Structure of Cationic Propene, 1-Butene, and *cis*-2-Butene Polymers. Mechanism of the Polymerization

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ABSTRACT: Propene, 1-butene, and *cis*-2-butene polymers prepared with cationic initiators in the 12–22 °C temperature range were analyzed for their olefin and backbone structure. Only internal (disubstituted and trisubstituted) olefins were detected by IR and ^{1}H NMR spectroscopy; they were quantitatively determined. The total olefin content was measured by hydrogenation. In propene and 1-butene polymers, the presence of tetrasubstituted olefins was inferred from olefin balance. In these polymers, the unsaturation was less than theoretical and decreased with the progress of polymerization, presumably because intramolecular alkylation of a tertiary carbon atom by the polymer double bond is a side reaction. Many structural fragments were identified by IR, ^{13}C NMR, and ^{1}H NMR spectroscopy, which, when pieced into a polymer skeleton, can be accounted for by isomerization polymerization involving intramolecular 1,2-hydride shifts in the propagation steps. "Side reactions" other than hydride shifts may also play some role in the formation of the very irregular polymer skeleton. In the case of propene polymerization, the kinetic results could also be explained by a rate-controlling initiation step instead of a slow, rate-controlling propagation as proposed in the literature. At a given polymerization temperature, the polypropene molecular weight was found to be independent of the monomer concentration and many other variables, including the initiator concentration. It is suggested that the various "side reactions" control the polymer molecular weight.

The various aspects of cationic polymerization of propene, 1-butene, and *cis*-2-butene monomers have been studied by many authors.[1] A very complex chemistry is associated with these polymerizations,[1] the details of which are not well understood. Much of our knowledge is derived from the publications of earlier authors who had to conduct their studies without the convenience of a modern laboratory well equipped for the ease of monomer handling, polymerization control, and monomer and product analysis. With the dramatic technical and analytical developments of the last 2 decades, the contemporary researcher should be in a better position to gain a better understanding of the chemistry involved.

Previously we showed how IR and ^{1}H NMR spectroscopy can be used to identify and determine the olefin types in low-molecular-weight isobutylene polymers.[2] The results revealed valuable information about the olefin-forming termination step. To explain the formation of some olefin types, skeletal rearrangements and even tail-to-tail monomer coupling had to be postulated. We found that the type of initiator as well as the experimental conditions markedly influence the termination mechanism and the nature of the olefin formed. Isomerization of the polymer double bond was also observed.

Our work has now been extended to illustrate how IR, ^{1}H NMR, and ^{13}C NMR spectroscopy can be applied to the structural analyses of cationic propene, 1-butene, and *cis*-2-butene polymers. Both the olefin and the backbone structure were analyzed. The olefin analyses, again, gave valuable information about the olefin-forming termination steps. The backbone analyses confirmed the basic conclusions of previous IR studies[3,4] that polypropenes and poly-1-butenes have very irregular structures with short branches but differed in the details. Finally, we have also conducted kinetic and molecular weight studies. Our results do not agree with the previously proposed[5] kinetic model of propene polymerization that postulates that the rate-controlling step is the propagation.

Experimental Section

Materials. The monomers and the propane and butane solvents were C.P. grade chemicals (min. 99% pure) from the Linde Division of Union Carbide. The butane had 0.4% 2-methylpropane impurity. The aluminum chloride had typically 99.3% $AlCl_3$ content; it was a fine powder ("Micropowder" grade) from Pearsall Chemical Co. The pentane or hexane used to transfer the aluminum chloride were a minimum of 99% pure from Phillips Petroleum Co.

Polymerizations. The polymerizations were carried out in a 0.5-gallon stirred stainless steel autoclave equipped as follows: (1) for the introduction of a measured volume of liquified feed; (2) for the introduction of the aluminum chloride as an unstable "slurry" in pentane or hexane; (3) with an internal cooling coil to give ±1 °C automatic control of the polymerization in case of moderate rates; and (4) with a bottom valve for taking liquid samples from the reactor prior to and during the polymerization for GC analyses (feed analysis and measurement of the monomer conversion) and for the determination of the molecular weight distribution. The samples taken during the polymerization were "quenched" with methanol to deactivate the initiator.

The polymerization feed was made up from the monomer and propane or butane solvent. The monomer concentration in the feeds varied between 30 and 50 mol % for propene and between 9 and 29 mol % for *cis*-2-butene, and the concentration was 25 mol % in the case of butene-1. The feed liquified under nitrogen pressure in a resevoir was passed through a drier filled with granular anhydrous calcium sulfate. Then 1.3 L of it was charged into the reactor. Its moisture content was determined by an on-line analyzer (Model 1000 aluminum oxide hygrometer from Panametrics); it was always below 1 ppm. In the case of propene polymerization, 2-chloropropane was often introduced into the feed in a 0.2 to 0.4 molar ratio to the aluminum chloride used. The temperature of the feed was adjusted to the desired polymerization temperature of 5, 12, 20, or 22 °C. The pressure was always autogenic. The feed was agitated, and a slurry of the aluminum chloride in pentane or hexane was introduced. The aluminum chloride levels were selected to give 350-to-500 olefin-to-aluminum chloride molar ratios for propene, 150 for 1-butene, and 70 to 120 for *cis*-2-butene. The rates of the polymerization were followed by withdrawing samples through the bottom valves for GC analyses. Final monomer conversions depended on the conditions. Nearly quantitative (>98%) conversions could be achieved with propene and 1-butene, within the indicated ranges of the reaction variables. However, in the case of *cis*-2-butene, the monomer conversions were only in the 68 to 92% range. When the polymerization stopped, or sometimes later, small amounts of methanol were introduced to deactivate the aluminum chloride and arrest secondary reactions.

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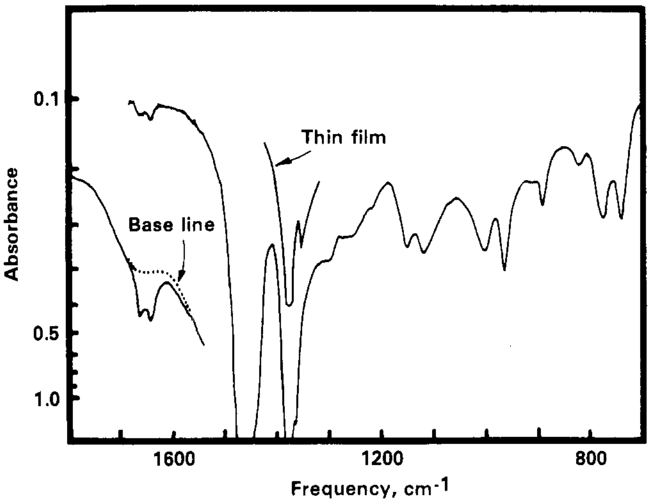


Figure 1. Partial IR spectrum of polypropene (neat, 0.1 mm and in part 0.5 mm).

Both the intermediate quenched samples and the final products were worked up the same way. The solutions were "degassed" and then heated to 100 °C at about 15 kPa. The residue was dissolved in hexane, filtered through Celite, and vacuum distilled for complete removal of the solvent.

Analytical Equipment and Procedures. The GC analyses were carried out on a Hewlett-Packard Model 5750 research chromatograph, using standard techniques.[6] It was assumed that the liquid-phase samples withdrawn from the reactor represented the total reactor composition (i.e., the gas-phase compositions were ignored). The number average molecular weight ($\bar{M}_n$) was determined with a Mechrolab Model 301 vapor-pressure osmometer.[7] The molecular weight distribution (MWD) was measured by gel-permeation chromatography (GPC) on a Waters Associates Model 200 instrument with a differential refractometer as a detector. Three 4 ft × $^3/_8$ in. columns packed with Styragel of 900, 400, and 45 Å diameter, respectively, were applied. Tetrahydrofuran was the eluent with 1.0 mL/min flow rate. Correction was applied for the change of the refractive index with the molecular weight. However, the change of the refractive index with the polymer structure has been ignored. Polystyrene and poly(propylene glycol) standards (from Waters Associates) were used in the calibration, and the Q factors were used for the conversion of the data. Since we were primarily interested in the differences rather than the absolute values of the molecular weight, this method of calibration was satisfactory. The unsaturation was measured by microhydrogenation,[8] and the results were expressed as percent of theoretical unsaturation (i.e., one double bond per polymer molecule).

The IR spectra were recorded on neat liquid polymers in calibrated cells on a Perkin-Elmer 237B grating spectrometer. Identifications were based on well-established characteristic absorptions.[9,10] Quantitative determination of the trisubstituted olefin content from the intensity of the 1662-cm^{-1} absorption band was possible as before[2] because of the fortuitous absence of interfering cis-disubstituted olefins. The 1642-cm^{-1} band served to measure the vinylidene content.[2] The molar absorptivity values previously derived for isobutylene polymers[2] were used in the calculations rather than determining them individually for the propene, 1-butene, and *cis*-2-butene polymers. Because measurements of the 1662- and 1642-cm^{-1} polypropene and poly-1-butene absorbances were uncertain due to uncertainties in the base line, hydrogenated polymers were used to determine the exact positions of the base lines, as illustrated in Figures 1 and 6. In the propene and 1-butene polymers, trans-1,2-disubstituted olefins were also determined quantitatively from their characteristic absorption around 967 cm^{-1}, according to the formula:

$$\text{TRANS} = \frac{A_{967}\bar{M}_n}{a_{967}bg \times 10}$$

where TRANS = trans-1,2-disubstituted olefin content, in percent of the theoretical unsaturation; A_{967} = measured absorbance of the 967-cm^{-1} band (since this band is a composite in propene polymers, the aborbance was taken as the difference between those of the original and the hydrogenated polymer; for 1-butene polymers, the peak height from the base line gave the absorbance directly); a_{967} = the molar absorptivity of the 967-cm^{-1} band, taken as a previously reported[10] value of 100 L/(mol cm); b = the cell thickness, cm; and g = the density of the polymer, g/cm^3.

The ^{1}H NMR spectra were obtained on Bruker HX-90 or JEOL MH-100 instruments as described previously.[2] Identifications were based on correlations between chemical shifts and olefin types.[11] Vinylidene content was measured by our techniques.[2] However, these techniques[2] could not be directly applied for the determination of the trisubstituted olefin content in propene and 1-butene polymers because 1,2-disubstituted olefins interfered. To circumvent this problem, the following method of calculation was adopted:

$$\text{TRI} = \frac{A^{\text{total}}\bar{M}_n\text{Wt}^{\text{dur}}100}{67\text{Wt}^{\text{pol}}A^{\text{dur}}} - 2(\text{TRANS})$$

where TRI = the trisubstituted olefin content as the percent of theoretical unsaturation; A^{total} = the area of the ^{1}H NMR peaks in the δ 4.9 to 5.6 region, arising from both trisubstituted and 1,2-disubstituted olefins (arbitrary units); A^{dur} = the area of the aromatic protons (δ 6.74) of the durene standard; Wt$^{\text{dur}}$ = the weight of the durene standard (grams) in carbon tetrachloride solution; Wt$^{\text{pol}}$ = the weight of the polymer sample (grams) in carbon tetrachloride solution; and TRANS = the trans-1,2-disubstituted olefin content determined by IR spectroscopy (see above).

Quantitative determinations of the olefin types by ^{1}H NMR and by IR were in reasonable agreement, confirming that the use of assumed molar absorptivity values in the IR analyses did not result in a great systematic error.

Carbon-13 spectra were obtained on a Varian CFT-20 spectrometer at 20.0 MHz. Samples were run as 80% (w/v) solutions in CDCl$_3$ with tetramethylsilane (Me$_4$Si) used as an internal standard. Data were obtained using a spectral width of 4000 Hz, 8192 data points, a pulse width of 8 μs (45°), and no delay between pulses.

Results and Discussion

Propene Polymers. (a) Olefin Analyses and the Mechanism of the Termination. Figure 1 shows the partial IR spectrum of a polypropene. This is very similar to those reported for several cationic polypropenes[3,4,12] but differs from the spectrum of a propene oligomer made in the gas phase with boron trifluoride.[13] The absorptions at 1662 and 825 cm^{-1} are assigned to trisubstituted, those at 1642 and 890 cm^{-1} to vinylidene, and that at 967 cm^{-1} to trans-disubstituted olefins.[9,10] The absence of absorption in the 985–995- and 905–915-cm^{-1} regions indicates that the polymer does not contain monosubstituted olefins.[9,10] The absence of significant amounts of cis-disubstituted olefins was inferred indirectly: the trans-disubstituted olefin content determined by IR analysis can totally account for the ^{1}H NMR absorption intensity of the δ 5.3 shoulder band in Figure 2, which otherwise could arise from both trans- and cis-disubstituted absorption.[11] The assignments of the olefinic absorptions have been confirmed by hydrogenation. The olefin bands disappeared with the exception of the 967-cm^{-1} band. The latter decreased in intentsity on hydrogenation; it is apparently a composite band arising from the absorption of the trans-disubstituted olefin and an unidentified nonolefinic group.

Table I summarizes the results of the olefin determinations. It can be seen that in polypropenes the unsaturation measured by hydrogenation is below the theoretical value. The various types of olefins determined by spectroscopy do not add up to the unsaturation value measured by hydrogenation. It is inferred from the difference that tetrasubstituted olefins are present in the polymers because the IR and NMR techniques do not detect and measure the tetrasubstituted olefins.

Table I
Olefin Determinations by Hydrogenation and Spectroscopy in Polymers of Propene, 1-Butene, and *cis*-2-Butene[a]

polymer	$\overline{M}_n$	*d*	olefin types (in % of the theoretical unsaturation)			
			vinylidene[b]	trans-disub[b]	trisub[b]	tetrasub[c]
polypropene	770-980	88-96	4-8	4-8	38-48	32-42
poly-1-butene	700-930	86-94	4-8	4-9	36-48	29-42
oligo-*cis*-2-butene	240-260	not measured	5-9	not found	74-88	

[a] The table shows the observed ranges in the samples made under the conditions defined in the Experimental Section. The individual polymers prepared under various experimental conditions differ distinctly in their olefin distribution. [b] Determined by IR and NMR spectroscopy. [c] The difference between the unsaturation measured by hydrogenation and the sum of the spectroscopically determined olefin types. [d] Unsaturation by hydrogenation (% of theoretical).

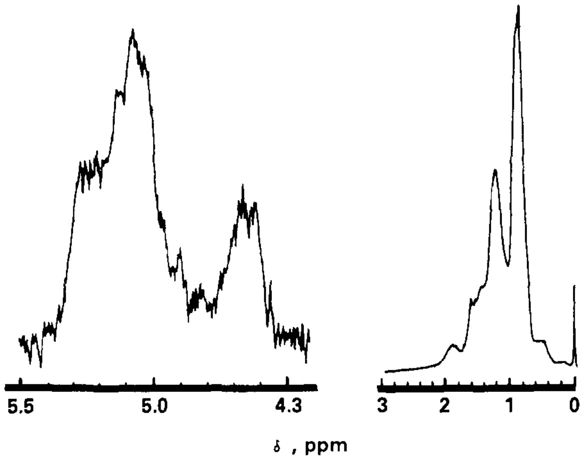


Figure 2. ^{1}H NMR 100 MHz spectrum of polypropene (in carbon tetrachloride).

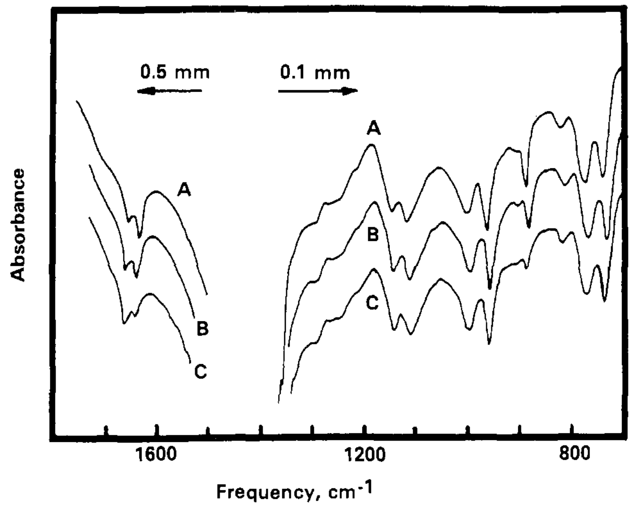


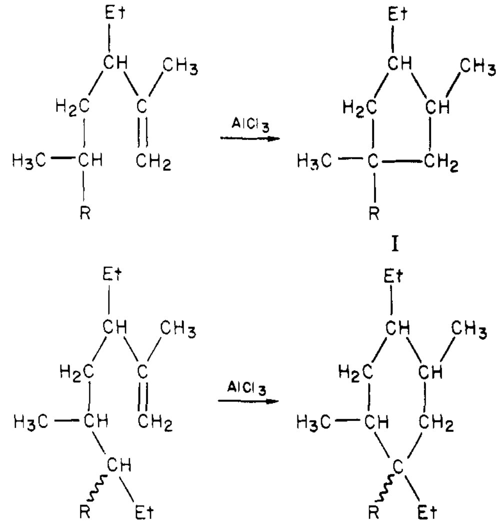
Figure 3. Changes in the IR spectrum of polypropene during and after polymerization.

Table II
Changes in Polypropene Unsaturation during and after Polymerization[a]

propylene conversion, %	unsaturation by hydrogenation, mol, %
70	97
93	96
>99[b]	90

[a] Propene (50%) in propane polymerized at 12 °C. The propene to $AlCl_3$ molar ratio was 350; the 2-chloropropene to $AlCl_3$ ratio is 0.37. [b] The polymerization mixture was stirred for an additional 30 min after the polymerization had stopped.

The less than theoretical polypropene unsaturation can be explained on the basis of some additional results. The data of Table II suggest that the loss of unsaturation continues after the monomer conversion is complete. The IR spectra of intermediate and final polymer samples reveal some changes which are probably related to the loss of unsaturation. In Figure 3, curves A and B represent polymer samples at 48 and 93% monomer conversion level, and curve C represents the final polymer isolated after the mixture warmed up from the polymerization temperature (12 °C) to 20 °C in the presence of the initiator. Although several minor changes are apparent from the spectra, the decrease in the 1642- and 890-cm^{-1} vinylidene absorptions is the most noticeable. Vinylidene contents of A, B, and C are 10.1, 7.2, and 4.9%, respectively. We propose that the vinylidene double bond easily alkylates a tertiary carbon atom intramolecularly under the catalytic influence of the aluminum chloride. The resulting molecule is saturated and contains a five- or six-membered ring, as shown by structures I and II.

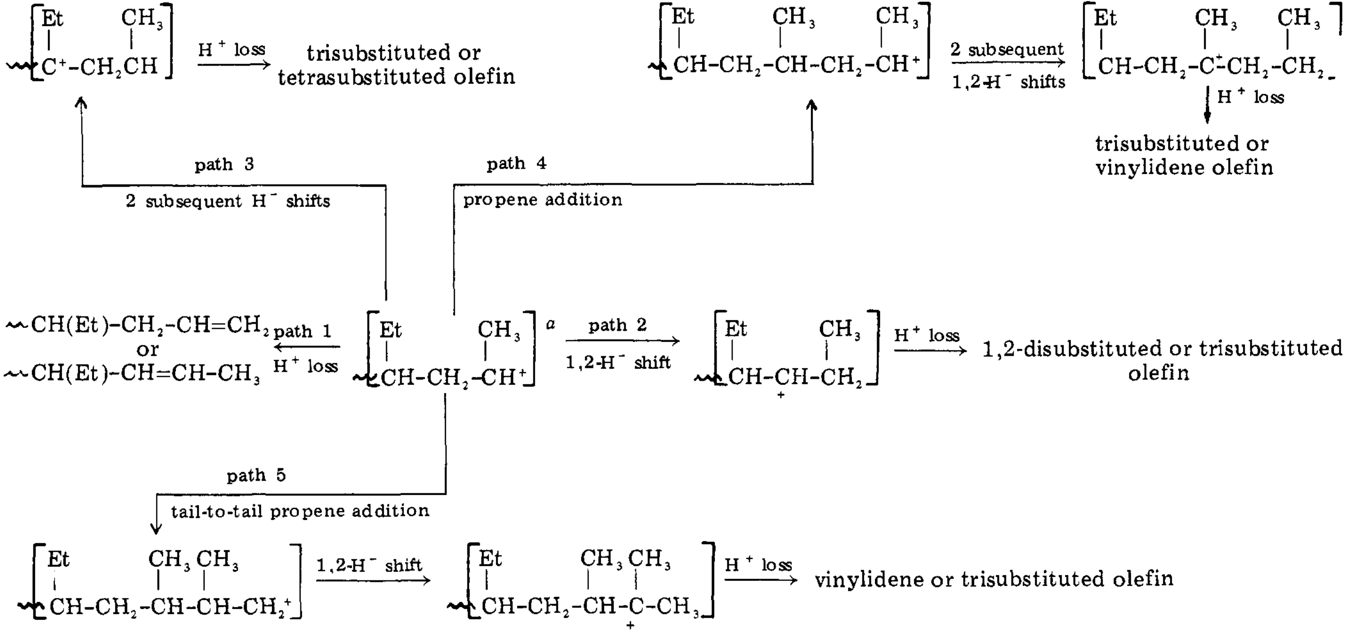


I

II

Scheme I illustrates the possible mechanistic routes in the termination step which can explain the formation of the observed olefin types. Path 1 shows the classical termination by proton expulsion. Our results refute this path. Because no monosubstituted olefins were observed and because a 100% selectivity for 1,2-disubstituted olefin by path 1 is unreasonable, even the small amounts of 1,2-disubstituted olefins that we detected cannot be explained by path 1. These results mean that a hydride shift or some other reaction must have occurred prior to the proton expulsion. Path 2 involves a 1,2-hydride shift prior to the proton expulsion. Because this is the only path giving 1,2-disubstituted olefin, it is almost certainly operative. Path 3 involves two subsequent 1,2-hydride shifts (or a 1,3-hydride jump) prior to the proton expulsion, resulting in trisubstituted and tetrasubstituted olefins. Since these are the major olefin types in polypropenes (see

Scheme I
Olefin-Forming Terminations during Propene Polymerization



[a] Since hydride shifts are known to take place during propagation, here an intermediate is shown with its penultimate C_3 unit rearranged by hydride shift.

Table I), we believe that path 3 is the most frequent in the termination. To explain the formation of the vinylidene olefins, paths 4 and/or 5 are suggested. In path 4, the penultimate propene addition is not followed by a hydride rearrangement. After the last propene addition, two subsequent 1,2-hydride shifts occur prior to the proton expulsion. In path 5, a tail-to-tail coupling takes place followed by a 1,2-hydride shift and then by a proton expulsion. Additional paths could also explain the observed olefin types. For example, the growing polymer cation could couple to a vinyl, vinylidene, or trisubstituted double bond of a polymer molecule to give vinyldene, trisubstituted, or tetrasubstituted olefins, respectively, after proton expulsion.

The proposed tail-to-tail coupling step (path 5 in Scheme I) involves the generation of a transient primary carbenium ion. This path may be objectionable because formation of a more stable secondary carbenium ion by the regular tail-to-head coupling would be favored energetically. However, the existence of a lower-energy variety of primary carbenium ions such as the protonated cyclopropane is well established in liquid-phase carbenium-ion rearrangements[14,15] and might also be acceptable in this case. Recently, even the existence of the $C_2H_5^+$ cation was demonstrated.[16] There are some indications that occasional tail-to-tail coupling may occur even during isobutylene polymerization[17,18] when the energetics is much less favorable for irregular coupling. Based on these arguments, the assumption of some tail-to-tail coupling during propene polymerization is reasonable but, as yet, there is no firm evidence to support this proposal.

(b) Kinetics of the Polymerization and the Molecular Weight Distribution. From a kinetic study of propene polymerization at low temperature with the homogeneous $AlBr_3$–HBr initiator system, Fontana and Kidder[5] have concluded that the propagation is the rate-controlling slow step. Although minor modifications have been proposed to the original kinetic scheme,[3,19] the basic ideas of rate-controlling slow polymer growth have been widely accepted through review articles. The best evidence for this scheme was a reported steady growth of the polymer molecular weight (viscosity) during the initial phases of the polymerization.[5] However, a careful review of their work raises some doubts about the validity of the proposed scheme. For a fundamental analysis, the kinetic data must be complete and very accurate because simplifications or small deviations may easily result in a different interpretation and consequently in an incorrect picture. For example, in the cited reference,[5] the kinetic consideration was limited to propagation only, ignoring initiation and termination. Furthermore, the precipitation of the initially homogeneous initiator system was noted,[5] but it was not mentioned whether the experimental data were corrected to account for this. Finally, it was stated that the butane solvent available from a pilot plant fractionator had 99% purity, but the impurities were not specified. Because it is very difficult to separate the butane and 2-methylpropane components of refinery C_4 mixtures, and because reliable analytical tools could hardly have been available at the time of their work (1944–1945) to detect the presence of small amounts of 2-methylpropane, it is reasonable to suspect that 2-methylpropane was present in the butane. The adventitious 2-methylpropane possibly left in Fontana's polymerization feed may have been responsible for the apparent molecular weight growth. It has since been well established[3,20] that 2-methylpropane acts as a powerful chain transfer agent during propene polymerization and causes an observable molecular weight decrease even at 0.5% concentration level.[20] However, this was not yet recognized at the time of Fontana's first publication.[5] Scheme II shows how the 2-methylpropane impurity could reduce the molecular weight of the polymer by hydride transfer, until it is "consumed" by incorpora-

Scheme II

$$[RCH^+CH_3] + HC(CH_3)_3 \xrightarrow[\text{by hydride transfer}]{\text{premature termination}} [RCH_2CH_3 + {}^+C(CH_3)_3]$$

$$[{}^+C(CH_3)_3] \xrightarrow{nC_3H_6} \text{polymer}$$

tion into the polymer. Subsequent polymerization to a higher molecular weight product would result in an apparent molecular weight growth. For these reasons, it might be worthwhile to repeat Fontana's work.

We have studied the polymerization with commercial powdered aluminum chloride at 12 °C. We believe that our initiation must have been homogeneous. It is known[21] that aluminum chloride has a low but finite solubility even in saturated hydrocarbons such as liquified butane. Its solubility in olefins would be expected to be much higher. However, as the monomer conversion progresses, the solubility would be expected to decrease, probably resulting in the precipitation of some of the dissolved initiator. Indeed, Fontana[5] was able to observe the precipitation of their "soluble" $AlBr_3$–HBr system probably due to similar causes by using glass equipment. We have also studied the kinetics of propene polymerization. The results are suitable for industrial modeling but not for fundamental studies since we could not measure the real concentration of the dissolved initiator. We have found that polymerization occurred without a coinitiator. In this case, initially there appeared to be a little monomer conversion, probably due to the presence of adventitious protogenic impurities, but then the polymerization stopped. However, after an induction period of several minutes, the polymerization started and continued to 97% conversion of the monomer. The induction period was reduced or practically eliminated, and the polymerization rate was drastically increased with addition of the 2-chloropropane coinitiator. We have obtained rate curves similar to those reported by Fontana[5] with the exception that we did not observe initial rate maxima. In agreement with Fontana's results, we have also found that the rate can be approximately described as independent of the monomer concentration within a wide monomer concentration range. Perhaps the rate might be independent of the monomer concentration in the real kinetic sense, but this contention is obscured experimentally by the changes in the dissolved initiator concentration. The observed polymerization kinetics could be explained either by a slow initiation—which is independent of the monomer concentration—followed by a fast chain propagation or by the mechanism of Fontana and Kidder.[5] Finally, we have found that the polymer molecular weight distribution is independent of the conversion and the concentration of the monomer. This is illustrated in Figure 4 by showing that polymer samples from a batch polymerization experiment at 26 and 85% propene conversion levels have identical molecular weight distributions. The molecular weight distribution was also determined on numerous propene polymers made under a great variety of experimental conditions: in propane and butane solvents, with different feed compositions and initiator levels within the limits specified in the experimental section, at intermediate and final conversion levels of the batch polymerizations. Surprisingly, at a given polymerization temperature (12 °C) all the polymer samples were found to have essentially identical molecular weight distribution within the experimental error of the determination, similar to those shown in Figure 4. In contrast to Fontana's report,[5] under our conditions we did not find evidence for a molecular weight growth with the progress of the polymerization.

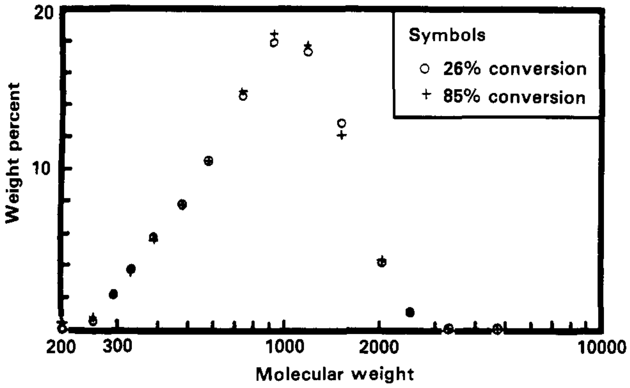


Figure 4. Polypropene molecular weight distributions at different stages of batch polymerization.

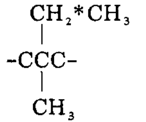
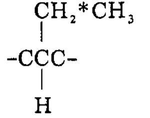
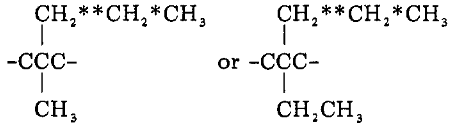
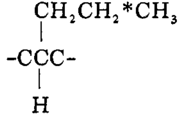
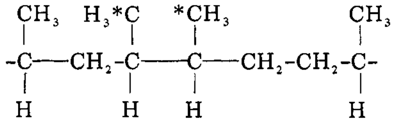
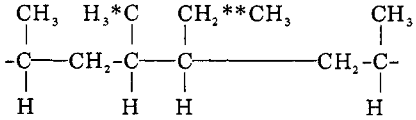
In agreement with our results, some other reports also seem to indicate that at a given temperature propene appears to polymerize to the same molecular weight under quite a wide variety of experimental conditions. Thus, the polypropene molecular weight was reported[22] to be independent of the monomer concentration in the −15 to −80 °C temperature range, with the boron trifluoride–methanol initiator system. Fontana et al.[23] have also made a general statement that "the molecular weights of polymers produced with unpromoted aluminum bromide are not very sensitive to changes, within reasonable limits, in the reaction conditions other than temperature". To explain this unique behavior, we propose that the polypropene molecular weight distribution is determined by the occurrence of "side reactions" such as the hydride transfers or irregular coupling during the propagation which can easily lead to termination (see Scheme I). This does not mean that, in Scheme I, the intermediates of the various paths cannot propagate further but rather that they have a relatively high tendency to terminate. Therefore, they will terminate the chain before the monomer concentration could become a limiting factor.

Previously, both intramolecular and intermolecular hydride shifts were postulated[3] to take place during propene polymerization. Based on the results of our molecular weight distribution studies, we argue against the intermolecular hydride transfer. Such a transfer would terminate a chain prematurely and would initiate another chain. However, in an overcrowded polymer structure, initiation inside the polymer chain could hardly result in further growth; we would rather expect a termination by proton expulsion. Thus, we would expect an overall effect of molecular weight decrease. Increasing monomer conversion (i.e., increasing polymer concentration) should result in increasing frequency of intermolecular hydride shift and, consequently, in a lowering of the molecular weight. Since our results do not agree with this model, we think that intermolecular hydride shifts do not play a significant role.

(c) Analysis of the Polymer Skeleton and the Mechanism of the Propagation. Fontana was the first to recognize[24] that cationic polypropenes have a "tree-branched" skeleton as a result of hydride transfer reactions during propagation. Subsequently, Ketley and Harvey[3] and Immergut et al.[4] have reported on the basis of IR studies that cationic polypropenes do not have the regular $[\text{-CH}_2\text{CH(CH}_3)\text{-}]_n$ skeleton but contain ethyl and propyl branches. To account for their formation, both inter- and intramolecular hydride shifts were postulated.[3] To find out more details about the polymer skeleton, we applied a combination of ^{13}C NMR and IR studies.

Figure 5 shows the ^{13}C NMR spectrum of the paraffin region of our polypropene. If Figure 5 is compared to the spectra of polypropenes made with Ziegler-Natta catalysts,[25] dramatic differences can be seen. The Ziegler-Natta polymers exhibit relatively simple spectra because the propene units are joined in a regular $[\text{-CH}_2\text{CH(CH}_3)\text{-}]_n$ fashion. In stereoregular polymers, the three kinds of

Table III
Calculated ^{13}C NMR Chemical Shifts of High-Field Methyl and Methylene Carbons in Various Structural Environments[a]

structure no.	structure	calcd chemical shift, ppm from Me_4Si	
		for *C	for **C
III	 $-C\overset{CH_2{}^{*}CH_3}{\underset{CH_3}{C}}C-$	8-9	
IV	 $-C\overset{CH_2{}^{*}CH_3}{\underset{H}{C}}C-$	11-12	
V	 $-C\overset{CH_2{}^{**}CH_2{}^{*}CH_3}{\underset{CH_3}{C}}C-$ or $-C\overset{CH_2{}^{**}CH_2{}^{*}CH_3}{\underset{CH_2CH_3}{C}}C-$	15	17.5-19.5
VI	 $-C\overset{CH_2CH_2{}^{*}CH_3}{\underset{H}{C}}C-$	14-15	
VII	 $-\underset{H}{\overset{CH_3}{C}}-CH_2-\underset{H}{\overset{H_3{}^{*}C}{C}}-\underset{H}{\overset{{}^{*}CH_3}{C}}-CH_2-CH_2-\underset{H}{\overset{CH_3}{C}}-$	14-16[b]	
VIII	 $-\underset{H}{\overset{CH_3}{C}}-CH_2-\underset{H}{\overset{H_3{}^{*}C}{C}}-\underset{H}{\overset{CH_2{}^{**}CH_3}{C}}-CH_2-\underset{H}{\overset{CH_3}{C}}-$	14-16[b]	11-12

[a] See ref 26. [b] As Table IV of ref 26 illustrates, calculated and experimental results do not agree well in sterically crowded groups. We corrected the calculated values to best fit the experimental results. For recent measurements, see A. Zambelli, P. Locatelli, and E. Rigamonti, *Macromolecules*, 12, 156 (1979).

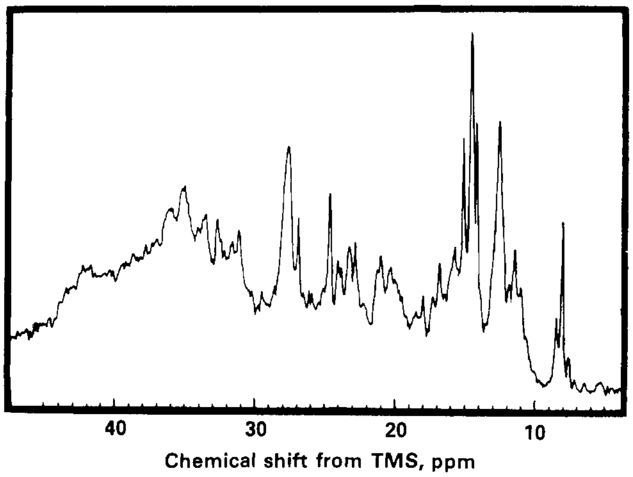


Figure 5. Partial ^{13}C NMR spectrum of polypropene (in deuteriochloroform).

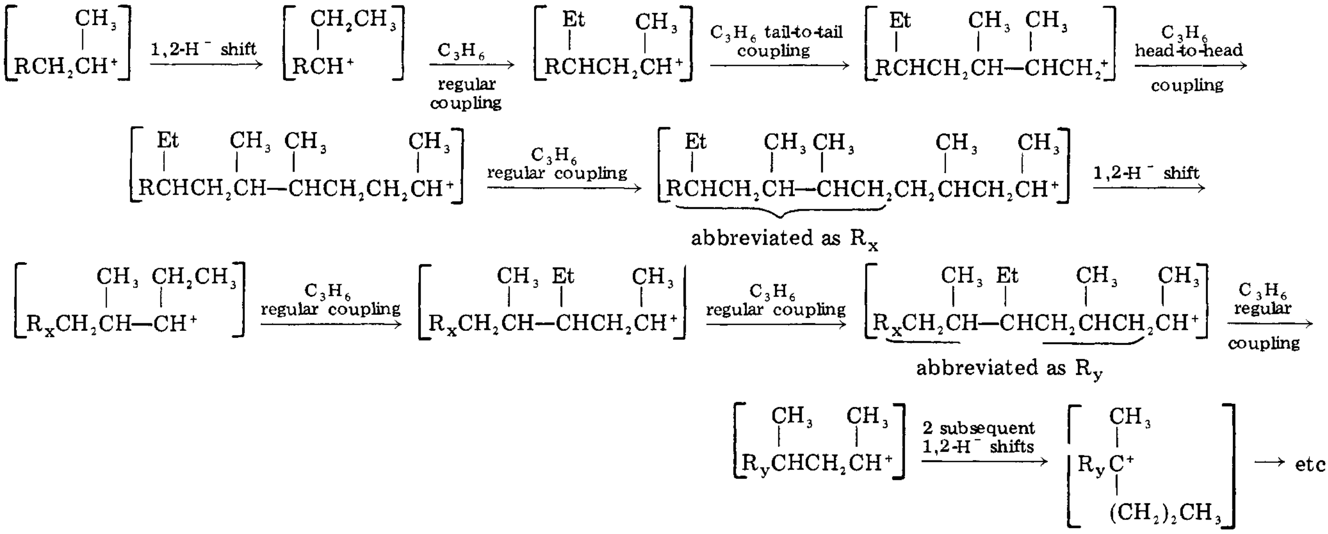
carbons give three sharp absorption bands. Variations in the stereochemistry, as occur in atactic fractions, result in a slightly more complex spectrum. In contrast, Figure 5 is extremely complex, indicating that the cationic polymers have a very irregular skeleton. However, in spite of its complexity, the spectrum can give valuable information.

It is possible to calculate[26] the chemical shifts of individual paraffinic carbons, and the calculated values are in good agreement with those obtained experimentally. Table III summarizes the calculated chemical shifts of the high-field (less than 18 ppm from Me_4Si) carbons in various structural environments which are expected to occur in polypropenes. Figure 5 can be analyzed by using these calculations. Absorptions at 7–9 ppm must arise from ethyl groups attached to the quaternary carbon as in III and those at 11–13 ppm from ethyls attached to the tertiary carbon as in IV. The intense absorptions at 14–16 ppm can originate either from V, VI, VII, or VIII. However, if V were responsible, absorptions of about equal intensity would be expected also at 17.5–19.5 ppm. Since there is no strong absorption in this region, V does not appear to be a major contributor to the 14–16-ppm absorption bands. This leaves VI, VII, and VIII for further consideration.

Previously,[3] the 739-cm^{-1} IR band (see Figure 1) was assigned to propyl and the 769-cm^{-1} band to ethyl branchings. Thus, interpretation based on both ^{13}C NMR and IR spectra may suggest that the 14–16-ppm ^{13}C NMR absorption arises mostly from structure VI. We do not doubt that an unsaturated variety of VI is present in small quantities, because as Scheme I shows, terminations by paths 3 or 4 can easily yield propyl groups. However, only a propagation mechanism could account for substantial amounts of VI, but we do not see how. Propyl groups resulting from a propagation step should have structure V rather than VI (see Scheme I, path 3, with the assumption that the intermediate propagates rather than terminates). An alternative interpretation of the results might be that the 739-cm^{-1} IR band is a composite band, only a fraction of its intensity is arising from propyl groups, and structures VII and VIII are responsible for much of the ^{13}C NMR absorptions in the 14–16-ppm range.

It may be of interest to find out whether unrearranged $-CH_2CH(CH_3)-$ units are present at all in cationic polypropenes. Previous studies[3] suggest that they are practically absent. However, these results may be questioned because they are based on a poorly defined IR absorption around 830 cm^{-1} which was identified in atactic poly-

Scheme III
Propagation during Propene Polymerization[a]



[a] The scheme is intended to illustrate the formation of the major probable structural fragments. This does not imply that the proposed reactions occur in the same sequence.

propylenes.[27] If the analyses were based on an absorption at 1154 cm^{-1}, which can be assigned[11] to isolated methyl groups of the type $\sim CH_2CH(CH_3)CH_2 \sim$, one should conclude that these groups are present in cationic polypropenes, even though in small amounts. This latter interpretation merits greater confidence, because it is based on a well-established absorption, even though it falls into the less characteristic fingerprint region of the spectrum.

Scheme III illustrates our understanding of the propagation and formation of the major structural units. For the sake of brevity, it does not incorporate the formation of the minor but still important unit III. To illustrate the complexity of the reactions, we wish to point out the presence of a very small peak in the IR spectrum at 1365 cm^{-1} (see Figure 1). This can be assigned to $C(CH_3)_2$ or $C(CH_3)_3$ groups. Scheme III does not account for this structure either.

1-Butene Polymers. Figure 6 shows the partial IR spectrum of a 1-butene polymer. The olefin absorption bands and, consequently, the olefin types are the same as those described for polypropenes. The absence of monosubstituted and cis-disubstituted olefins is also inferred analogously.

Table I summarizes the results of the quantitative olefin analyses. The unsaturation is less than theoretical. Tetrasubstituted olefins are undoubtedly present because the spectroscopically measured unsaturation is less than that determined by hydrogenation. The formation of the identified olefin types and the loss of polymer unsaturation can be explained in the same way as was done for the case of polypropene.

The quantitative IR analyses for the determination of the trisubstituted olefins (Table I) gave results which seem to be quite reasonable, even though we used assumed molar absorptivity values for the 1662-cm^{-1} absorption. An alternative way to determine trisubstituted olefin content is to use the intensity of the 825-cm^{-1} trisubstituted out-of-plane =CH deformation band. A range of 33 to 48 L/(mol cm) was given in the literature[10] for the molar absorptivity of this absorption. Selecting a median value of 40 L/(mol cm), we would calculate about 20 times lower unsaturation than that given in Table I. We know that the molar absorptivity value of the 1662 cm^{-1} C=C stretching band is reasonable (see Experimental Section). Consequently, the molar absorptivity of the 825 cm^{-1} =CH band must be 20 times smaller in 1-butene polymers (2 L/(mol cm)) than that assumed on the basis of literature reports.[10]

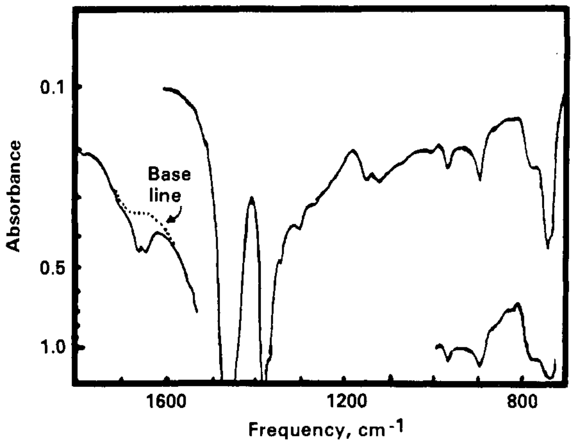


Figure 6. Partial IR spectrum of poly-1-butene (neat, 0.1 mm and in part 0.5 mm).

Ketley and Harvey[3] have recognized that cationic poly-1-butenes have an irregular skeleton. The presence of ethyl, propyl, and butyl branches was postulated.[3] A very recent[28] paper based on ^{13}C NMR analysis has indicated that the two major structural elements are VI and $-C(R_1)(R_2)-$, where R_1 = butyl and R_2 = methyl or ethyl or propyl. The minor units are[28] III, IV, and V, and in polymers made at higher polymerization temperature, the *tert*-butyl group is included. We have also studied the polymer skeleton from IR (Figure 6) and ^{13}C NMR (Figure 7) spectra. Surprisingly, in the ^{13}C NMR spectra of polypropene and polybutene-1, in the 0–20-ppm region, the chemical shifts of all the significant peaks (but not the intensities!) were found identical. This raises some questions: Is it due to identical groups or is it only coincidental? For example, there can be no doubt about the presence of the $-C(R_1)(R_2)-$ group, where R_1 = butyl and R_2 = methyl, ethyl, or propyl, based on the 14.1-ppm ^{13}C NMR signal, the 730-cm^{-1} IR shoulder band, and mechanistic considerations. But it is also possible that the 14.1-ppm signal assigned to the methyl carbon of the butyl

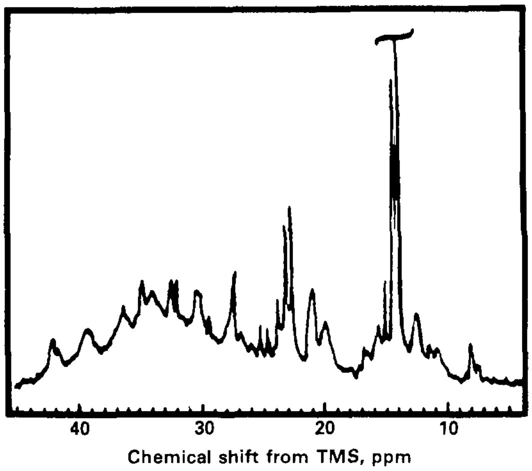


Figure 7. Partial ^{13}C NMR spectrum of poly-1-butene (in deuteriochloroform).

groups,[28] in part, originates from crowded methyl groups of the type $-C(CH_3)CH(R)-$, where R = propyl. In an alternative interpretation to that given,[28] the weak 15.1-ppm signal may also be assigned to crowded methyls instead of V.

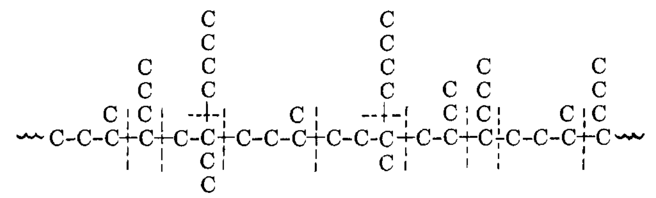
The crowded methyl group could originate from a 1,2-hydride transfer in one of the possible directions:

$$[RCH_2CH^+CH_2CH_3] \xrightarrow{1,2\text{-}H^-\text{ shift}} [RCH^+(CH_2)_2CH_3]$$

$$\Big\downarrow \text{ 1,2-H}^-\text{ shift}$$

$$[RCH_2CH_2CH^+CH_3] \xrightarrow[\text{2. 1,2-H}^-\text{ shift}]{\text{1. propene addition}} \text{“crowded” methyl}$$

There is very little indication of tail-to-tail coupling in polybutene-1,[28] and this may be associated with the individual monomer structure. Another point of interest is the presence of isolated methyl groups in 1-butene polymers. The IR spectrum (Figure 6) shows a weak absorption band at 1154 cm^{-1} which could be assigned[10] to isolated methyl groups. With these interpretations, the structure of polybutene-1 can be represented as something like this:



Concerning the kinetics and chain growth of butene-1 polymerization, a very small number of experiments suggest great similarity to those observed during propene polymerization.

***cis*-2-Butene Oligomers.** Cationic polymerization of *cis*-2-butene gives only low molecular weight oligomers.[13] Figure 8 shows a typical IR spectrum of our oligomers. The bands at 1662 and 825 cm^{-1} are assigned to trisubstituted and those at 1642 and 890 cm^{-1} to vinylidene olefins.[9,10] No other olefin type could be detected. Figure 9 shows the ^1H NMR spectrum. The 4.67 ppm band can be assigned to vinylidene protons[11] and the distorted quadruplet at 5.12 ppm (J = 6.3 Hz) to trisubstituted olefins with the structure $\sim C(CH_3)=CHCH_3$.[2] The results of the quantitative determinations of the olefin types are summarized in Table I. The trisubstituted and vinylidene olefins nearly account for the theoretical unsaturation. The balance may be due to analytical error, to the presence of tetrasubstituted olefins, or to less than theoretical unsaturation.

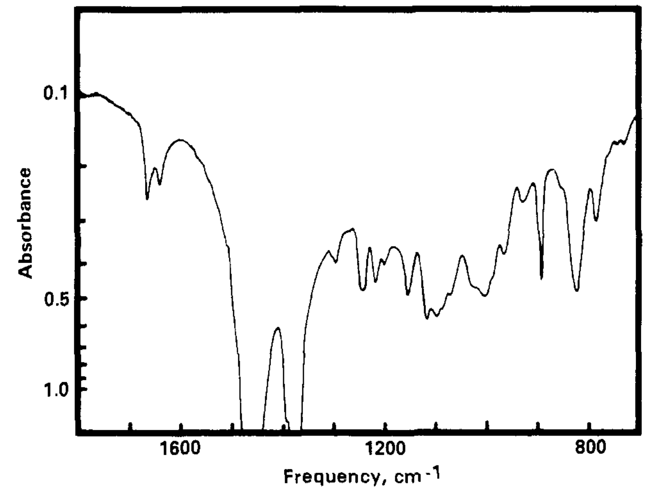


Figure 8. Partial IR spectrum of oligo-*cis*-2-butene (neat, 0.1 mm).

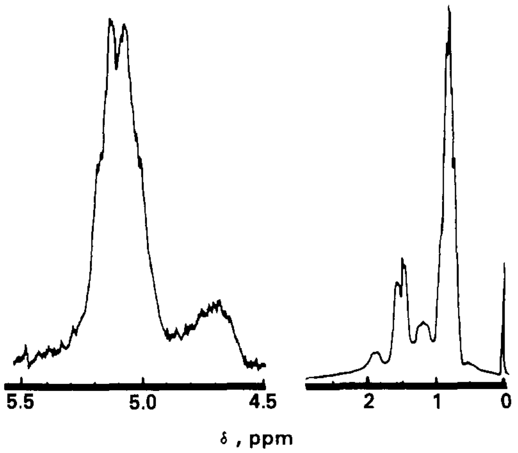


Figure 9. ^1H NMR 100 MHz spectrum of oligo-*cis*-2-butene (in carbon tetrachloride).

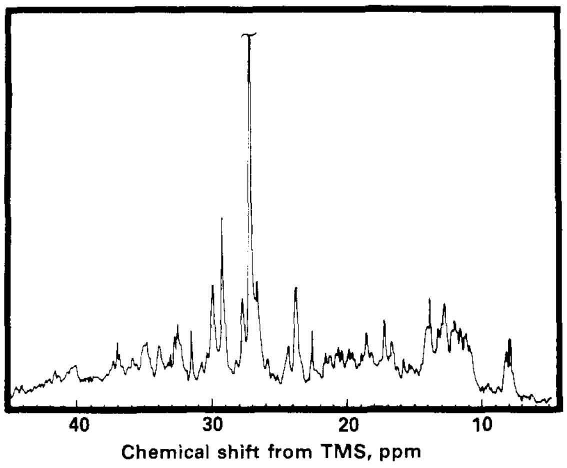
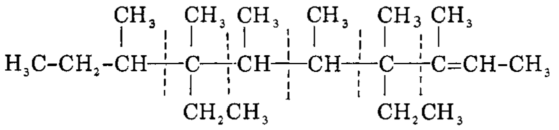


Figure 10. ^{13}C NMR spectrum of oligo-*cis*-2-butene (in deuteriochloroform).

The ^{13}C NMR spectrum (Figure 10) reveals by the absorption at 8 ppm that ethyl groups attached to a tetrasubstituted carbon (III in Table III) are present. The absorptions in the 11–15-ppm range can be assigned to crowded methyls on subsequent tertiary chain carbons and, in part, to methyl carbons of ethyl groups attached to a tertiary carbon (type IV). In the IR spectrum (Figure 8), the absorption at 1120 cm^{-1} is assigned to neighboring tertiary carbons ($\sim CHR_1-CHR_2\sim$) and that at 780 cm^{-1}

to ethyl branches. A structure (see structure X of a pentamer) conforming to these features can be derived if we assume that in every second propagation step a 1,2-hydride shift occurs. If hydride shifts occur in two subsequent propagation steps, the resulting carbenium ion is unable to propagate and terminates. Termination can give either a trisubstituted (as in X) or a vinylidene double bond but not a tetrasubstituted one. This line of thought is also in agreement with our ideas that the molecular weight distribution is controlled by side reactions during the polymerization of these monomers.



$$H_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}C(CH_3)(CH_2CH_3)\text{-}CH(CH_3)\text{-}CH(CH_3)\text{-}C(CH_3)(CH_2CH_3)\text{-}C(CH_3){=}CH\text{-}CH_3$$

X

These interpretations of the various spectroscopic techniques for the structure of *cis*-2-butene oligomers appear to be in good agreement and give confidence in the results. Yet they overlook a very important aspect of the oligomerization. Meyer had demonstrated in 1950[13] that the *cis*-2-butene oligomers made with $AlBr_3$ or $AlCl_3$ are extensively fragmented products not conforming to the expected $(C_4H_8)_n$ formula. Lachance and Eastham[29] demonstrated well this fragmentation for the oligomers made with $BF_3{\cdot}CH_3OH$. It was confirmed by field ionization mass spectrometry[30] that very extensive fragmentation also occurred with our oligomers. Although the fragmentations are overlooked by our spectroscopic analyses, they do not seem to change the expected structural units of the oligomers. However, the fragmentation may play an important role in the termination and may be a very important limiting factor to the growth of the molecular weight.

Finally, it is worth considering briefly how propene, 1-butene, and *cis*-2-butene polymerizations fit into the overall picture of cationic polymerization. They can be classified as "isomerization polymerizations with intromolecular hydride shift" because, as the name implies, the propagating species isomerize by 1,2-hydride shifts. The known varieties of isomerization polymerization, including the hydride shift polymerization, have been reviewed in the literature.[31-33] In most of the previously reported cases, the hydride shift polymerization occurs when the formation of a tertiary cation is the driving force for the hydride shift. With propene and 1-butene, this is not always the case; they often propagate through a secondary cation which had been generated from another secondary cation by hydride shift. However, beyond hydride shift isomerization, other "side reactions" may also be important during the propagation, such as fragmentation in the case of *cis*-2-butene and possibly irregular tail-to-tail coupling in the case of propene. Other side reactions not part of the propagation step, such as the formation of saturated hydrocarbons, were also observed. This latter reaction together with the formation of conjugated olefins are the major reaction types during "conjunct" polymerizations.[34] The polymerizations of propene, 1-butene, and *cis*-2-butene under our conditions are definitely not conjunct polymerizations even though both saturated hydrocarbons and conjugated olefins[35] are detectable in the product.

Acknowledgment. We are indebted to Drs. D. A. McCaulay and E. M. Eastham and Professor J. P. Kennedy for their helpful discussions and invaluable suggestions. The contributions to the various analyses by Messrs. R. W. Dunlap, J. J. Oita, and B. Bidlingmeyer are gratefully acknowledged.

References and Notes

(1) For an excellent review, see J. P. Kennedy, "Cationic Polymerization of Olefins: A Critical Inventory", Wiley-Interscience, New York, 1975, pp 57-86.

(2) I. Puskas, E. M. Banas, and E. G. Nerheim, *J. Polym. Sci., Polym. Symp.*, **56**, 191 (1976).

(3) A. D. Ketley and M. C. Harvey, *J. Org. Chem.*, **26**, 4649 (1961).

(4) E. H. Immergut, G. Kollmanan, and A. Malatesta, *J. Polym. Sci.*, **51**, S 57 (1961).

(5) C. M. Fontana and G. A. Kidder, *J. Am. Chem. Soc.*, **70**, 3745 (1948).

(6) "ASTM Book of Standards", Method D-1717, Published yearly by the American Society for Testing and Materials, Philadelphia, Pa.

(7) Reference 6, Method D-2503.

(8) C. L. Ogg and F. J. Cooper, *Anal. Chem.*, **21**, 1400 (1949).

(9) See, e.g., L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, 1956, pp 13 and 34, or any textbook on IR spectroscopy.

(10) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

(11) F. C. Stehling and K. W. Bartz, *Anal. Chem.*, **38**, 1467 (1966).

(12) C. Y. Liang and W. R. Watt, *J. Polym. Sci.*, **51**, S 14 (1961).

(13) R. L. Meyer, *J. Chem. Soc.*, 3656 (1950).

(14) C. J. Karabatsos, *Prep., Div. Pet. Chem., Am. Chem. Soc.*, **16**, C-22 (1971), and references therein.

(15) D. M. Brouwer and J. M. Oelderik, *Recl. Trav. Chim. Pays-Bas*, **87**, 721 (1968).

(16) M. Siskin, *J. Am. Chem. Soc.*, **98**, 5413 (1976).

(17) Y. M. Slobodin and N. I. Matusevich, *Vysokomol. Soedin.*, **5**, 774 (1963); *Chem. Abstr.*, **41**, 7804a (1963).

(18) In ref 2, a tail-to-tail coupling step was postulated to explain the formation of an unusual olefin type during isobutylene polymerization with aluminum chloride. This olefin was incorrectly described to account for all of the trisubstituted olefins. It accounts only for a fraction of the trisubstituted olefins.

(19) F. R. Mayo and C. Walling, *J. Am. Chem. Soc.*, **71**, 3845 (1949).

(20) C. M. Fontana, R. J. Herold, E. J. Kinney, and R. C. Miller, *Ind. Eng. Chem.*, 44, 2955 (1952).

(21) Standard Oil of Indiana, U.S. Patent 3 121 125 (Feb. 11, 1961).

(22) T. Szell and E. M. Eastham, *J. Chem. Soc. B*, 30 (1966).

(23) C. M. Fontana, G. A. Kidder, and R. J. Herold, *Ind. Eng. Chem.*, 44, 1688 (1952).

(24) C. M. Fontana, *J. Phys. Chem.*, **63**, 1167 (1959).

(25) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

(26) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).

(27) See, e.g., J. L. Koenig, L. E. Wolfram, and J. G. Grasselli, *Spectrochim. Acta*, **22**, 1233 (1966).

(28) C. Corno, G. Ferraris, A. Priola, and S. Cesca, *Macromolecules*, **12**, 404 (1979).

(29) P. Lachance and A. M. Eastham, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1843 (1975).

(30) S. Meyerson and I, Puskas, unpublished results.

(31) J. P. Kennedy in "Encyclopedia of Polymer Science and Technology", Vol. 7, Interscience, New York, 1967, p 762.

(32) J. P. Kennedy and A. W. Langer, *Adv. Polym. Sci.*, **3**, 523 (1964).

(33) A. Tsukamoto and O. Vogl, *Prog. Polym. Sci.*, **3**, 223 (1971).

(34) For a review, see L. Schmerling, *Ind. Eng. Chem.*, **45**, 1448 (1953). The "conjunct polymerization" term was originated by V. N. Ipatieff and A. V. Grosse, *J. Am. Chem. Soc.*, **58**, 915 (1936).

(35) Detectable in very small amounts by UV spectroscopy.