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Head-to-Head Polymers X:* High Resolution NMR Spectroscopy of Polystyrene and Poly(Vinyl Cyclohexane)

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INTRODUCTION

Proton NMR spectroscopy was first proven as a useful tool for the description of the polymer stereochemistry 20 years ago (BOVEY, et al. 1963) and has since become a very important tool supplementary to x-ray spectroscopy (NATTA, et al. 1955) to describe stereospecific isotactic or syndiotactic polymers or atactic polymers (BOVEY 1972) (HARWOOD 1965). These "regular" or head-to-tail polymers, where the substituent groups are located in the 1,3 position of a polyethylene backbone chain (MARVEL, DENSON 1938), have been extensively studied and are described in NMR spectroscopic terms as triads and as diads.

In 1965 the first long range effect of stereochemistry on polyacetaldehyde was described using an experimental 200 MHz proton spectrometer with a superconducting magnet (BRAME, VOGL 1965) (BRAME, VOGL 1967) (VOGL 1978). It was shown that at least six of the expected ten (RAMEY 1967 a;1967 b)doublets could be recognized and the individual stereochemical structures could be described by analyzing the spectrum with a curve resolver. Better resolved spectra of pentad placements were later described with poly(methyl methacrylate) (FERGUSON 1969), when the 220 MHz with temperature probes became available. It is now well known that in the earlier work of NMR spectroscopy, line broadening and first indication of splittings were often believed to be viscosity effects of polymer solutions.

Further development of the long range order analysis has since been done by tetrad and hexad analysis.

Additional advances were made by the development of ^{13}C NMR spectroscopy and the availability of suitable spectrometers (SCHAEFER 1971).

In H-T polymers (olefins, acrylates, and vinyl polymers) the side group is placed in the 1,3,5,7 position of the polymer chain. More recently, systematic work has been undertaken to prepare H-H polymers where

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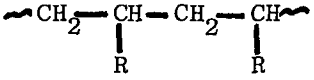
the side group is in 1,2,5,6 position of the polymer chain with two methylene groups separating the carbon atoms which have two adjacent R groups in threo or erythro position to each other (KINCAID, et al. 1974) (INOUE, et al. 1977) (HELBIG, et al. 1978).

In the last few years several pure H-H polymers have been prepared, most importantly polystyrene (INOUE, et al. 1977), poly(vinyl cyclohexane) (HELBIG, et al. 1978), poly(vinyl chloride) (BAILEY, et al. 1964), polypropylene (KLHOK,et al. 1976) and polyacrylates (OTSU, et al. 1970) (TANAKA, VOGL 1974) (TANAKA, VOGL 1974) (TANAKA, VOGL 1974). Initial work on the ^{1}H NMR and ^{13}C NMR spectra using the 100 MHz proton spectrometer or the equivalent 22.6 MHz ^{13}C mode has been undertaken for polystyrene (INOUE, et al. 1977), polypropylene (KHLOK, et al. 1976) and poly(vinyl cyclohexane) (HELBIG, et al. 1978).

Threo and erythro placements could be identified in H-H polystyrene and related to the portion of cis and trans double bonds of the 1,4 poly(2,3-diphenylbutadiene), the precursor from which H-H polystyrene was obtained by chemical stereospecific reduction.

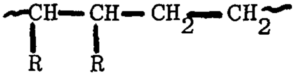
It was the purpose of this work to evaluate in detail the high resolution ^{1}H and ^{13}C NMR spectra of H-H polystyrene and poly(vinyl cyclohexane) in an attempt to identify long range order of the stereochemistry of these polymers and compare them with the regular H-T polymers.



$$\sim CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}\sim$$

1,3
H-T

Polymer



$$\sim\underset{R}{CH}-\underset{R}{CH}-CH_2-CH_2\sim$$

1,2
H-H

EXPERIMENTAL PART

Materials:

H-H polystyrene (H-H PS) was prepared from 1,4-poly (2,3-diphenylbutadiene) by reduction with K and ethanol. This polymer was in turn prepared from 2,3-diphenylbutadiene by radical polymerization with AIBN as the initiator in a bulk polymerization and was, according to NMR and IR spectroscopy, free of 1,2 monomer placements. H-H PS had an η of approximately 1,5 dl/g and a $\bar{M}_n$ of over 40,000 with a $\bar{M}_w/\bar{M}_n$ of about 2 (INOUE, et al. 1977).

Polystyrene (H-T-PS) was prepared by radical polymerization of styrene with AIBN and had a $\bar{M}_n$ of 45,000 and a polydispersity of 2.

H-H poly(vinyl cyclohexane) (H-H PVCH) was prepared from 1,4-poly(2,3-diphenylbutadiene) by catalytic hydrogenation with Pd/charcoal at 1500 psi and about 200°C. The polymer had a lower inherent viscosity as some molecular weight degradation occurred during the hydrogenation (HELBIG, et al. 1978).

H-T poly(vinyl cyclohexane) (H-T PVCH) was obtained by catalytic hydrogenation of atactic polystyrene with Pd/charcoal catalyst similar to the hydrogenation of H-T PS to H-H PVCH.

Measurements:

NMR measurements were carried out on solutions of approximately 3% polymer in C_2Cl_4 for PS and $CDCl_3$ for PVCH on a CAMECA superconducting magnet NMR spectrometer, at 250 MHz for ^{1}H and 62.86 MHz for ^{13}C. No significant improvement in the resolution was obtained at higher temperatures; it was found more efficient to lower the concentration of the polymer in the solution and to increase the number of accumulations which were typically of the order of 10,000 for one ^{13}C spectrum with an acquisition time of 0.65 sec. and a resolution of 1.25 Hz/point. Undecoupled spectra and spectra with gated or off resonance decoupling were performed when necessary to distinguish between quaternary, methylene and methine carbon atoms. All chemical shifts were measured in δ(ppm) relative to TMS.

RESULTS AND DISCUSSION

Head to Head Polystyrene

The ^{1}H spectrum of H-H PS in Figure 1 shows five resolved bands of the aromatic protons at 7.0 - 6.9 - 6.8 - 6.5 - 6.2 ppm which result from the overlapping multiplets of the five spin system. The CH and CH_2 bands are

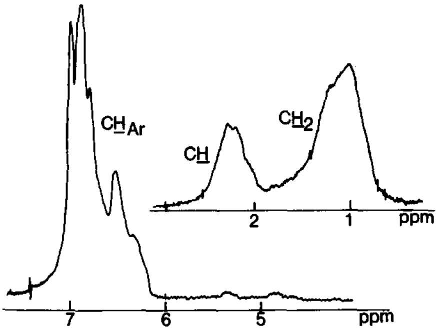


Fig. 1: ^{1}H NMR Spectrum of H-H polystyrene in C_2Cl_4

largely separated but individually are not resolved. Two very small bands at 4.85 and 5.35 ppm can be attributed to a small amount of non-hydrogenated cis and trans double bonds.

The aromatic part of the ^{13}C spectrum is shown in Figure 2. The five bands at 125.4 - 127.2 - 127.9 - 128.2 - 128.8 ppm arise from the five phenyl CH as shown by the undecoupled spectra which can be generated using a single coupling constant J ~150 Hz. No direct assignment of the ortho, meta and para carbon atoms can be made on the basis of this spectrum.

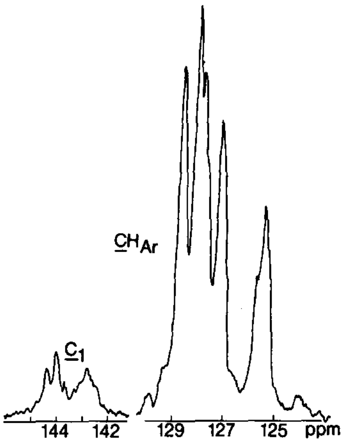


Fig. 2: ^{13}C Spectrum of H-H Polystyrene in C_2Cl_4: Ring Carbons

The high field line at 125.4 shows two shoulders suggesting the influence of longer range tacticity and appears very conclusively on the signal of the phenyl C_1. The two bands previously observed and attributed (INOUE, et al. 1977) to threo (high field) C_1 and erythro (low field) C_1 placements are well separated. The relative area of these bands are in the ratio 54/46 which is in good agreement with the values obtained from lower frequency spectra. The erythro band now shows three well resolved lines and the threo band two clearly established shoulders indicative of differences in long range order similar to pentads in head to tail polymers (BRAME, VOGL 1965) (BRAME, VOGL 1967).

Further evidence of the influence of long range order is provided by the methylene and methine part of the ^{13}C spectrum as shown in Figure 3. Attribution of the band near 31 ppm to CH and near 51 ppm to CH_2 has been made on the basis of

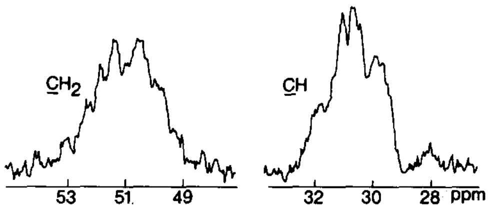


Fig. 3: ^{13}C NMR spectrum of H-H Polystyrene in C_2Cl_4: Backbone Carbons

our undecoupled spectra. The CH band shows at least four lines and the CH_2 clearly five but most probably seven lines whose chemical shifts are reported in Table 1.

TABLE 1

^{13}C NMR Chemical Shifts in H-H Polystyrene, δ in ppm, Relative to TMS

Phenyl C_1:	142.8 (threo 54%); 143.7 - 144.0 - 144.4 (erythro 46%)
Phenyl CH:	125.4 - 127.2 - 127.9 - 128.2 - 128.8
Backbone CH:	30.0 - 30.7 - 31.1 - 31.8
Backbone CH_2:	(49.3) - 50.0 - 50.4 - 51.4 - 51.9 - 52.4 - (53.1)

Head to Head Poly(vinyl cyclohexane)

The ^1H spectrum is shown in Figure 4. There is no distinction between the backbone and the ring protons.

The ^{13}C spectrum is shown in Figure 5. The three low field bands which are nicely split correspond, from off resonance spectra, to two methine and one methylene group resonance (J ~123 Hz). The signal of the five remaining methylene groups is spread over a broader region between 27 and 30 ppm. The approximate chemical shifts (concerning the line width and the overlap of the bands) are given in Table II. The assignment is based on the shift of substituted cyclohexanes (DALLING, GRANT 1967).

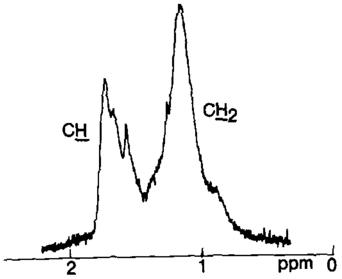
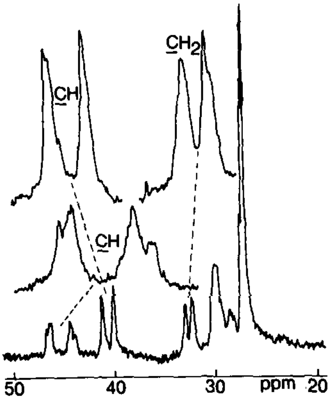


Fig. 4: ^1H NMR Spectrum of H-H Poly(vinylcyclohexane) in $CDCl_3$



^{13}C NMR Spectrum of H-H Poly(vinylcyclohexane) in $CDCl_3$

TABLE II

^{13}C NMR Chemical Shifts in H-H Poly(vinyl cyclohexane)
δ in ppm, Relative to TMS

Backbone CH:	44.0 - 44.5 - 46.6 - 46.9
Backbone CH_2:	32.3 (shoulders) - 33.0
Ring CH:	40.2 - 41.3 (shoulders)
Ring CH_2(5):	30.0 (shoulders) - 28.5 - 28.0 - 27.5 - 27.28 - 27.06

The major splitting in the three low field bands is attributed to the difference of chemical shift for the erythro and threo placement. In the three cases there is a small but significant difference in the area under the two components corresponding to a 48/52 ratio, with the smaller at low field for the 45 ppm methine group and the 33 ppm methylene group but the reverse for the 41 ppm methine group. Considering the cis-trans ratio in the parent 1,4-poly(2,3-diphenylbutadiene) (INOUE, et al. 1977), this may help to assign separately the threo and erythro placement.

Of more interest are the further splittings corresponding to the influence of long range order. They are only apparent as two shoulders in the low field component of the 41 ppm methine band and in the high field component of the 32 ppm methylene band, but are clearly resolved in the two components of the low field CH with lines at 44.0 - 44.5 - 46.6 - 46.9 ppm.

The ^{13}C NMR spectra of both the H-H PS and H-H PVCH show, for some of the carbon atoms, splittings which go beyond the simple difference between threo and erythro placement and reveal the influence of long range order, similar to the tetrad and pentad placements in H-T vinyl polymers (RAMEY 1967; 1967) and pentad placements in polyacetals (BRAME, VOGL 1967) (VOGL 1978). The number of possible stereochemical sequences to consider in H-H polymers is different from the traditional H-T polymers and is not only a function of the threo or erythro nature of the neighboring unit but also of the respective signs of the two neighboring asymetric carbons in successive units. Denoting the absolute configuration by S and R one should therefore consider the following sequences:

R - R - 0 - 0 - R - R or S - S - 0 - 0 - S - S (mmm)
S - R - 0 - 0 - R - R or R - S - 0 - 0 - S - S (rmm)
or S - S - 0 - 0 - S - R
or R - R - 0 - 0 - R - S

S - R - 0 - 0 - R - S or R - S - 0 - 0 - S - R (rmr)
R - R - 0 - 0 - S - R or R - S - 0 - 0 - R - R (rrm)
or S - R - 0 - 0 - S - S
or S - S - 0 - 0 - R - S
S - R - 0 - 0 - S - R or R - S - 0 - 0 - R - S (rrr)
R - R - 0 - 0 - S - S or S - S - 0 - 0 - R - R (mrm)

Taking the central sequence X - 0 - 0 - Y as a meso or racemic dyad, one sees that the classification corresponds to the six "tetrad" placements in a head to tail polymer as given in the parenthesis. Their probabilities are however quite different. Denoting by P_m the probability of a meso sequence, the probabilities of the different sequences are:

m m m	$1/2\ P_m^2$
m m r	$P_m\ (1 - P_m)$
r m r	$1/2\ (1 - P_m)^2$
m r m	$1/2\ P_m^2$
r r m	$P_m\ (1 - P_m)$
r r r	$1/2\ (1 - P_m)^2$

With $P_m = 0.5$ there should be two strong lines and four of half magnitude which could overlap to give the pattern observed in the ^{13}C signal of the methylene group in H-H PS.

The question is even more complicated in the case of the methine group or of any of the carbon of the side group. In that case one should enumerate the possible hexads, such as:

R - S - 0 - 0 - R - R - 0 - 0 - R - R (r r m m m)

There is no hope to observe all the possible structures with present day equipment. Even in the three signals which represent the most favorable cases of this type and where we have observed some splittings beyond the simplest erythro-threo difference, i.e. phenyl C_1 and backbone methine of H-H PS, backbone methine of H-H PVCH, no more than four or five lines were clearly resolved.

CONCLUSIONS

The ^{13}C NMR spectra of H-H PS and H-H PVCH show the influence of the long range order on the chemical shift of several carbons. There is some hope to improve the resolution by the choice of appropriate solvents. The attribution of the lines to specific stereosequences would require the preparation and separation of optically pure dimers and trimers. It is, however, already possible to compare the microstructure of H-H polymers prepared by different chemical ways.

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REFERENCES

1. F.E. BAILEY, J.P. HENRY, R.D. LUNDBERG and J.M. WHELAN: J. Polym. Sci., Part B, 2, 447 (1964)
2. F.A. BOVEY and G.V.D. TIERS: Fortschr. Hochpolymer Forschung 3, 139 (1963)
3. F.A. BOVEY: High Resolution NMR of Macromolecules, Academic Press (1972)
4. E. BRAME and O. VOGL: Brooklyn Polytechnic Inst., N.Y., January, 1965
5. E. BRAME and O. VOGL: J. Macromol. Sci. (Chem.) A1(2), 277 (1967)
6. D.K. DALLING and D.M. GRANT: J. Am. Chem. Soc. 89, 6612 (1967)
7. R. FERGUSON: Macromolecules 2, 237 (1969)
8. H.J. HARWOOD: Angew. Chem. Int. Ed. 4, 1051 (1965)
9. M. HELBIG, H. INOUE and O. VOGL: J. Polym. Sci., Symposium Edition (1978)
10. H. INOUE, M. HELBIG and O. VOGL: Macromolecules 10(6), 1331 (1977)
11. D. KHLOK, Y. DESLANDES and J. PRUD'HOMME: Macromolecules 9(5), 809 (1976)
12. P. KINCAID, T. TANAKA and O. VOGL: Preprints, ACS Polym. Div. 15(2), 222 (1974)
13. C.S. MARVEL and C.E. DENSON: J. Am. Chem. Soc. 60, 1045 (1938)
14. G. NATTA, P. PINO, P. CORRADINI, F. DANUSSO, E. MANTICA, G. MAZZANTI and G. MORAGLIO: J. Am. Chem. Soc. 77, 1708 (1955)

15. T. OTSU, S. AOKI and R. NAKATANI: Makromol. Chem. 134, 331 (1970)
16. K.C. RAMEY: Preprints, ACS Polym. Div. 8(2),1017 (1967a); Polymer Letters B5, 859 (1967b)
17. J. SCHAEFER: Macromolecules 4, 107 (1971)
18. T. TANAKA and O. VOGL: Polymer J. (Japan) 6, 522 (1974)
19. T. TANAKA and O. VOGL: J. Macromol. Sci. (Chem.) A8(6), 1059 (1974)
20. T. TANAKA and O. VOGL: J. Macromol. Sci. (Chem.) A8(8), 1299 (1974)
21. O. VOGL: Polymer News 10 (1978)

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