Monthly
 Ecumenical
  Letters from
   Laboratories
   Of
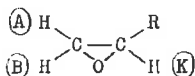   N - M - R

     No. 10

SHELL DEVELOPMENT COMPANY
### EMERYVILLE, CALIFORNIA

July 13, 1959

Dr. A. A. Bothnerby
Mellon Institute
440 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

Jerry Swalen and I recently completed the analysis of spectra from some simple epoxides of the structure:

Analysis with the ABX approximation accounted satisfactorily for the positions of all lines (better than ± 0.1 cps) but not for the intensities. Extension of the analysis to an ABK (perturbed ABX) approximation accounted for the intensities as well. The K proton was identified by its resonance position in styrene oxide and the A proton by its coupling constant to this proton. It was first established from doubly substituted epoxides of the structure
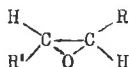
that the "trans" coupling constant is about 2 cps in these compounds. The results may be summarized as follows (spectra at 40 Mcps with SiMe$_4$ as an internal reference):

R	Approx.	J_{AB}	J_{AK}	J_{BK}	$\eta H_0(1-\sigma_A)$	$\eta H_0(1-\sigma_B)$	$\eta H_0(1-\sigma_K)$
∅	ABX	5.66	2.41	4.11	100.4	112.3	144.5
	ABK	5.65	2.50	4.04	100.4	112.4	144.3
CN	ABX	5.57	2.88	3.84	124.3	119.9	140.4
	ABK	5.54	2.59	4.15	124.3	120.0	140.2
COCH$_3$	ABX	5.80	1.51	5.66	117.5	119.6	135.1
	ABK	5.99	1.86	5.24	117.7	120.1	134.5
COOH	ABX	6.36	1.46	5.40	117.3	119.3	139.4
	ABK	6.47	1.84	5.05	117.4	119.6	139.0

I would like to point out two implications of these results for the analysis of NMR spectra. First, the "cis" coupling constant is larger than the "trans" one. Second, use of the inadequate ABX approximation can lead to considerable errors in the coupling constants derived (in the present cases up to almost 0.5 cps) even though the line positions are fitted to within ± 0.05 cps by either the ABX or the ABK approximation. Preprints of this work are available from either Jerry or me.

Preprints of the following paper are also available: "Ionization of Strong Electrolytes. VII. Temperature Coefficient of Dissociation of Strong Acids by Proton Magnetic Resonance" by G. C. Hood and C. A. Reilly.

Sincerely yours,

Charlie

C. A. Reilly

CAR:jel

$f = J/\Delta\omega$

ABK	f_{AB}	f_{AK}	f_{BK}
∅	1.471	0.057	0.127
CN	~1.288	0.163	0.205
COCH$_3$	2.496	0.111	0.364
COOH	2.741	0.085	0.260

REQUIREMENTS TO BE MET BY PAPERS CONCERNED WITH NMR SPECTRAL DATA

(1) <u>Convert all "chemical shift" data from cps to ppm units.</u>
The use of cps for "chemical shifts" is <u>quite</u> <u>unacceptable</u>,
as the numerical values cited depend upon the operating
frequency. Essentially all NMR experts agree on this point.
In the past there was a time when nearly all spectrometers
operated at 40 mc, so that a tenuous justification for the
listing of cps values could be made. Now, however, some
spectrometers operate at 60 mc, some at <u>ca.</u> 56 mc, and quite
a few will remain at 40 mc., and to list values in cps
represents a callous indifference to the convenience of the
reader (which it is certain that authors do not intend!).
Suppose for example that many chemists reported m.p. and b.p.
data in <u>millivolts</u>, usually (but not always!) stating the
type of thermocouple used, and leaving it to the reader to
make the conversion to degrees! One cannot believe that such
laziness would be condoned by the Journal.

(2) <u>State the type of calibration on which measurement of peak</u>
<u>separation is based.</u> In other words, how do we know that the
peak separations are correctly measured? The Varian spectro-
meter <u>is</u> <u>not</u> calibrated and <u>contains no</u> "standard" for measure-
ment, and the audio-oscillator usually supplied with it may be
<u>several per cent</u> in error at different points on the dial.
<u>A frequency counter is strongly recommended.</u> To pursue the
thermocouple analogy, one would not even report "millivolts"
unless one's potentiometer were at some point checked against
a standard cell!

(3) <u>Measure peak positions in a meaningful, reproducible way.</u>
(a) The use of an "external-reference" compound is invalid
unless measurements are extrapolated to infinite dilution
(J.A.C.S. <u>79</u>, 5361 (1957)). Temperature should be stated
<u>particularly</u> if external H_2O is used as a reference.
Measurements made at low concentration, (for example below
5%) probably do not require extrapolation unless superior
accuracy is needed. Measurements made in one solvent
cannot as a rule be compared to those made in another
solvent unless conversion is established by use of special
techniques (which should be explained).

(b) Many difficulties are avoided by use of a good "internal-
reference" such as tetramethylsilane. (However this
compound is insoluble in D_2O, so that a conversion method
similar to that in (a) is required if such data are to
be compared.) When tetramethylsilane is used, it is best
to report results on the scale defined in J. Phys. Chem.
<u>62</u>, 1151 (1958), as this is now fairly well accepted.

The thermocouple analogy is helpful here also. Millivolt read-
ings, however precise and accurate, can only be converted to
degrees centigrade if the reference junction is held at a known
temperature. If this latter were not done comparison of
temperature data between laboratories would become largely
meaningless.

(4) <u>State solvent, concentrations and temperature.</u>
This is, of course, most important when the peak positions for
OH (or other "hydrogen-bonded" protons) are given.

(5) <u>Give standard deviations for averaged numerical data.</u>
The standard deviation <u>for an averaged value</u> is obtained by
dividing the standard deviation for a single measurement by
the square root of the number of measurements. Reasonable
values in 1959 are: $\pm$ 0.004 ppm for sharp peaks, $\pm$ 0.010 ppm
for fairly sharp analyzable multiplets, and perhaps $\pm$ 0.025 ppm
for broad peaks.

(6) <u>Multiplets not satisfactorily analyzed must be indicated.</u>
It is often possible visually to estimate the position of the
center-of-area of a complex multiplet even though a proper
analysis is not performed. Such values may be quite useful,
and should not be omitted, but should be marked "mult." to
indicate their lesser certainty. Broad peaks also should be
specified.

(7) <u>Describe analyzable multiplets, and give coupling constants</u>
<u>in cps.</u> Where possible, identify the nuclei responsible for
the multiplicity. The symbol J is customarily (though perhaps
unfortunately) used for the coupling constant, the <u>only</u>
accepted units being cycles per second.

(8) <u>Omit figures showing NMR spectra if data can be tabulated.</u>
Very often the detailed appearance of the spectrum results
from the particular choice of operating variables (much more
so than in infrared spectroscopy!), consequently figures are,
as a rule, not especially helpful. Complex, incompletely-
analyzed spectra merit publication, but <u>only</u> if the horizontal
coordinates are <u>very carefully</u> entered, so that other workers
in the future may profit by the "buried" data.

George V. D. Tiers

POLYMER NSR SPECTROSCOPY.   II.[*]

THE HIGH RESOLUTION SPECTRA OF

ISOTACTIC AND "ATACTIC" POLYMETHYL METHACRYLATE

F. A. Bovey and G. V. D. Tiers

Communication No. 163,

Central Research Laboratories,

Minnesota Mining and Manufacturing Company

St. Paul, Minnesota

(Received   )

WE have observed significant differences between the high
resolution NSR spectra of methyl methacrylate polymers prepared
with free radical and anionic initiators.   Isotactic polymers
were prepared in toluene at -60°, -10° and 25°, and in toluene:
dioxane mixtures at -60° using n-butyllithium as initiator.[1]
The "atactic" polymers were prepared in toluene solution at
50° and in bulk and solution at 100°, using benzoyl peroxide
as initiator.   A sample of commercial molding resin, assumed to
have been prepared using a free radical initiator, was also
examined.   Spectra were obtained on 15% solutions of the polymers
in chloroform, using 0.5 ml. of solution in 5 mm. O.D. Pyrex
tubes.   A Varian V-4300-2 40.00 Mc per sec. spectrograph was
employed, together with a Varian heated probe, sample spinner,
audio-oscillator, Hewlett-Packard 522-B frequency counter and
Varian recorder.   In order to achieve the required spectral
resolution, all samples were maintained at approximately 90°.

Typical spectra in the region of interest, embracing the
methylene and α-methyl resonances, are shown in Fig. 1.   The
peak at the extreme right is that of the internal reference
standard, tetramethylsilane; the scale is expressed in parts
per million, referred to this peak as 10.00.   Values on this
scale, termed τ-values,[2] were reproducible to ca. $\pm$ 0.02 p.p.m.
standard deviation in the present work.   The ester methyl group
appears at 6.40 τ in all the polymers, and is not affected by
the chain conformation.   There are three α-methyl peaks, at
8.78 τ, 8.95 τ, and 9.09 τ, whose relative heights vary greatly
with the method of polymer preparation.   Polymers prepared with
n-butyllithium show a very prominent peak at 8.78 τ, the others
being much smaller (Curve a).   Polymers prepared in solution
with benzoyl peroxide initiator (Curve b) show the same three
peaks, but now the 9.09 τ peak is the most prominent; in the
bulk and commercial polymers (Curve c), the 8.95 τ peak is nearly
as large.   In both bulk and solution polymers, the 8.78 τ peak
is smaller but is always clearly discernible.

We interpret these very marked differences as follows.
Polymethyl methacrylate prepared with n-butyllithium initiator
is believed to be predominantly isotactic,[1] as is also the
polymer prepared in hydrocarbon solvents using 9-fluorenyl-
lithium.[3]   The peak at 8.78 τ must therefore be due to the α-
methyl groups of monomer units which are flanked on both sides
by units of the same configuration, i.e. d d d or l l l.   This
we term an isotactic configuration, the central unit being
termed an "i" unit.   The most prominent peak in free radical
polymers, - at 9.09 τ -, is attributed to α-methyl groups of

3.

central monomer units in syndiotactic configurations, ("s" units) l d l or d l d, since in free radical polymers, at least when prepared at low temperatures, this structure tends to predominate.[3] The peak at 8.95 τ is believed to be due to α-methyl groups of central monomer units in heterotactic configurations ("h" units), l d d, d l l, d d l, or l l d. The 8.78 τ, 8.95 τ, and 9.09 τ peaks will be proportional to the numbers of l, h, and s units.

The "backbone" methylene resonance would be expected to be a single peak in a syndiotactic polymer, as observed, because from simple geometrical considerations both protons must experience the same magnetic environment. In an isotactic polymer, however, this is not true; the two protons will be differently shielded and may therefore be expected to show electron-coupled spin-spin splitting to give a four-fold resonance. (A somewhat parallel situation has been studied by Wiberg.[2f]) This will consist of two "non-equivalent" doublets having nearly equal peaks if the difference in shielding considerably exceeds the coupling constant J; whereas if the shielding difference is approximately equal to J, the peaks will be more closely spaced and the outer peaks will be weaker[4]. In Fig. 1, b and c, the

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[4] E. L. Hahn and D. E. Maxwell, Phys. Rev. **88** 1070 (1952).

methylene resonance is a single peak at 8.14 τ. In Fig. 1, a, three of the expected four peaks can be seen; the fourth is assumed to be under the α-methyl resonance. The center of the quartet is in the same position, 8.14 τ, as the single peak of b and c. The coupling constant J is found to be 15.5 cycles-

sec.$^{-1}$ and the shielding difference 0.60 p.p.m. The observation of the methylene resonances provides absolute, independent confirmation of the structures deduced from X-ray fiber diagrams.

One system of nomenclature which we prefer has already been indicated. In considering the methylene resonances, however, another system is more convenient. The fraction of methylenes giving a quartet resonance will be equal to the fraction of d d or l l units, i.e. we now must consider the chain structure in terms of dyads of monomer units rather than in terms of triads as above. The fraction of monomer units involved in d l or l d configurations we shall designate as the fraction of racemic or "r" units; the fraction of d d or l l, i.e. meso units, we shall designate as "m".

NSR spectroscopy appears to provide a simple means of examining polymer chain configurations with a high degree of discrimination. It should be particularly valuable in the study of those polymers which are not sufficiently regular to crystallize. We shall describe our results in greater detail in a subsequent publication.

Fig. 1 NSR Spectra of Methyl Methacrylate Polymers (in CHCl₃) prepared (a) with n-butyllithium at 25°; (b) with benzoyl peroxide in toluene at 100°; (c) with benzoyl peroxide in bulk at 100°.

HAMILTON COLLEGE
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DEPARTMENT OF CHEMISTRY

June 30th, 1959

Dr. A.A. Bothner-By
Mellon Institute
440, Fifth Avenue
PITTSBURGH 13, Pennsylvania

Dear Dr. Bothner-By:

Dr. R.F.M. White of University College London and I are writing a review on Structural Applications of N.M.R. in Inorganic Chemistry. We would be very grateful for any reprints relevant to this topic that readers of M.E.L.L.O.N.M.R. might care to send to either or both of us.

Perhaps you would be kind enough to publish this request in the next letter if you consider it appropriate.
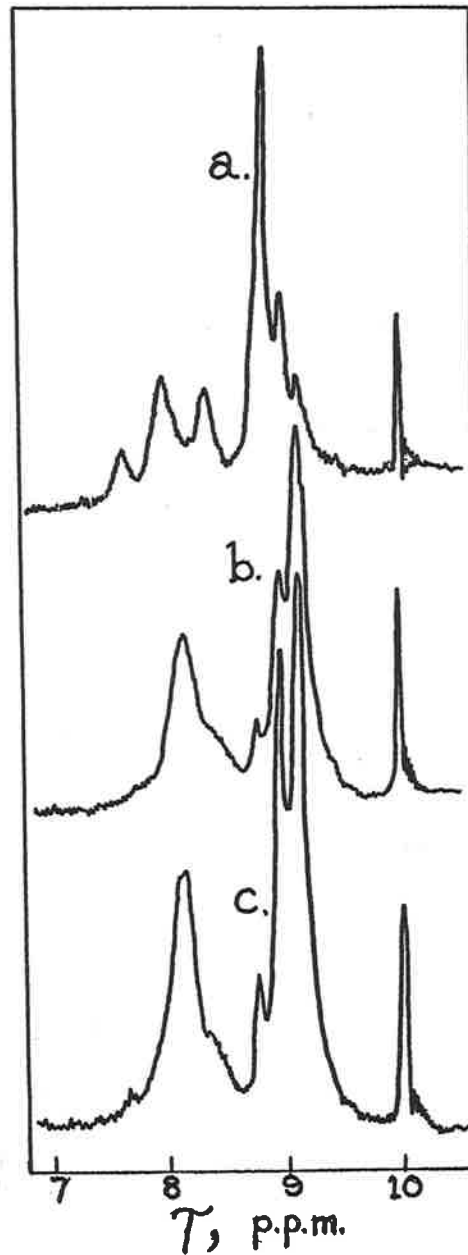
Yours sincerely,

R. J. Gillespie

RJG:bm

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