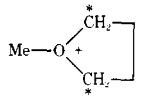
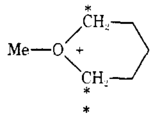
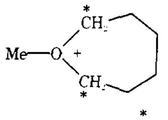
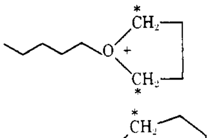
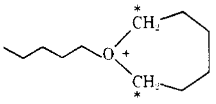
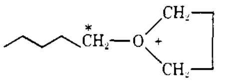
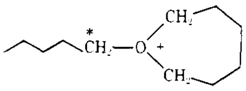
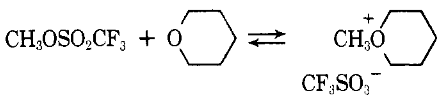
Table II
^{13}C NMR Chemical Shifts of the "Oxonium" α-Methylene Carbons

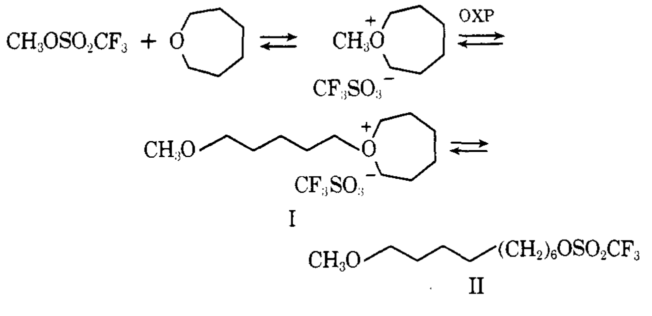
Assignments[a]	^{13}C chemical shift[b]
	90.1
	92.1
	93.5
	87.5
	90.5
	89.6
	92.8

[a] The carbon atoms of interest are marked by an asterisk. [b] Chemical shifts are given in ppm with respect to internal TMS.

ppm, which is due to the α-methylene carbons of the methyl tetrahydropyranylium ring.



Finally, the top scan (Figure 2C) shows the oxonium region in the spectrum of a polymerization mixture containing the seven-membered ring oxepane (OXP).[11] The largest signal (at 93.5 ppm) is due to the α-methylene carbons of the initially formed methyl oxonium ring, which was present in higher concentration in this case because of a high initiator concentration. No macroester signal is found under these conditions. In the presence of higher monomer–initiator ratios (oxepane–$CH_3OSO_2CF_3$ = 4:1, in nitromethane, 70 wt. %) the methyl oxonium signal at 93.5 ppm was absent after 60 min, and the molar ratio of macroion I to macroester II (at 79.5 ppm) was found to be 3:7.



The chemical shifts of the oxonium methylene carbons of Figure 2 are listed in Table II.

The pronounced ring-size effect in these systems is evident, resulting in a downfield shift of about 1.7 ppm per ring expansion by one methylene group, from the five-membered to the seven-membered ring. A corresponding downfield shift of the open-chain and ring methylene carbons in the α position to the propagating chain end of the larger ring is also observed. Carbon-13 NMR spectroscopy may therefore allow quantitative measurement of the different propagating chain ends in ionic copolymerization of cyclic ethers.

Similar chemical shifts have been found in polymerizations initiated by ethyl esters ($EtOSO_2F$ or $EtOSO_2CF_3$), or by free acid (CF_3SO_3H). The clear separation of the different oxonium ions, which in some cases cover a range of almost 10 ppm, and the sensitivity of ^{13}C measurements may permit an estimation of the so-called "dormant" oxonium ions. Such open-chain oxonium ions have been postulated to be present in these polymerization systems.[12] Carbon-13 NMR spectroscopy therefore appears to be a very powerful tool for studying the detailed mechanisms in the cationic polymerization of cyclic ethers.

Acknowledgment. We wish to thank Dr. D. W. Ovenall for helpful discussions and for the spectra of model compounds.

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^{13}C-{^{1}H} Nuclear Magnetic Resonance Study of Poly(isopropylthiiranes) Prepared from Racemic and Optically Active Monomers

Polymerization of monosubstituted thiirane has been extensively studied during recent years and special attention has been devoted to obtaining stereoregular polymers.[1] Use of optically active pure enantiomers allowed the preparation of corresponding optically active polymers and gave information on the ring-opening mechanism and the structure of the polymers. Thus, *S*(−)-methylthiirane[2] and *S*(−)-*tert*-butylthiirane[3] were prepared and polymerized with various initiators. Stereoregularity was studied by ^{13}C-{^{1}H} NMR on undeuterated polymers[4–7] and by ^{1}H NMR on deuterated polymers.[5,8,9]

In the case of methylthiirane it was shown that the tertiary carbon of the chain (A) was sensitive only to dyad ef-

Table I
Polymerization of Racemic and Levorotatory Isopropylthiiranes[a]

	Monomer α^{25}D (neat, dm)	Initiator system	Polymer $[\alpha]^{25}$D[c]
I	Rac	Sodium	
II	−11°	Sodium	−47
III	−11°	Cadmium tartrate	−45
IV	−22.9°	Sodium	−111
V	−58.8°	Sodium	−282
VI	−58.8°	$ZnEt_2$–H_2O (1:1)	−213
VII	Rac	$ZnEt_2$–(−)3,3-dimethyl-1,2-butanediol (1:1)	+93[b]

[a] All polymerizations were carried out at room temperature and in bulk, except VI which was performed in toluene solution. [b] Polymerization was stopped at 33% conversion; residual monomer α^{25}D −11° (neat, dm). [c] $CHCl_3$, c = 0.4 g/100 ml.

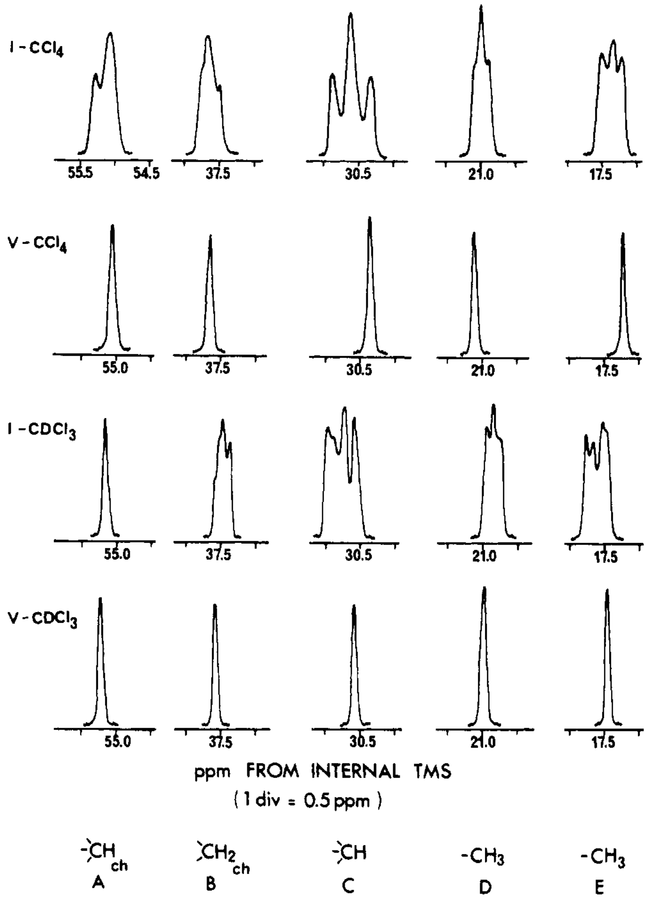
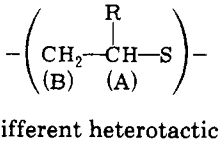


Figure 1. ^{13}C-{^{1}H} NMR spectra (25.15 MHz) of heterotactic and isotactic poly(isopropylthiiranes) in CCl_4-C_6D_6 and $CDCl_3$ solutions at room temperature. Samples I and V, see Table I.



$$-\left(\underset{(B)}{CH_2}-\underset{(A)}{\overset{R}{CH}}-S\right)-$$

fects,[4,5] as the two different heterotactic triads, *rm* and *mr*, overlap respectively the isotactic *mm* and syndiotactic *rr* triads.[6] This means that (A) is affected by the configuration of only one of the two vicinal asymmetric centers (the right one, in the case of the unit shown above). No stereosensitivity at all was found for the methylenic carbon (B) and for the side-chain methyl carbon. On the other hand, the methine (A) and methylene (B) carbons of poly(*tert*-butylthiirane) show triad effects.[5] It was thus interesting to study the behavior of poly(isopropylthiirane) which bears a side group of bulkiness intermediate between methyl and *tert*-butyl.

Experimental Section

Racemic poly(isopropylthiirane) was recently prepared.[10] It was shown that the polymer obtained by anionic polymerization was the only one soluble in common solvents. Other polymers prepared with stereospecific initiators were insoluble.

S(−)-Isopropylthiirane was prepared[12] in the usual way, starting from the corresponding optically active 1,2-diol.[2,3,11] The monomer obtained shows an optical activity α^{25}D −58.8° (neat, dm).

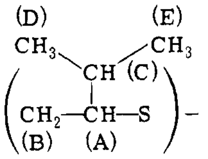
Polymerizations with different initiator systems (Table I) were carried out using a high-vacuum technique.[2,3,10] Details concerning these polymerizations will be reported later.[12] Diethylzinc-(−)3,3-dimethyl-1,2-butanediol (1:1) system was used in the stereoelective polymerization as described previously.[13,14] Results of polymerizations are given in Table I. All the polymers were soluble in C_6H_6, CCl_4, and $CHCl_3$, except polymer VII which was soluble only in $CHCl_3$ after heating.

^{13}C-{^{1}H} NMR spectra of these polymers were observed in CCl_4-C_6D_6 and $CDCl_3$ solutions on Varian XL-100 and JEOL PS-100 FT spectrometers. Assignments of the peaks to specific carbons were made by using partial C–H decoupling.

Results and Discussion

Typical spectra of heterotactic and isotactic polymers are shown in Figure 1 and the chemical shifts and basic assignments are given in Table II.

Five resonance patterns are observed, the two upfield ones (D) and (E) corresponding to the two magnetically nonequivalent methyl groups. At high temperature in *o*-dichlorobenzene, peaks (D) and (E) move toward each other, but separation still remains significant (δ = 3.5 ppm at 25°C and 2.5 ppm at 125°C). This indicates a preferred conformation of the isopropyl group toward the nearby asymmetric center and this observation is in agreement with the existence of two nonequivalent methyl groups in the monomer isopropylthiirane (21.56 and 21.35 ppm from TMS in *o*-dichlorobenzene at room temperature). Analogous behavior was also observed by ^{1}H NMR by Naegele on poly(isopropyloxiirane)[15] and by Roberts et al.[16] in the case of isopropylalkyl carbinols $(CH_3)_2CH$-CH(OH)R, where the degree of nonequivalence of methyl groups increases rapidly with increasing bulkiness of the alkyl substituent on the vicinal asymmetric center.



It appears that all carbons of the monomer unit are stereosensitive but this stereosensitivity depends on the solvent used. Triad effects are observed for side group carbons (C), (D), and (E) of the heterotactic polymers. In CCl_4-C_6D_6 solutions, triplets are obtained, particularly well resolved for the (C) methine carbon, whereas $CDCl_3$ solutions exhibit four-peak patterns for (C) methine and (E) methyl carbons (Figure 1). This last observation is consistent with different shifts for the two heterotactic triads h_i and h_s (*mr* and *rm*), but overlapping of the peaks does not allow quantitative resolution.

Chain methine (A) and methylene (B) carbons are much less stereosensitive in both solvents. In CCl_4-C_6D_6 solution, two peaks are observed for (A), but we are as yet unable to specify if they result from triad effects, or from dyad effects as in polypropylene sulfide. The first interpretation

Table II. Chemical Shifts (ppm from TMS) and Stereosensitivity of Chain and Side-Group Carbons for Heterotactic and Isotactic Poly(isopropylthiiranes)

Polymer structure	Solvent	⩾CH (A) chain			>CH$_2$ (B)			⩾CH (C) side group			–CH$_3$ (D)			–CH$_3$ (E)		
								s	*h*	*i*	*i*	*h*	*s*	*s*	*h*	*i*
Isotactic (samples	CCl$_4$–C$_6$D$_6$			55.06	37.62					30.34	21.11					17.22
III,V,VI,VII)	CDCl$_3$			55.21	37.58					30.58	20.96					17.46
Heterotactic (samples	CCl$_4$–C$_6$D$_6$	55.27		55.07	37.73(sh)	37.66	37.48(sh)	30.86	30.59	30.34	21.09(sh)	20.98	20.86(sh)	17.62(sh)	17.34	17.22(sh)
I,II,IV)	CDCl$_3$		55.17		37.53(sh)	37.48	37.38(sh)	30.96	30.84,30.72	30.57	20.94(sh)	20.85	20.72(sh)	17.76	17.67,17.53	17.46

Table III. Calculated and Experimental Amounts of Triads for Optically Active Poly(isopropylthiiranes)

Polymer	Monomer α^{25}D (neat, dm)	R–S	*r*	*i*		($h_i + h_s$)		*s*	
				Calcd	Exptl[a]	Calcd	Exptl[a]	Calcd	Exptl[a]
I	0	50:50	1	0.25	0.25	0.50	0.50	0.25	0.25
II	–11	41.5:58.5	1.41	0.28	0.27	0.48	0.50	0.24	0.23
IV	–22.9	32.4:67.6	2.09	0.34	0.36 (0.33)[b]	0.44	0.41 (0.45)[b]	0.22	0.23 (0.22)[b]

[a] Experimental determinations were done on (C) methine carbon resonance pattern, from CCl$_4$–C$_6$D$_6$ solutions. Accuracy = ±0.03. [b] Values in parentheses correspond to determinations on the same carbon but in CDCl$_3$ solution.

seems more reasonable; as for samples I and II the large difference in peak intensities fits with a (s) and ($h_s + h_i + i$) assignment. No stereosensitivity at all was found for this carbon in CDCl$_3$ solution. As to the methylenic (B) carbon, the resonance pattern is so poorly resolved that any tentative assignment would be doubtful.

Positions of isotactic peaks in triads were determined by using polymers III and VI prepared with convenient stereospecific catalysts known to give highly isotactic polythiiranes.[17,18] It is interesting to note that polymer VII, obtained using a stereoelective initiator, is also highly isotactic, as in the case of poly(*tert*-butylthiirane).[14] The isotactic peak observed in the different heterotactic samples is upfield for carbons (C) and (E) and downfield for (D). Thus resonance lines of (D) and (E) methyl carbons are closest, and the degree of magnetic nonequivalence less, in syndiotactic polymers than in isotactic ones. Careful study of this point should probably give information on the allowed chain conformations.

The distribution of different triads according to the enantiomeric composition of the polymers was examined. In a previous work on methylthiirane,[9] it was demonstrated that the triad distribution could be simply calculated from enantiomeric composition in a polymer obtained by a nonspecific initiation, e.g., a simple anionic noncoordinated polymerization. If the starting monomer mixture has an enantiomeric composition R–S = 1/r then the relative amounts of triads in polymer are given by

$$i = \frac{r^3 + 1}{(r + 1)^3}$$

and

$$s = h_s = h_i = \frac{r(r + 1)}{(r + 1)^3}$$

Polymer V prepared from a monomer of optical activity α^{25}D –58.8° (neat, dm) shows by ^{13}C NMR a tacticity at least as high as 90%, which means that the optically pure monomer should not have an optical activity higher than –65° (neat, dm). Using this value the enantiomeric distribution and then the relative amount of i, s, and h triads in the heterotactic polymers I, II, and IV were determined and compared to the values obtained by resolution of the overlapping peaks of the (C) methine resonance. As shown in Table III, the NMR experimental values are in good agreement with the calculated ones.

Further work on these problems is in progress and will be reported later.

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CORRECTION

"Electron-Deficient Trisubstituted Olefins", by H. K. Hall, Jr., and Robert C. Daly, Volume 8, Number 1, January–February 1975, page 22.

On page 29, right-hand column, in the paragraph headed **Trimethyl 1,1,2-Ethanetricarboxylate,** line 10, add "... overnight at room temperature. Methanol was removed by rotary evaporation."