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POLYMERIZATION OF 2,3-DIHYDROFURAN DERIVATIVES. VI.
ISOTACTIC POLYMER OF 2-METHYLENETETRAHYDROFURAN

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The microfine structure of poly(2-methylenetetrahydrofuran) obtained by various cationic catalysts was studied by NMR spectroscopy. Only a quartet was observed for the backbone methylene protons of the ethyl methyl ketone-insoluble polymer, which was found to be crystalline by X-ray analysis. The polymer is suggested to be primarily isotactic in nature.

It is well known that exo methylene cyclic compounds can not be polymerized through the opening of the double bond in the exo position to high molecular weight polymers. Methylene cycloalkanes, for example, homopolymerize reluctantly by cationic catalysts.[1] Recently, a new type of the ring-opening polymerization of methylene cyclobutane has been reported.[2,3] The predominant structures were of the cyclised or uncyclised polyene type. Bicyclic compounds with the exo methylene group, such as β-pinene[1] and methylenenorbornene[4], can not also polymerize without accompanying rearrangements of bonds, and give polymers consisting of unique types of reccuring units. Hachihama et al.[5] first reported on the polymerization of 2-methylenetetrahydrofuran(THMF) with various cationic catalysts, and suggested from IR analysis that the polymerization occurred by the opening of the exo double bond. Therefore, THMF is the only exo methylene cyclic compound which converts through the opening of the carbon-carbon double bond in the exo position to high molecular weight polymers. However, there have been only one investigation on the polymerization of THMF and little attention has been paid to the microstructure of the polymer obtained by the cationic polymerization of THMF.

The monomer was prepared from tetrahydrofurfuryl chloride by dehydrochlorination with potassium hydroxide according to the Ansell's method.[6] Polymerizations were carried out as follows: Freshly distilled monomer and solvent were introduced into an ampoule equipped with a three-way stopcock under dry nitrogen atomosphere. After the ampoule reached thermal equilibrium, appropriate amounts of catalyst were introduced into the system by a syringe. The crude polymer was collected by precipitation in excess methanol and was purified by repeated dissolution and precipitation in chloroform and methanol, respectively. The purified polymer was then fractionated by extraction with boiling ethyl methyl ketone(MEK) into soluble and insoluble parts.

The NMR spectra of the polymers were obtained at 160 °C with JNM-PS-100 spectrometer of JEOL at 100 MHz on a 5-10 w/v % polymer solution in o-dichlorobenzene. Tetramethylsilane was used as an internal standard.

In Table 1 are shown the results of the polymerization of THMF by various cationic catalysts.

Table 1. Cationic Polymerization of 2-Methylenetetrahydrofuran at -78 °C

Catalyst		Solvent	Time	Conv.	Polymer				
					MEK-insol. fraction			MEK-sol. fraction	
	(mmol)	(20 ml)	(hr)	(wt %)	wt %	$\eta_{sp/c}$ [a]	mp(°C)	$\eta_{sp/c}$ [a]	mp(°C)
$SnCl_4$,	0.2	Toluene	20	80.2	71.6	0.27	124	0.08	93
$TiCl_4$,	0.2	Toluene	20	70.2	92.4	----	113	0.05	--
$HClO_4$,	1.0	Toluene	20	93.4	80.1	0.11	124	0.03	84
$AlEt_2Cl$,	0.1	n-Hexane	22	84.3	82.1	0.42	143	----	--
$AlEt_2Cl$,	0.1	Toluene	22	87.3	84.1	0.31	141	----	--
$AlEt_3/TiCl_4$,	0.1/0.1	Toluene	20	80.3	72.7	0.33	136	0.08	96
$AlEt_3/TiCl_4$,	0.1/0.1	n-Hexane	20	78.8	90.2	0.38	143	----	--

a) Solution Viscosity, determined in chloroform solution(0.5 g/dl) at 30 °C.

PTHMF obtained with different cationic catalysts gave essentially identical IR and NMR spectra. Besides, both soluble and insoluble fractions of PTHMF fractionated with boiling MEK showed no differences in their IR and NMR spectra. The differences in solubility of these two fractions are probably attributed to differences in molecular weight rater than stereoregularity. A strong absorption at 1360 cm^{-1} which corresponds to CH_3 asymmetric bending and which is characteristic of poly(5-methyl-2,3-dihydrofuran)[7] was not found in PTHMF obtained. This observation consists with the results from NMR analysis. Therefore, it is indicated that THMF does not undergo the isomerization polymerization under the conditions employed, although it is known to isomerize into the endo isomer, i.e., 5-methyl-2,3-dihydrofuran, in the presence of trace amounts of acid.[8]

The MEK-soluble PTHMF is stable in o-dichlorobenzene on aging at room temperature. At elevated temperatures it becomes unstable and decomposes gradually, whereas the MEK-insoluble PTHMF is stable in the medium even at an elevated temperature at 160 °C. In Figure 1 is shown typical NMR spectrum for 5 % solution of the MEK-insoluble PTHMF prepared with $Al(C_2H_5)_2Cl$ catalyst in toluene at -78 °C. In the spectrum there are six well-resolved peaks in two distinct groups. The signal at 6.18 τ is reasonably attributed to the α'-methylene protons adjacent to oxygen atom in the tetrahydrofuran ring, since the peaks of

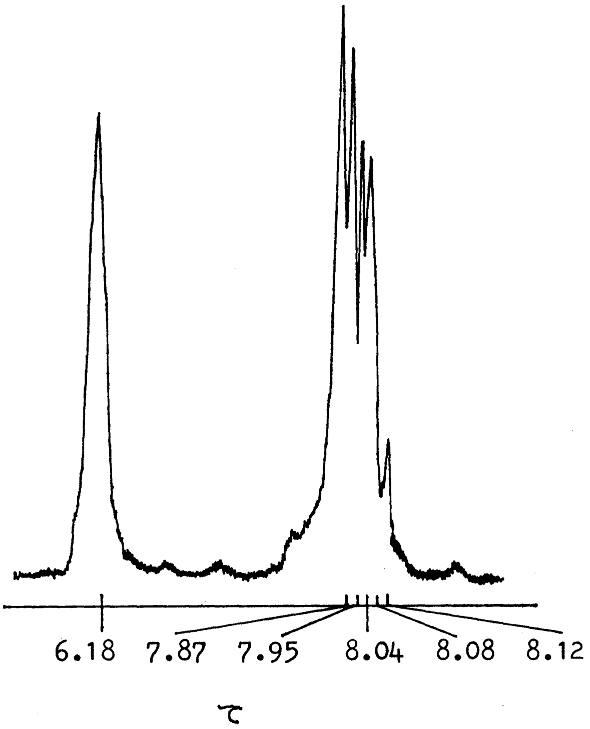


Figure 1. NMR spectrum of MEK-insoluble PTHMF obtained by $Al(C_2H_5)_2Cl$ catalyst in toluene at -78 °C(measured in o-dichlorobenzene solution at 160 °C).

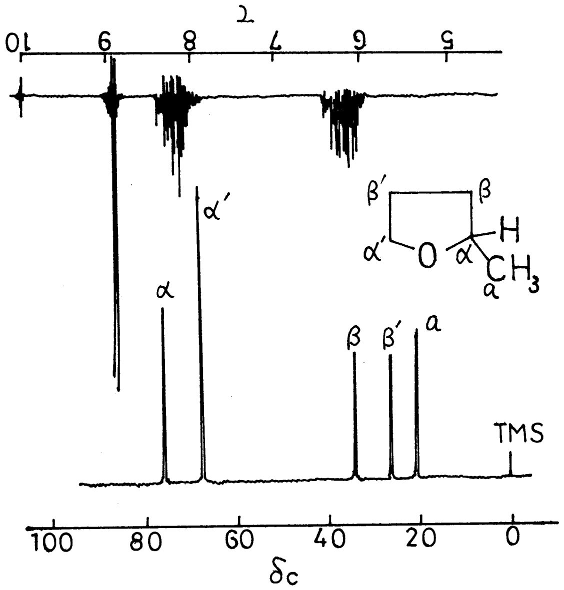


Figure 2. ^{1}H- and ^{13}C-NMR spectra of 2-methyltetrahydrofuran measured in CDCl$_3$ at 25 °C and in neat liquid at 22 °C, respectively.

O-methylene protons of poly(2,3-dihydrofuran) and poly(5-methyl-2,3-dihydrofuran)[7] appear at similar regions(6.24 and 6.25 τ, respectively). The assignments of the peaks at 7.87 and 7.95 τ were determined from a comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data with 2-methyltetrahydrofuran(MTHF), which might be regarded as the simple monomeric units of PTHMF. In the ^{1}H-NMR spectrum of MTHF(Figure 2), both the complex multiplets of β- and β′-methylene protons overlap each other, and hence one can be unequivacally indistinguishable from the other. On the other hand, in the ^{13}C-NMR spectrum of the model compound, the resonances of the two methylene carbons fall into two distinct signals which are assigned as indicated in Figure 2. Therefore, the β-methylene protons are expected to resonate at a lower field than the β′-methylene protons. For this reason, the peaks at 7.87 and 7.95 τ should be assigned to the resonances of β- and β′-methylene protons, respectively. The spectra of the methylene protons attached to the carbon atom constituting the skeletal bonds of the polymer chain appeared at around 8.06 τ. It was found in PTHMF that the backbone methylene protons spectra were sensitive to the configuration of the polymer and the resolution of the spectra depended on the kind of solvent media for NMR measurements. When the spectra were measured in CDCl$_3$, the resonances of the backbone methylene protons are rather broadened and overlapped with those of the β- and β′-ring methylene protons. In chlorobenzene solution the resonances of the backbone methylene protons still remained a singlet, but those of the two methylene protons were split into two components. As shown in Figures 1 and 3, in o-dichlorobenzene the backbone methylene protons are considered to consist of an AB quartet, wherein the upper three signals are observed at 8.04, 8.08, and 8.12 τ, but the lowest field perhaps overlaps with the signals of ring methylene protons. We observed only a quartet signal for the methylene protons of the MEK-insoluble fractions of polymers obtained regardless of polymerization conditions employed. This observation indicates that these polymers acquire primarily one stereochemical configuration.

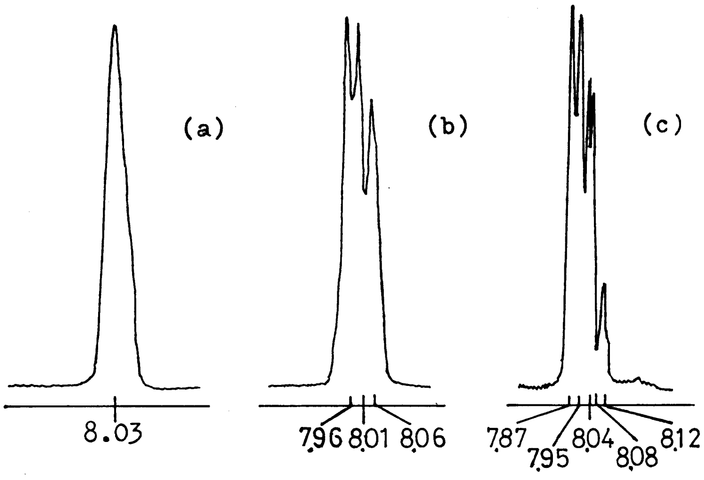
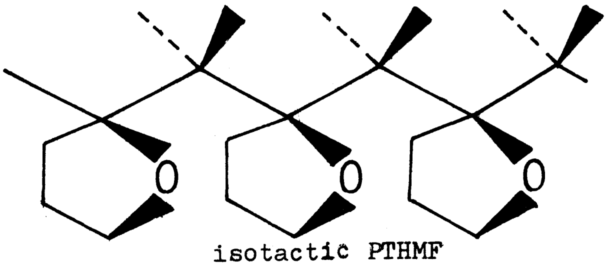
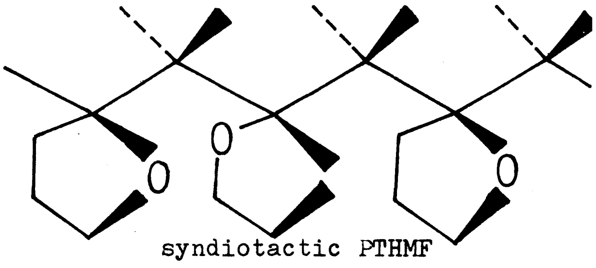


Figure 3. NMR spectra of the upper field part of PTHMF observed in (a) CDCl$_3$ at 50° (b) chlorobenzene at 120° (c) o-dichlorobenzene at 160 °C.



isotactic PTHMF



syndiotactic PTHMF

In the isotactic form, the methylene protons become nonequivalent and should yield an AB quartet. In the syndiotactic structure, the methylene protons become equivalent and yield a singlet. We observed only a quartet for the backbone methylene protons of PTHMF, which supports the hypothesis that the polymer is primarily isotactic. Were the quartet for the methylene protons in PTHMF to arise from an isotactic structure we would, in general, expect the polymer to be crystalline.

The X-ray pattern of the powder sample of MEK-insoluble PTHMF obtained by $HClO_4$ catalyst in toluene at -78 °C is shown in Figure 4. Crystalline reflections appear at 2 θ degrees of 12 and 18.5°. It is interesting that, through cationic polymerization, typical α,α'-disubstituted vinyl monomers, such as poly(α-methylstyrene)[9] and poly(α-methylvinyl methyl ether)[10] which have similar structure to PTHMF form predominantly syndiotactic polymers, while THMF gives primarily isotactic polymers. We think that this difference in main-chain configurations arises probably as a result of steric hindrence of five-membered ring directly attached to the α-carbon atom constituting the skeletal bonds of the polymer chain, which governs the stereochemical configuration of the main chain.

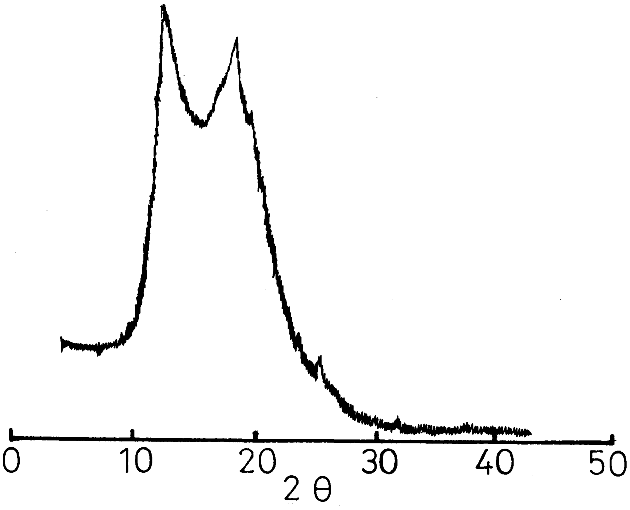


Figure 4. X-ray diffraction pattern of MEK-insoluble PTHMF obtained by $HClO_4$ catalyst in toluene at -78°C.

Further studies are needed to clarify the mechanism and presently in progress.

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