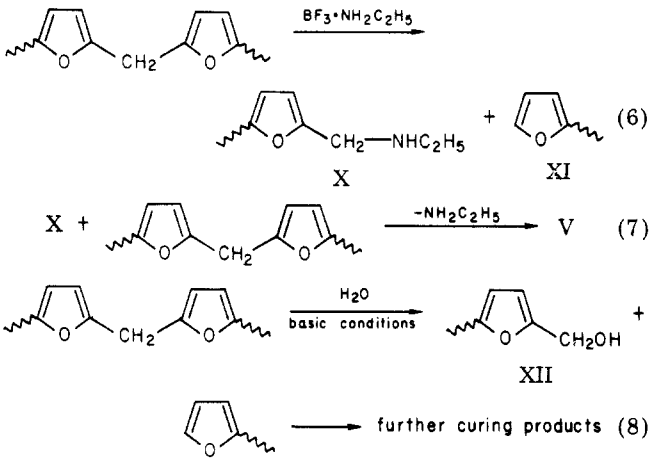
VIII IX

of conformational differentiation is absent in short chains that have been studied in the liquid state, where rapid conformational exchange can occur, but could be present in more rigid solids. A priori, the doublets could be attributed to terminal furan rings or furan rings directly attached to methylol groups or dimethylene ether linkages. However, these three possibilities are ruled out by the absence of the corresponding peaks for terminal furan rings, methylol groups, or dimethylene ether linkages in the ^{13}C CP/MAS spectra obtained in this study.

Another possible explanation of the doublets concerns branching brought about by the oxidation of furfuryl alcohol moieties to furfural groups and condensation with two other furan rings to form a branching linkage (e.g., via hydration of furfural groups to acetal (diol) groups). However, the absence of ^{13}C NMR intensity around 36 ppm in resins 67-1 and 67-2, which would correspond to the >CH moiety, rules out this possibility. According to the conformational interpretation, during the curing of furfuryl alcohol resins the specific conformations giving rise to the individual peaks in a doublet start to become distorted by the strains imposed by cross-linking; therefore, the doublets start to merge into single peaks.

Because there is no evidence in the ^{13}C spectra indicating the existence of methylol groups, dimethylene ether linkages, or formaldehyde in resin 67-1 and in view of the

severe conditions employed in curing and neutralization, the most likely possible routes for cross-linking are assumed to be as follows:



These two schemes are supported by the increase in intensity of the peak around 142 ppm, corresponding to the 5-position of terminal furan rings, with increasing cure time.

The ^{13}C NMR spectra show that if amine species (X) or alcohols (XII) are formed during curing, they do not accumulate. If they are formed, they must be consumed by condensing with methylene bridges to form the species V, perhaps a very few of them condensing with the 3- and 4-positions of the furan ring. Another possible way for consuming the alcohol (XII) is elimination of formaldehyde.[14] The fate of the evolving formaldehyde would be either to condense with two methylene bridges to form species IV, as shown in eq 3, or to form paraformaldehyde. The peak around 90 ppm indicates that there is some accumulated paraformaldehyde, which decreases somewhat for longer curing time.

In summary, ^{13}C CP/MAS NMR studies of furfuryl alcohol resins provide no evidence for the existence of appreciable concentrations of formaldehyde, methylol groups, or dimethylene ether linkages in the very early stages of the curing process. The ^{13}C results indicate that the cross-linking process is brought about by cleavage of methylene linkages by the curing agent, $BF_3{\cdot}NH_2CH_2CH_3$, or by OH^-. Experiments designed to distinguish between these kinds of possibilities are in progress. The ^{13}C CP/MAS NMR studies point to an interesting feature of fixed polymer conformations in these solid resins.

Acknowledgment. We are grateful to the U.S. Department of Agriculture, Forest Products Laboratory, for partial support of this research.

Registry No. Poly(furfuryl alcohol) (homopolymer), 25212-86-6.

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) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(5) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, Chapter 1.
(6) Maciel, G. E.; Chuang, I-S.; Myers, G. E. *Macromolecules* **1982**, *15*, 1218.
(7) Conley, R. T.; Metil, I. *J. Appl. Polym. Sci.* **1963**, *7*, 37.
(8) (a) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042. (b) Fukushima, E.; Roeder, S. B. W. "Experimental Pulse NMR: A Nuts and Bolts Approach"; Addison-Wesley: London, 1981; Chapter IV.
(9) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(10) (a) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854. (b) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5856.
(11) Fawcett, A. H.; Dadamba, W. *Makromol. Chem.* **1982**, *183*, 2799.
(12) (a) Bose, A. K.; Srinivasan, P. R. *Tetrahedron* **1975**, *31*, 3025. (b) Sarneski, J. E.; Surprenant, H. L.; Molen, F. K.; Reilley, C. N. *Anal. Chem.* **1975**, *47*, 2116.
(13) Milkovic, J.; Myers, G. E.; Young, R. A. *Cellulose Chem. Technol.* **1979**, *13*, 651.
(14) Wewerka, E. M. *J. Polym. Sci., Part A-1* **1971**, *9*, 2703.

Comparison of Static with Gas-Chromatographic Solute Infinite-Dilution Activity Coefficients with Poly(dimethylsiloxane) Solvent

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ABSTRACT: Replicate gas–liquid chromatographic based specific retention volumes, activity coefficients, and interaction parameters of ten solutes with poly(dimethylsiloxane) (PDMS) solvent at 303 K are reported. The average relative standard deviation of the former (three GLC columns) is 0.82%. The values moreover compare favorably with those reported previously for four PDMS used commonly as stationary liquids in analytical GLC. Static-determined activity coefficients and interaction parameters are also reported and compared with the GLC results. The internal consistency of the former lies within ±1.2%, while the averages of these agree with the GLC values to within ±0.5%, thus providing validation of the latter. Previously reported discrepancies between static and GLC-based activity coefficients and interaction parameters with PDMS solvents are therefore attributed to experimental artifact rather than fundamental principle.

The potential advantages of gas–liquid chromatography for measurement of physicochemical properties were recognized within 2 years of the inception of the technique.[1,2] There is moreover little question today that, for example, activity and partition coefficient data derived from the GLC method do in fact agree to well within the experimental errors arising with more traditional (static) apparatus of various designs.[3,4]

Application of the GLC technique to polymer solvents

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