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Notes

^{13}C NMR Spectroscopic Study of the Microstructure of Poly(3-methyltetrahydrofuran)

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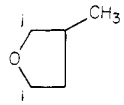
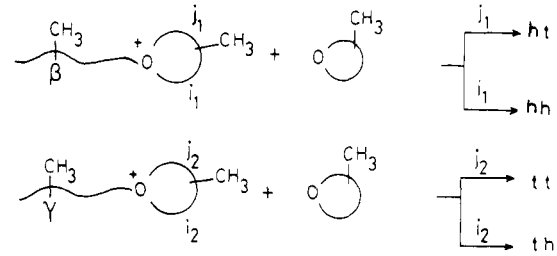
From thermodynamic considerations it was concluded in the past that substituted tetrahydrofuran could not polymerize due to the fact that substitution of hydrogen atoms by methyl groups in heterocyclic compounds render the free energy of polymerization positive.[1] However, Chiang and Rhodes[2] accomplished the polymerization of 3-methyltetrahydrofuran at several temperatures. The polymers obtained were of low molecular weight because transfer reactions probably took place during the polymerization process. More recently, the kinetic and thermodynamic aspects of the cationic polymerization of 3-methyltetrahydrofuran were studied at temperatures lying in the range 0 to −12 °C using an initiator with a very stable counterion: acetyl hexafluoroantimonate.[3] With this catalyst, "living polymers" were obtained. On the other hand, it was found that the ceiling temperature of 3-methyltetrahydrofuran is 4 ± 1 °C, a value significantly lower than that reported for the polymerization of tetrahydrofuran (THF), which is in the vicinity of 86 °C.[4] The enthalpy and entropy of polymerization also were calculated and their values were −5.4 kcal mol^{-1} and −19.5 cal K^{-1} mol^{-1}, respectively.[3] The former value is similar to that obtained for THF, but the latter is lower than that found for the entropy of bulk polymerization of THF (−12.5 cal K^{-1} mol^{-1})[4-9].

3-Methyltetrahydrofuran presents two different adjacent carbon atoms to the monomeric oxygen atom; as a consequence, the ring opening of the heterocycle can occur at i or j bonds in the monomer ring



and therefore different structures may be formed. In this work we report preliminary results on the microstructure of poly(3-methyltetrahydrofuran), as determined by ^{13}C NMR spectroscopy.

Scheme I



Experimental Part

Materials. The monomer (3-methyltetrahydrofuran) (Fluka), acetyl chloride (Merck), and silver hexafluoroantimonate (Ventron) were purified as previously described.[3] The initiator acetyl hexafluoroantimonate was prepared according to procedures described elsewhere.[3]

Polymerization. Bulk polymerizations of the monomer were carried out under high vacuum at −4 °C (polymer A) and −25 °C (polymer B) using initiator concentrations of 2.6 × 10^{-2} and 0.85 × 10^{-2} mol L^{-1}, respectively. The polymerization reactions were terminated with an aqueous solution of sodium carbonate, and the polymers were extracted with benzene, precipitated with methanol, and, finally, freeze-dried from benzene solutions at room temperature. The values of the number-average molecular weight of the polymers, determined at 37 °C in chloroform solutions with a Knauer vapor pressure osmometer, are shown in Table II.

^{13}C NMR Analysis. The ^{13}C NMR spectra of the polymers were recorded at 26 °C with a Bruker HX-90E Fourier transform spectrometer at 22.63 MHz, using deuterated chloroform as solvent and tetramethylsilane as internal reference. Quantitative spectra were obtained by using long pulse delay times (>10 s) and inverse gated decoupling techniques in order to eliminate the nuclear Overhauser enhancement.

Results and Discussion

In a recent work[3] it was reported that the mechanism of the cationic polymerization of 3-methyltetrahydrofuran is similar to that of tetrahydrofuran. The polymerization reaction is produced by nucleophilic attack of the monomer oxygen atom on the carbon atom in α position relative to the oxonium ions, according to the mechanism shown in Scheme I, where hh, ht, th, and tt refer, respectively, to head-to-head, head-to-tail, tail-to-head, and tail-to-tail structures. As in the case of poly(2-methyloxacyclobutane), the fraction of the different structures along the chains can be quantitatively estimated by ^{13}C NMR spectroscopy.[10,11] The ^{13}C NMR spectrum of the polymer, shown in Figure

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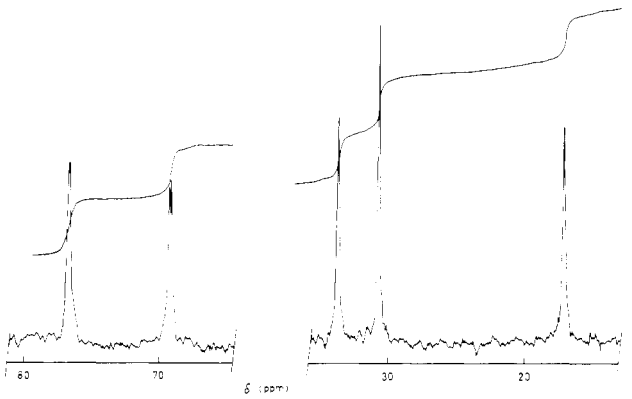

Figure 1. ^{13}C NMR spectrum of poly(3-methyltetrahydrofuran) (polymer B) at 22.63 MHz (2000 scans).

Chart I

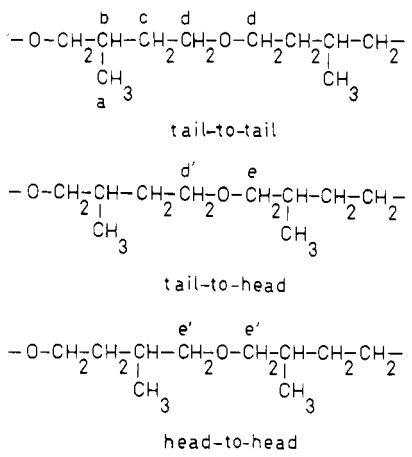

Table I
Chemical Shifts (ppm) for the Different Carbon Atoms Indicated in Chart I

carbon	chem shift, calcd	chem shift, exptl
a	16.1	17.2_4
b	36.4	33.6_5
c	34.2	30.7_6
d	67.4	69.0_4
d′	67.7	69.2_1
e	76.8	76.4_2
e′	77.1	76.5_3

1, presents seven resonance signals corresponding to the same number of different carbons indicated in Chart I, and it clearly corresponds to structures which differ from those that could be formed by simple repetition of head-to-tail units. Since the effect of neighboring carbons diminishes with distance so that the ϵ effect is very small, only the signals corresponding to the oxymethylenic carbons appear split.

As can be seen in Table I, the differences between the resonances of the split signals, of the oxymethylenic carbons are only 0.11–0.17 ppm, in fair agreement with the values calculated[12] by using the contributions from groups in α, β, γ, and δ position relative to the observed carbon. The signals at 17.24, 33.65, and 30.76 ppm are assigned to the resonance of the methyl, methinic, and methylenic carbons not adjacent to the heteroatom, respectively. The doublet signals at 69.04 and 69.21 ppm are attributed, respectively, to carbons d and d′, corresponding to tail-to-tail and tail-to-head (or head-to-tail) dyads. In the same way, the peaks at 76.42 and 76.53 ppm are assigned to methylenic carbons e and e′ of the structure tail-to-head

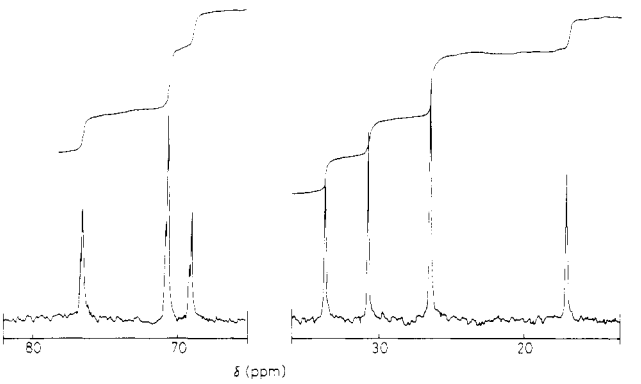

Figure 2. ^{13}C NMR spectrum of a tetrahydrofuran/3-methyltetrahydrofuran copolymer.

Table II

polymer	T, °C	M_n	P(ii) + P(jj)	P(ij) = P(ji)	P(i)	P(j)
A	−4	5000	0.60	0.20	0.73	0.27
B	−25	17000	0.58	0.21	0.70	0.30

(or head-to-tail) and head-to-head, respectively. It can be argued that the splitting of the signals around 69.1 and 76.5 ppm may also be due to stereoisomerism. However, preliminary spectrometric determinations carried out on tetrahydrofuran/3-methyltetrahydrofuran copolymers seem to rule out this possibility.[13] Actually, the ^{13}C NMR spectrum corresponding to a copolymer in which the molar fraction of tetrahydrofuran is 0.50 (see Figure 2) shows[13] that, besides the resonance signals given above, three additional signals appear centered at 26.51 ppm, corresponding to the central methylenic groups of the tetrahydrofuran unit, and at 70.47 and 70.65 ppm, corresponding to the oxymethylenic groups of the same unit. The presence of these two last signals may be attributed to the different chemical environment of the dyads $OCH_2CH_2CH_2CH_2OCH_2CH(CH_3)CH_2CH_2$ and $OCH_2CH_2CH_2CH_2OCH_2CH_2CH_2CH_2$, which appear along the copolymeric chain as a consequence of the ring opening of 3-methyltetrahydrofuran through bonds of type i. Since the difference between the chemical shifts of the two signals is 0.18 ppm, a value very near to that for the analogous oxymethylenic group in poly(3-methyltetrahydrofuran), it is reasonable to assume that the split signals observed in poly(3-methyltetrahydrofuran) are due to the different dyads that would appear in the chains as a consequence of the ring opening of 3-methyltetrahydrofuran through bonds of type i and j.

It has been pointed out recently that only dyad sensitivity should be expected for polymers similar to poly(3-methyltetrahydrofuran), with five skeletal bonds in the structural unit.[14] The values of the different dyads were calculated from the areas of the resonance peaks corresponding to the doublets, and the results obtained are shown in Table II. These data were used to determine the global microstructure of poly(3-methyltetrahydrofuran). In order to carry out this analysis it was assumed that the position of the methinic carbon with respect to the oxonium ion, indicated by β or γ in the reaction mechanism given in Scheme I, does not affect the scission of the monomer ring through bonds of type i and j. With this assumption in mind, we may write the probability of ring opening through bonds of type i as

$$P(\mathrm{i}) = k_\mathrm{i}/(k_\mathrm{i} + k_\mathrm{j})$$

where k_i and k_j are the ring-opening rate constants through

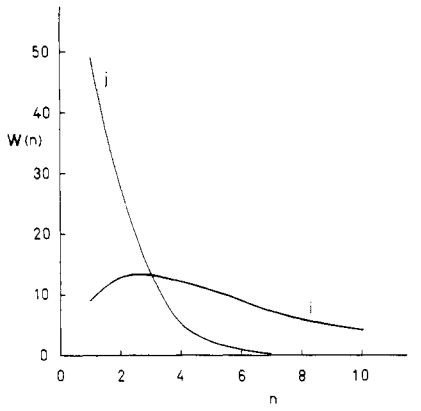

Figure 3. Weight fraction % sequences of length n for the structures i and j of Chart I.

bonds of type i and j, respectively. The probability of occurrence of a dyad will be determined by the equations

$$P(ii) = P(i)P(i) = P(i)^2$$

$$P(ij) = P(i)P(j) = P(ji)$$

The resonance data of Figure 1 in conjunction with these equations were used to estimate the values of $P(i)$ and $P(j)$, shown in Table II, where bond scission through bonds of type i was arbitrarily considered more probable than through bonds of type j. These data suggest the microstructure of poly(3-methyltetrahydrofuran). For illustrative purposes, the weight fractions of sequences of length n for structures of type i and j in the polymer prepared at lower temperature (polymer B) are shown in Figure 3. It can be observed that 49% of the structures of type j are isolated whereas the sequences of type i present a wide distribution with a maximum for $n = 3$.

The similarity of values of $P(i)$ for the two polymers prepared at −4 and −25 °C should not lead to the conclusion that the k_i/k_j ratio is independent of the reaction temperature. In fact, owing to the low ceiling temperature of poly(3-methyltetrahydrofuran) ($T_c = 4$ °C), the polymerization can only be carried out over a very limited interval of temperature, which precludes reaching any reliable conclusion regarding the influence of temperature on the structure of the polymer, although it can be expected that more regular polymers form at lower temperatures. The data at hand suggest that the ring opening occurs preferably through one of the bonds (70% of the total scission), but they do not allow one to establish which carbon is preferentially attacked over the interval of temperature that we have studied. It can be argued that the steric hindrance of the methinic carbon presumably influences a preferential attack at the methylenic carbon, adjacent to the oxonium ion, situated further away from the methinic carbon, in a way similar to that which occurs in poly(propylene oxide), where the cationic ring opening takes place between oxygen and the methinic carbon to the extent of 30%.[15] This conclusion is highly speculative since the steric factor is not predominant in all the cases. For example, in the cationic polymerization of bicyclic ethers such as 2-oxabicyclo[2.2.2]octane,[16] the ring opening occurs predominantly by attack on the tertiary carbon adjacent to the oxonium ion. However, for *trans*-7-oxabicyclo[4.3.0]none[17] and *trans*-2-oxabicyclo[3.3.0]octane,[18] where severe steric hindrances are present, the attack of the monomer takes place preferably at the methylenic carbon.

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Registry No. 3-Methyltetrahydrofuran, 13423-15-9; poly(3-methyltetrahydrofuran), 25607-91-4.

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Vacuum-Ultraviolet Circular Dichroism of Poly(γ-ethyl *N*-methyl-L-glutamate)

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We report here the vacuum-ultraviolet circular dichroism (VUCD) of poly(γ-ethyl *N*-methyl-L-glutamate).

The polymer was synthesized as previously described by Cosani et al.[1,2] Purity was established by amino acid analysis and infrared spectroscopy, and the degree of polymerization was determined to be greater than 500. The polymer was dissolved in 2,2,2-trifluoroethanol (TFE) (Gold Label, Aldrich Chemical Co.) to form 5.2 mg/mL solutions. Films were cast by applying 0.03 mL of solution to a circular CaF_2 disk 1 mm thick and 1.9 cm in diameter and drying under nitrogen. The VUCD spectrometer has been described previously.[3,4] Spectra were insensitive to repeated 90° rotations of the disk in the light path, indicating an absence of linear birefringence.

The film spectrum is shown in Figure 1. The negative and positive bands at 229 and 200 nm, respectively, are 1–4 nm red shifted relative to the CD spectra of TFE solutions.[2] We also find a positive band at 175 nm not previously reported. We observed apparent negative ellipticity in the region 145–160 nm, but the signal–noise ratio was unacceptably small (<4) so those data are not included in Figure 1. In our previous VUCD studies of peptide films[3,4] we were able to obtain satisfactory spectra

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