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H-H Polymers XI:* High Resolution NMR Spectroscopy of Poly(Methyl Acrylates)

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INTRODUCTION

Polymers prepared by bond opening polymerization of α-olefins, vinyl and acrylic monomers have mainly H-T linkages in the polymer backbone chain (MARVEL, DENSON 1938); in some cases lower percentages of H-H linkages have been observed (OTSU, et al. 1965) (WILSON, SANTEE 1967). In the last few years, successful attempts have been made to prepare pure H-H polymers and characterize them properly (KINCAID, et al. 1974); especially noteworthy are the reports for the preparation of H-H polyolefins particularly polystyrene (INOUE, et al 1977), polypropylene (KHLOK, et al. 1976) and poly(vinyl cyclohexane (HELBIG, et al. in press).

One of the first investigations on H-H polymers' was the preparation and characterization of H-H acrylates (OTSU, et al. 1970) (TANAKA, VOGL 1974) (TANAKA, VOGL 1974) which were synthesized by an indirect route. Maleic anhydride was copolymerized with AIBN as the radical initiator at 60°C. with ethylene, cis- and trans-stilbene followed by complete esterification. These polymers were characterized and their thermal degradation was studied and an initial investigation of the ^{1}H NMR spectrum of these polymers at relatively low resolution was undertaken (TANAKA, VOGL 1974). It was suspected that ^{1}H NMR and ^{13}C NMR spectroscopy at high resolution could give a clear picture of the stereochemistry of these polymers. Stereochemistry in the maleate or fumarate portion of the macromolecule would give an indication of the stereochemistry of addition of the methylene terminated polymer radical as compared to the succinyl anhydride radical to ethylene. For substituted ethylenes, both cis- and trans-butene-2 stilbene were used for the copolymerization with maleic anhydride. Identical structures from the copolymerization would mean that only one radical of the olefin terminated polymer radical plays an important role in this part of the propagation, as has been observed in the high pressure polymerization of internal olefins (ANDERSON, et al. 1969) (ANDERSON, et al. in press).

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*Part X: G. Weill and O. Vogl, Polymer Bulletin, in press.

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Qualitatively speaking the line broadening of the characteristic chemical shift peaks as we go from H, to methyl, phenyl substitution in β-proton was expected to give an indication of the polymer chain stiffness.

The study of H-H polystyrene and H-H poly(vinyl cyclohexane) by 250 MHz spectroscopy and the corresponding ^{13}C NMR spectroscopy have shown that long range order of the stereochemistry of H-H polymers similar to that of the pentad and hexad placement in H-T polymers could be observed.

EXPERIMENTAL PART

Materials:

H-H Poly(methyl acrylate) was prepared from alternating copolymers of ethylene with maleic anhydride with AIBN as the initiator in chloroform solution (OTSU, et al. 1970); the polymer was esterified by treatment with methanol/sulfuric acid which gave the polymeric acid ester. Complete esterification was achieved by treatment of these polymers with diazomethane.

H-H Poly(methyl crotonate) was obtained from copolymers of cis-butene-2/maleic anhydride (STOLARCZYK, et al. 1977) and trans-butene-2/maleic anhydride (TANAKA, VOGL 1974). Esterification of butene/maleic anhydride was done in a way similar to the esterification of ethylene/maleic anhydride copolymers.

H-H Poly(methyl cinnamate): Copolymers of maleic anhydride with trans-stilbene were prepared with AIBN as the initiator in benzene solution. Long reaction times were needed to achieve high yields of polymers and high molecular weights (TANAKA, VOGL 1974). Cis-stilbene was copolymerized with maleic anhydride under similar conditions (STOLARCZYK, et al. 1977). It was also determined that cis-stilbene did not isomerize to trans-stilbene under these reaction conditions. Alternating stilbene/maleic anhydride copolymers were esterified by saponifying the copolymer in aqueous alkali and treating the aqueous solution of the polymeric acid salt with dimethyl sulfate.

All copolymers had inherent viscosities between 0.4 and 1.4 dl/g.

Measurements:

Measurements have been carried out on ~4% solutions in $CDCl_3$ at room temperature on a CAMECA superconducting magnet NMR spectrometer at 250 MHz for ^{1}H and 62,86 MHz for ^{13}C. Up to 100,000 accumulations had to be performed in the most unfavorable cases due to the unusually broad line width in the ^{13}C spectrum. Undecoupled spectra were recorded for the assignment of the CH and CH_2 signals of poly(methyl acrylate). All chemical shifts were measured from TMS.

RESULTS

H-H Poly(methyl acrylate)

The ^{1}H spectrum of H-H poly(methyl acrylate) is not reproduced since it consists of three relatively structureless bands whose chemical shifts and line width are given in Table I.

TABLE I

^{1}H and ^{13}C Chemical Shifts of H-H Poly(methyl acrylate) δ(in ppm) from TMS

$C\underline{H}$	5.25	(= 30 Hz)	$\underline{C}H$	46.14 - 46.75
$C\underline{H}_2$	2.98	(= 30 Hz)	$\underline{C}H_2$	26.24 - 26.50
$O\text{-}C\underline{H}_3$	7.35	(= 3 Hz)	$O\text{-}\underline{C}H_3$	51.8
			$\underline{C}{=}O$	173.97 - 174.07

The ^{13}C spectrum of H-H poly(methyl acrylate) is displayed in Figures 1 and 2. Chemical shifts are indicated in Table I.

The splittings observed in the $\underline{C}H_2$, $\underline{C}H$ and $\underline{C}{=}O$ signals are attributed to the difference in chemical shift of threo and erythro units in an essentially 1/1 ratio. The $O\text{-}CH_3$ signal which has a line width of 8 Hz (0.125 ppm) does not show any splitting, while a 6 Hz splitting is clearly resolved in the broader

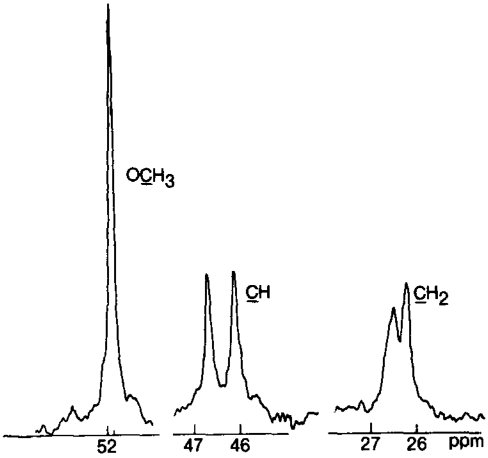


Fig. 1: ^{13}C spectrum of H-H Poly (methyl acrylate): $O\text{-}CH_3$, CH and CH_2 signals

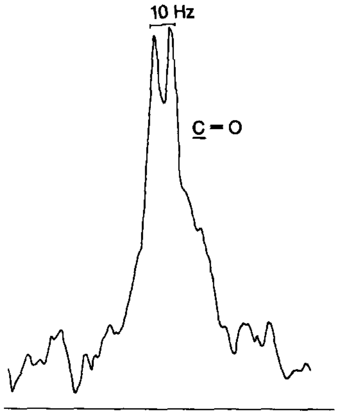


Fig. 2: ^{13}C Spectrum of H-H Poly(methyl acrylate): 6 Hz Splitting in the C=O Signal

$\underline{C}$=O signal. The absence of sensitivity of the O-$\underline{C}H_3$ signal to microtacticity both in the ^{1}H and ^{13}C spectrum in line with a similar observation in the case of H-T poly (methyl methacrylates) of different tacticity (JOHNSON, et al. 1970).

H-H Poly(methyl crotonate): ^{13}C spectra obtained for the two polymers prepared from cis- and trans-butene are shown in Figures 3 and 4. The two ^{13}C spectra are quite similar; the slight differences in resolution and in relative line heights are probably due more to differences in line width, due for example, to the influence of the molecular weight, than to differences in the microstructure of the polymers obtained from cis- and trans-butene. The assignment of the $\underline{C}H$ and $\underline{C}H_3$ signals are based on undecoupled spectra and comparison of the shifts with that of H-H poly (methyl acrylate), as it may be seen in Table II.

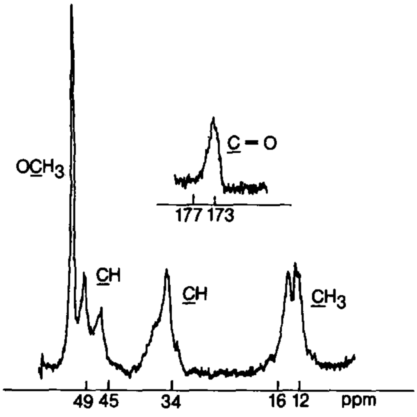


Fig. 3: ^{13}C Spectrum of H-H Poly(methyl crotonate) from Trans-Butene

One should remark about the 30 Hz line width of the O-$\underline{C}H_3$ signal. This is essentially due to the increased stiffness resulting from the presence of bulky side groups on each carbon of the backbone. It is also reflected in the ^{1}H spectrum by a more than 1 ppm wide unresolved band for the CH protons.

It can also be seen clearly that the signals of the carbon atom of the methine group in a butane unit are distinctively split as a result of threo or erythro placement. Indications of unresolved splittings appear in the CH and C=O (cis-butene) signals of the maleate unit.

H-H Poly(methyl cinnamate): The ^{1}H spectrum reflects once again the substantial rigidity of this polymer backbone chain. The broad spectrum extends from 2 to 9 ppm with broad maxima around 7, 3 and 2 ppm. The overlap is such that the separation of aromatic, O-CH_3 and CH protons is not possible from the integral.

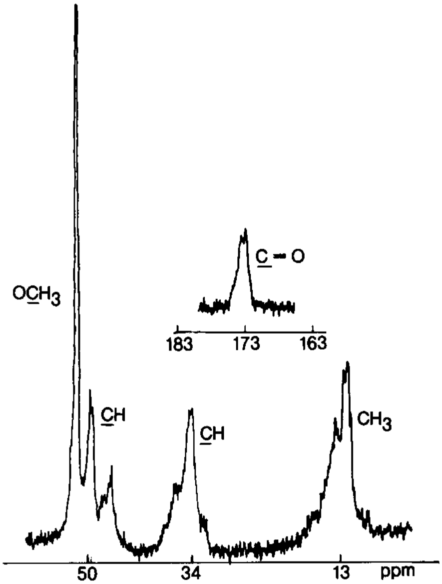


Fig. 4: ^{13}C Spectrum of H-H Poly(methyl crotonate) from Cis-Butene

TABLE II

^{13}C Chemical Shifts in H-H Poly(methyl crotonate) δ(in ppm) from TMS

CH (butene-2 unit)	49.5 - 46.3
CH (maleate unit)	34.4 (high field shoulder)
CH_3	11.7 (12.1) - 13.3
O-CH_3	51.4
C=O	173 (possibly a 30 Hz splitting)

This rigidity of the polymer chain is also reflected in the ^{13}C spectrum in a line width of 50 Hz of the O-CH_3 line. This is, however, the only line which shows a clearly resolved splitting of 20 Hz; it is also seen in each of the polymers from cis- or trans-stilbene. The two H-H poly(methyl cinnamates) are undistinguishable by NMR spectroscopy and only one of them is therefore displayed in Figure 5. No resolved splitting is observed in either of the other

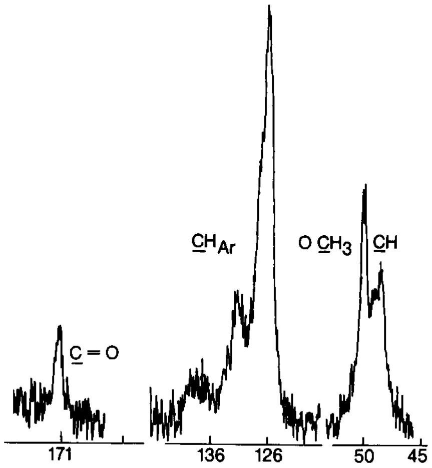


Fig. 5: ^{13}C Spectrum of H-H Poly(methyl cinnamate) from Trans-Stilbene

bands; this is caused by the inherent broader line width of the signal and the higher number of possible stereosequences with different chemical shifts which are expected in a polymer where all carbon atoms are asymmetric and where the aromatic ring effect is expected to largely influence the particular chemical shift of each long range stereosequence. In particular, the 138 ppm band which can be attributed to the phenyl C_1 is spread over nearly 4 ppm. These factors lower considerably the S/N ratio and therefore precludes any detail analysis of the fine structure.

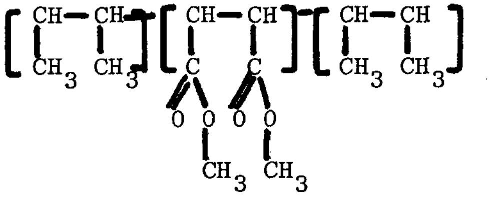
TABLE III

^{13}C Chemical Shifts in H-H Poly(methyl cinnamate)
δ(in ppm) from TMS

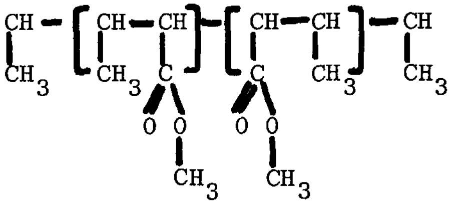
CH (backbone unresolved)	47.6
$O-CH_3$	50.44 - 50.75
CH (phenyl ring)	126.7 - 132 - 138
C=O	172

DISCUSSION

The microstructure of H-H poly(methyl acrylate) and β-substituted H-H poly(methyl acrylates) can be analyzed in terms of threo and erythro sequences within the maleate unit, but the NMR spectrum does not permit to identify further influence of long range order. In the case of H-H poly(methyl crotonate) and H-H poly(methyl cinnamate), both the influence of the stiffness due to bulky side groups on each carbon atom and of the number of possible microstructures in the case where all carbon atoms are asymmetric contribute to a poor resolution of the spectra. Moreover, in cases where splittings can be identified, the question is raised whether the difference in chemical shift of a meso or racemic dyad, which is the first order explanation for such a splitting, should be considered <u>inside</u> of a monomer unit or using a <u>mixed</u> dyad with one carbon from each monomer as represented schematically below in the case of polymethylcrotonate:



inside dyads



mixed dyads

This is especially clear in the case of the O-CH$_3$ signal of H-H poly(methyl cinnamate), since it has been shown in the case of H-H-PMA and H-H poly (methyl crotonate) that its chemical shift is insensitive to the threo or erythro nature of the maleate unit. Therefore the observed splitting must be essentially due to the relative placement of the corresponding positions of the neighboring phenyl ring, but if that is the case results appear to be very insensitive to the stereochemistry of radical bond opening of the individual double bonds.

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