^{13}C n.m.r. study of optically active polymers: 2. Relaxations in poly [(S)-4-methyl-1-hexene]

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(Received 13 June 1978; revised 12 July 1978)

T_1, T_2 and *NOE* were measured in ^{13}C n.m.r. spectra of two fractions of poly [(S)-4-methyl-1-hexene] obtained by selective solvent extraction (diethyl ether and cyclohexane) of the polymers prepared in the presence of isospecific catalysts. T_1 measurements provide evidence in the two fractions for the existence of different conformational weightings about side chain bonds according to conclusions from vibrational spectroscopy studies. Subtle configurational differences of the two substantially isotactic samples are suggested to explain this result. A discussion of the dynamic parameters related to the correlation time is also presented which supports the above explanation.

INTRODUCTION

In a previous paper[1] we reported that poly[(S)-4-methyl-1-hexene] fractions of different molecular weights obtained by selective solvent extraction showed peculiar differences in their ^{13}C n.m.r. spectra.

In particular it was shown that some of the signals arising from the side chain carbon atoms exhibited different linewidths despite the rather high and apparently very similar degree of isotacticity of the two samples as shown by infrared, X-ray and polarimetric measurements. This observation was tentatively interpreted in terms of conformational effects in the side chain.

As an additional probe and to gain a better insight into these effects, n.m.r. parameters directly related to molecular motions and to correlations time, i.e. T_1, T_2 and the nuclear Overhauser enhancement (*NOE*), were measured. The results constitute the subject of this paper.

EXPERIMENTAL

Polymers

(S)-4-methyl-1-hexene was obtained as previously described[2,3].

Polymerization experiments were carried out in the presence of $TiCl_3$ 'ARA' or VCl_4 and $Al(iso\text{-}C_4H_9)_3$ catalysts. The resulting polymers were fractionated by extraction with different solvents as previously reported[4].

The properties of some typical samples which were analysed have previously been reported[1].

^{13}C n.m.r. measurements

Proton decoupled ^{13}C n.m.r. spectra were measured using 5% solutions in $CDCl_3$ at room temperature (28°C), on a Bruker HFX90 instrument operating at 22.63 MHz.

^{13}C T_1 values were determined by the partly relaxed Fourier transform method.

$^{13}C-^{1}H$ nuclear Overhauser effect factors (*NOE*) were determined by the gated decoupling method (waiting time between 20° pulses = 25 sec).

The T_1 values for the methyls were estimated according to the equation:

$$A = A_0(1 - 2e^{-t/T_1})$$

where A_0 is observed in the *NFT* spectrum (3000 scans) and t is the time interval between 180° and 90° pulses (error $\leqslant 5\%$).

The small difference in chemical shift of the signals due to CH_2 and CH resonance in the samples studied limited the plot of $\log(A_0-A)$ (see *Figures 3a* and *3d* of ref 1). Thus, T_1 measurements represent the range in which the corresponding signal is still negative or positive in 5 msec intervals (15000 scans) following the disequations:

$$t \text{ signal negative} < T_1 \ln 2 < t \text{ signal positive}$$

T_2 was simply taken according to the equation:

$$T_2 = (\pi \times \text{linewidth})^{-1}$$

RESULTS AND DISCUSSION

Conformations in poly[(S)-4-methyl-1-hexene]

In *Table 1* the ^{13}C n.m.r. parameters are reported for the fractions obtained by the extraction with diethyl ether (polymer I) and cyclohexane (polymer II). These two poly-

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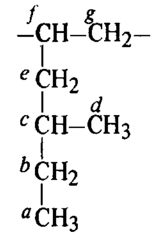
Table 1 Relaxations time (T_1 and T_2) and nuclear Overhauser effect factor (*NOE*) for fractions of poly[(S)-4-methyl-1-hexene]obtained by extraction with diethylether (polymer I) and cyclohexane (polymer II)[c]

Assignment	Value (ppm)[a]		T_1		T_2		
	Calculated	Experimental	Polymer I	Polymer II	Polymer I	Polymer II	*NOE*[b]
C*a*	10.87	11.51	404 ± 10	433 ± 10	76	53	1.6
C*b*	29.60	31.13	66 ± 3	98 ± 3	71	76	1.2
C*c*	32.52	31.74	55 ± 3	35 ± 4	33	21	1.2
C*d*	19.63	19.52	153 ± 10	151 ± 10	60	49	1.3
C*e* (or C*g*)	41.67	42.77	23 ± 2	23 ± 2	20	18	1.0
C*f*	30.84	29.72	35 ± 2	33 ± 2	42	35	0.6
C*g* (or C*e*)	39.98	41.20	20 ± 2	20 ± 2	16	14	1.0

[a] From TMS as internal standard [b] Error within 10%. Polymer I and II show *NOE* within the experimental error [c] $\bar{M}_v$ 0.2 x 10^6 for polymer I and 1.4 x $10^6$for polymer II

mers have comparable degrees of isotacticity and $\bar{M}_v$ 0.2 x 10^6 and 1.4 x 10^6, respectively.

It can be seen that the relaxation times of the C*g*, C*f*, C*e* and C*d* carbon atoms are practically the same in the two fractions.



Signals due to C*a* and C*b* carbon atoms show a longer T_1 in polymer II while methine C*c* has a much longer T_1 relaxation in polymer I.

The fact that no appreciable change in the T_1 parameters is observed for C*g*, C*f*, C*e* and C*d* carbon atoms is in agreement with the findings of Allerhand and Hailstone[5] for polystyrene samples having different molecular weights. In order to explain the variations of longitudinal relaxations for carbon atoms C*a*, C*b* and C*c* no difference in the main chain or around the torsional angles related to *fg*, *fe*, *ec* and *cd* bonds can be invoked.

Thus, the appreciably different T_1 values for C*a*, C*b* and C*c* atoms in the two fractions should arise only from the side chain conformations around the *cb* bond.

The conformation of each side chain depends on the conformation of backbone as its β methyl group can give rise to the different energetic interactions depending on the arrangement (*trans–trans*, *gauche–trans* or *gauche–gauche*) of the two main chain bonds[6]. A possible approach is to assume for the isotactic main chain the lowest energy conformation, that is the helical conformation assumed in the crystalline state, and to discuss the conformations of the side chains[6,7] consequently allowed.

Let us consider the allowed conformations 1a and 1b (*Figure 1*) of the monomeric units inserted in an isotactic macromolecule having a left-handed 3_1 helical structure. These conformations, derived from a consideration of molecular models[7], are substantially in agreement with X-ray data[8] and they differ only in the spatial position of the methyl group C*a*.

In the conformation 1a, the side chain forms a left-handed helical section, and the structure, as a whole, is noticeably rigid. It can be seen that the C*c* methine is held rigidly between two helices (the main chain and the side chain). Under these conditions the methylene C*b* and the methyl C*a*, which is *trans* to methyl C*d*, are quite well exposed to the solvent.

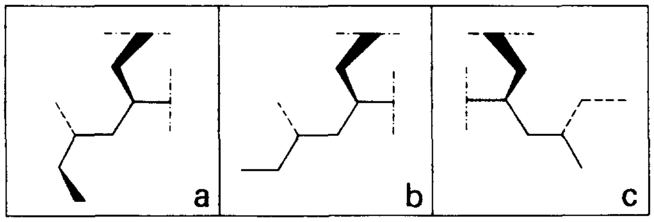


Figure 1 Allowed conformations of poly[(S)-4-methyl-1-hexene] monomeric unit inserted in an isotactic chain: (a) and (b) left-handed helices; (c) right-handed helix. (a) $[\phi]_D + 300$; (b) $[\phi]_D + 180$; (c) $[\phi]_D - 300$

In the second conformation, 1b, the side chain, as a whole, is more relaxed but the methyl group C*a* has only limited freedom due to long range interactions with the *gauche* methyl C*d*. It must also be noted that methylene C*b* is not well exposed to the solvent, while methine C*c* is less tightly packed than in structure 1a.

The diethyl ether soluble fraction (polymer I), showing a lower T_1 value for C*a*, C*b* and C*d* atoms and a higher T_1 value for C*c* atom, should have 1b as the dominant conformer, while the cyclohexane soluble fraction (polymer II), whose behaviour is completely opposite, should have 1a as the dominant conformer.

For the conformer 1c derived by the insertion of the monomeric unit in the allowed right-handed 3_1 helix, the n.m.r. parameters should be very similar to those for 1b. In fact the conformational requisites for C*a*, C*b*, C*c* and C*d* are practically the same, because these atoms are involved in two right-handed helices formed by the main chain and by the side chain, respectively.

Thus, the discussion can be centred on the forms 1a and 1b since optical rotation is positive and very high ($[\alpha]_D^{25}$ = +250–+280) in both fractions. This suggests the presence of relatively long left-handed helical sections which may be interspaced with much shorter right-handed helical sections[9,12]. These results are in keeping with i.r. spectroscopic findings[13], where the spectral differences for poly[(S)-4-methyl-1-hexene] fractions having different degrees of isotacticity can be interpreted as due to different positions of the conformational equilibrium. Of particular interest in this connection is the spectral region around 1000 cm^{-1} where the coupling of normal modes involving the sec-butyl group in the side chains occurs. The latter is confirmed by normal coordinate calculations performed on monomeric structural models[14].

In this region (*Figure 2*) two strong bands, at 995 and 964 cm^{-1}, and a shoulder at 973 cm^{-1} are present. This latter absorption which is rather pronounced in the solid-state spectra of low molecular weight ($\bar{M}_n = 5 \times 10^3$) isotactic samples, is responsible, at least in part, for enhancing the intensity of the 964 cm^{-1} band and is associated with the conformer 1b.

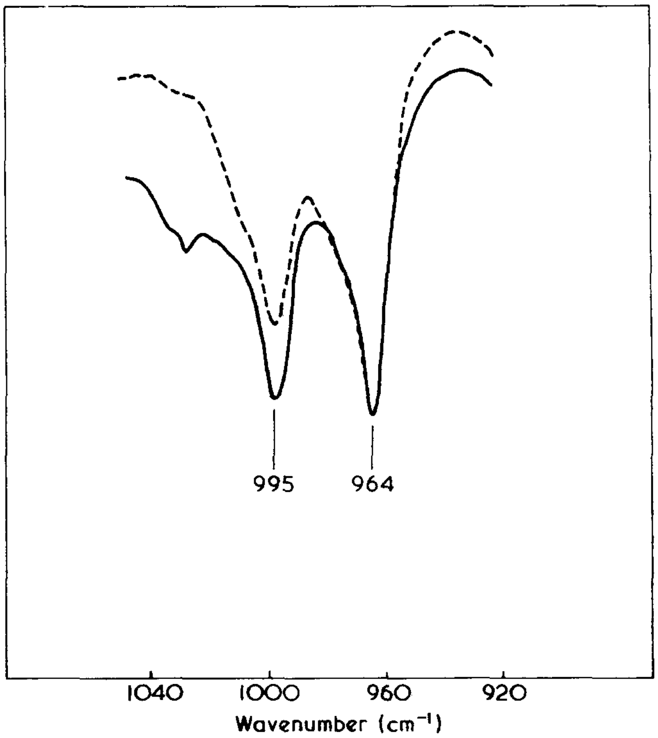


Figure 2 Infra-red spectra in the 1000 cm^{-1} region (CS_2 solution)

The different values of the ratio $R = D_B 995\ cm^{-1}/D_B 964\ cm^{-1}$, for polymer I ($R = 0.84$) and polymer II ($R = 0.96$) are then in complete agreement with the ^{13}C n.m.r. data as they suggest the prevailing population of conformation 1a with respect to 1b in the latter.

In fact the absorption band at higher frequency (995 cm^{-1}) can be attributed predominantly to the 1a conformational situation, whereas the absorption at 973 and 964 cm^{-1} can be considered to arise principally from the conformers 1b and 1c, which have the two terminal methyl groups in a *gauche* arrangement.

In conclusion, this separation of the two conformers cannot be explained easily unless configurational differences are present in polymer I and polymer II. These configurational differences may result from:

(i) differences in the extent of steric defects in the side chain (distribution and/or content of enantiomeric monomer units[16]);

(ii) differences in the extent of steric defects in the backbone (degree of tacticity);

(iii) a combination of the above considerations.

While none of these hypotheses can be excluded rigorously the overall extent of these defects is apparently quite low in both fractions and beyond our sensitivity limits, as is shown by the single resonance line due to C*d* methyl signal (see Figures in refs 1 and 17).

DYNAMIC PARAMETERS

Data in *Table 1* show that n.m.r. parameters (T_1, T_2, *NOE*) do not significantly differ for C*g*, C*f* and C*e* carbon atoms in polymers I and II. The T_1 value of the skeletal CH_2 carbon

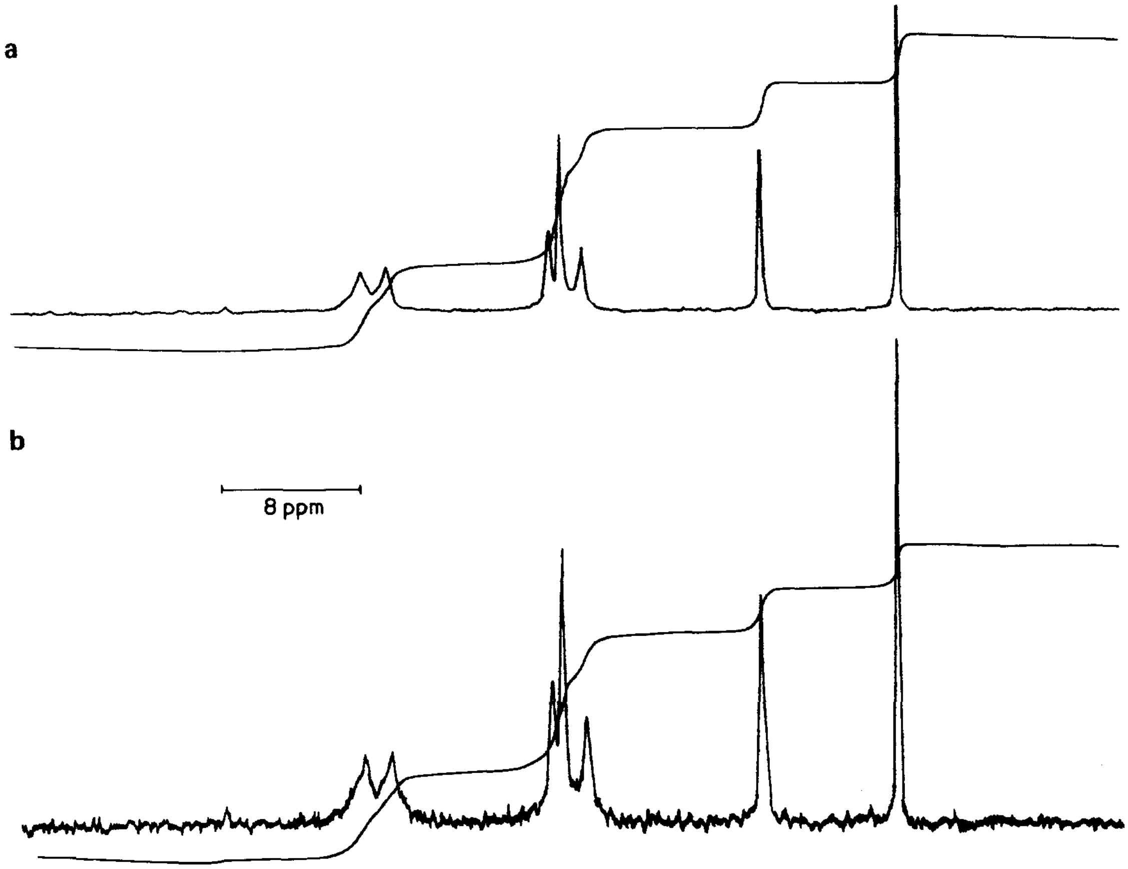


Figure 3 Polymer I ^{13}C n.m.r. spectrum with (A) and without (B) Overhauser enhancement. Spectrum amplification, (b)/(a) = 4 and integral amplification, (b)/(a) = 1. Chemical shifts are reported in *Table 1*

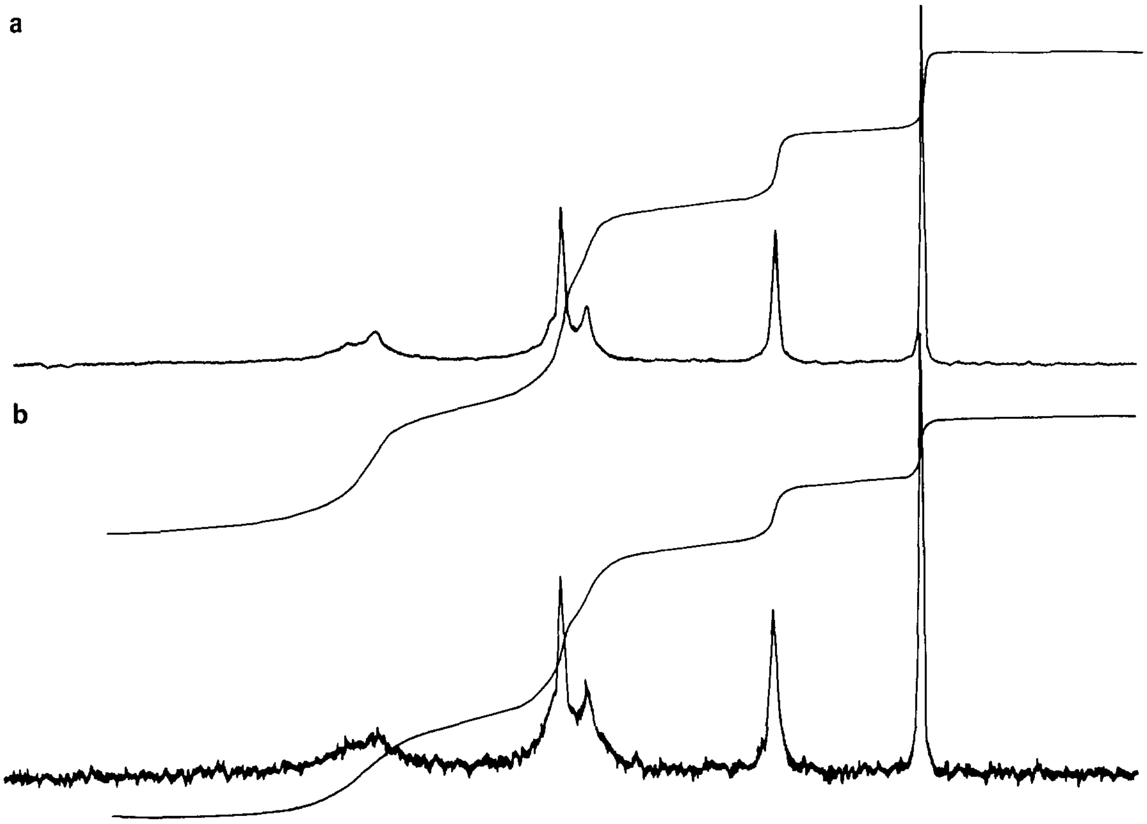


Figure 4 Polymer II ^{13}C n.m.r. spectrum with (a) and without (b) Overhauser enhancement. Spectrum amplification, (b)/(a) = 4 and integral amplification, (b)/(a) = 2. Chemical shifts are reported in *Table 1*

atom is about ½ that of the skeletal CH carbon atom. Where N represents the number of protons attached to C*g*, C*f* and C*e* respectively, the products $N \times T_1$ are nearly equal to each other. The same is true for $N \times$ *NOE* (Overhauser enhancement factor), (*Figures 3* and *4*).

These observations demonstrate that the dominant relaxation mechanism in the backbone (and for the C*e* methylene) of these polymer systems is the dipolar interaction with the attached protons, as is usually found in the ^{13}C relaxation of macromolecules[18]. Consequently, one can assume that the correlation times for the skeletal carbon atoms are nearly identical.

It is worth noting that the T_1 value and the *NOE* of the signals attributed to C*e* and C*g* methylenes are also almost the same. Thus, on this basis, no unequivocal assignment of the peaks is possible. However, one can deduce that the correlation times for the two kinds of carbon atoms are nearly the same, as has been previously reported for vinyl polymers with a bulky substituent[19].

If, as these observations suggest, an isotropic reorientation of the polymer molecular motions and a dominant ^{13}C–^{1}H dipolar relaxation mechanism are assumed, one can estimate the effective correlation time for the relaxation of the polymer on the basis of the measured T_1 and *NOE* values[20]. The relationship between τ and T_1 at 22.63 MHz was calculated according to the Allerhand's theoretical treatment[21,22]. Attention should be drawn to the fact that in this treatment a value of T_1 is not readily understood since it is slightly shorter than the minimum possible value while the *NOE* is quite high.

Although, the T_1 determination is imprecise, because it accidentally lies on a flat minimum, the present data (T_1, T_2 and *NOE*) may be interpreted in terms of a single correlation time model. A self-consistent explanation of the parameters and of the discrepancy found in the calculated value of τ can also be obtained in terms of a distribution of correlation times[20].

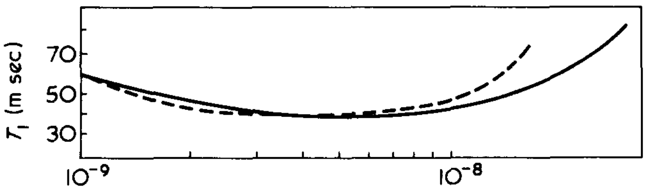


Figure 5 T_1 as a function of correlation time. ———, According to refs 21 and 22; — — — —, according to ref 20, p = 100

Note that Schaefer's model has to be used not because of discrepancies between the T_1 and T_2 values, as originally proposed[20], but because of the discrepancy between T_1 and *NOE* when calculated as a function of a unique correlation time. A logχ^2 distribution function can be used for this purpose[20]. In this formulation a given distribution is characterized by a width parameter p, a mean correlation time $\bar{\tau}$, and a logarithmic time scale of base, b. The larger the value of p, the narrower the width of the distribution.

For poly[(S)-4-methyl-1-hexene] at 28°C values of $p \simeq 100$ and $\tau \simeq 3 \times 10^{-9}$ satisfactorily explain the combined T_1 and *NOE* data for the backbone carbon atoms (*Figures 5* and *6*). Some uncertainty remains in the p and τ values due to the fact that T_1 lies on a flat minimum in the function of p and τ. A large value of p is characteristic of a system with many degrees of freedom and poor cooperativity. This is in agreement with the proposed model[9,12] for poly[(S)-4-methyl 1 hexene] consisting of segments of different length of left-handed helices joined to shorter segments of right handed

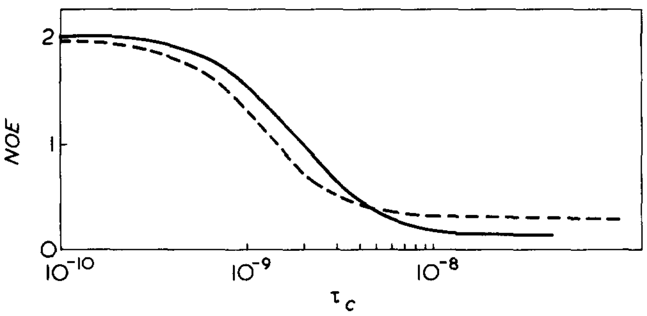


Figure 6 *NOE* as a function of correlation time. ———, According to refs 21 and 22; — — — —, according to ref 20, p = 100

helices. In fact, for a polymer with a segmented structure of this type many degrees of freedom in the segmental motions are likely.

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