Anomalous Carbon Numbers in Cationic Oligomers of Propylene and Butylenes

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Field-ionization mass-spectral analysis of the volatile fractions of cationically initiated polymers of propylene, 1-butene, *cis*-2-butene, and isobutylene reveal that substantial fractions of these polymers (20 to 80%) do not have the expected polymeric formulas. Specifically, they exhibit carbon numbers other than integral multiples of those of the monomers from which they were prepared. Although products with anomalous carbon numbers have been reported for triptene dimers[1] and *cis*-2-butene oligomers,[2-4] our data suggest that formation of such products during cationically initiated polymerization of olefins is more general than has been recognized. Aluminum chloride as a polymerization initiator appears to give more anomalous carbon-number product than boron trifluoride. Chain transfers involving carbon–carbon bond cleavages are responsible for their formation. These reactions appear to be more frequent at higher polymerization temperatures.

Introduction

Cationically initiated oligomers and polymers of olefins are generally assumed to have carbon numbers that are integral multiples of that of the monomer. However, two exceptions are known from the literature. In 1950, Whitmore et al.[1] reported that about half the product from the dimerization of triptene (2,3,3-trimethyl-1-butene) by sulfuric acid initiation was not the expected C_{14} olefin but a mixture of C_6, C_8, C_9, C_{10}, C_{11}, C_{12}, and other unidentified olefins. In the same year, Meier[2] reported that oligomers of *cis*-2-butene made with BF_3 initiator contained substantial amounts of C_9 and C_{10} hydrocarbons and that the distillation curve of the higher components was continuous. Lachance and Eastham[3,4] subsequently provided firm evidence that, indeed, oligomers of *cis*-2-butene contain substantial quantities of molecules not conforming to the $(C_4H_8)_n$ molecular formula. These authors also observed the presence of products with anomalous carbon numbers in propylene oligomers[3] but far less than in the *cis*-2-butene oligomers. To our knowledge, such products of anomalous carbon number have not been reported for polymers derived from other monomers.

We suspected that formation of products with anomalous carbon numbers during cationic polymerizations may, as a result of side reactions, be more general than has been recognized. Many side reactions, or secondary reactions, are known to take place during cationic polymerization. For example, carbonium-ion rearrangements by hydride or methide shifts are known to accompany the polymerization of many monomers;[1,2,5] carbon–carbon bond cleavages by β-fission are well established in certain cases;[1,2] double-bond isomerizations and intramolecular alkylations can occur;[6,7] etc. Such "side" reactions are often, in fact, integral parts of the polymerization chain reactions. Evidence for these side reactions comes largely from the identification of unexpected products in case of dimers or trimers;[1-4] identification of individual molecular species becomes increasingly difficult in higher molecular weight polymers. The presence of unexpected structural features in a polymer has usually been revealed by some type of spectroscopic analysis.[5-8] However, both the interpretation of the spectroscopic results and the rationale offered to account for the structural features inferred are often not completely unambiguous. The production from side reactions of polymer molecules of anomalous carbon number seems never to have been considered in the interpretation of the spectroscopic analyses. We decided, therefore, to make a deliberate effort to find out whether formation of products of anomalous carbon number is common to cationic polymerizations. We have now reexamined the carbon-number distributions of *cis*-2-butene oligomers and have also measured those of polymers of propylene, 1-butene, and isobutylene.

We employed field-ionization mass spectrometry (FIMS)[9] as our method of choice for the analysis of the volatile fractions of these polymers. Under the mild conditions of FI, molecules suffer much less fragmentation than under electron impact. Extensive branching, such as that expected in the oligomers with which we are concerned, increases fragmentation even in FI spectra, but an olefinic double bond reduces fragmentation, tending to counterbalance the effect of the branching.[10] This technique should be able to reveal whether our polymers are, indeed, true polymers, corresponding to integral multiples of the monomeric formula or not.

Experimental Section

Polymer Preparations and Sources. The preparation of the *cis*-2-butene and 1-butene polymers has been described.[6] The isobutylene polymers were prepared similarly but with lower

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[1] Whitmore, F. C.; Ropp, W. S.; Cook, N. C. *J. Am. Chem. Soc.* **1950**, *72*, 1507.

[2] Meier, R. L. *J. Chem. Soc.* **1950**, 3656.

[3] (a) Lachance, P.; Eastham, A. M. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1843. (b) *J. Polym. Sci., Polym. Symp.* **1976**, *no. 56*, 203.

[4] Lachance, P.; Eastham, A. M. *Can. J. Chem.* **1981**, *59*, 2621.

[5] For a review, see: Kennedy, J. P. "Cationic Polymerization of Olefins: A Critical Inventory"; Wiley-Interscience: New York, 1975; pp 57–86.

[6] Puskas, I.; Banas, E. M.; Nerheim, A. G.; Ray, G. J. *Macromolecules* **1979**, *12*, 1204.

[7] Puskas, I.; Banas, E. M.; Nerheim, A. G. *J. Polym. Sci., Polym. Symp.* **1976**, *no. 56*, 191.

[8] Corno, C.; Ferrari, G.; Priola, A.; Cesca, S. *Macromolecules* **1979**, *12*, 464.

[9] (a) Beckey, H.-D. "Field Ionization Mass Spectrometry"; Pergamon Press: Elmsford, NY, 1971. (b) "Principles of Field Ionization and Field Desorption Mass Spectrometry"; Pergamon Press: Elmsford, NY, 1977. (c) In "Biochemical Applications of Mass Spectrometry"; Waller, G. R., Ed.; Wiley-Interscience: New York, 1972; Chapter 30.

[10] (a) Beckey, H.-D.; Schulze, P. *Z. Naturforsch.* **1965**, *20a*, 1335. (b) Wanless, G. G.; Glock, G. A. *Anal. Chem.* **1967**, *39*, 2. (c) Weiss, M. J.; Hutchison, D. A. *J. Chem. Phys.* **1968**, *48*, 4386. (d) Reference 9a; pp 261–263.

0022-3263/84/1949-0258$01.50/0

Table I. Description of the Polymers Analyzed[a]

monomer	sample ID	initiator	solvent	polymerization temp, °C	$\overline{M}_n$[b]
propylene		*c*	*c*	*c*	~920
1-butene		$AlCl_3$	butane-pentane	0-20	~900
cis-2-butene		$AlCl_3$	butane-isobutane-pentane	20	252
isobutylene	A	$AlCl_3$	isobutane-pentane	−10	*d*
isobutylene	B	$AlCl_3$	isobutane-pentane	17-27	~700
isobutylene	C	BF_3	butane	0	1229
isobutylene	D	$BF_3 \cdot H_2O$	butane	0-8	876
isobutylene	E	$BF_3 \cdot {}^1/_2AcOH$	butane	0-8	557

[a] Unless otherwise specified, the polymers were subjected to mild "stripping" to remove the solvents. [b] Number-average molecular weight. [c] Proprietary information. [d] Overhead oligomeric fraction; estimated $\overline{M}_n$ 200-260.

initiator concentrations. The propylene polymer was also cationically initiated. Table I gives a brief description of these polymers.

Mass-Spectral Analysis. The analyses were performed on a CEC Model 21-110B mass spectrometer equipped with a razor-blade emitter; experimental details have been described.[11] The samples were introduced either through a heated batch inlet or via direct probe insertion into the ionization chamber (ion source). For the sample introductions through the batch inlet, the tables[12] show the temperatures of the vapor reservoir and the ionization chamber. For direct insertion, we employed a quartz temperature-programmable probe[13] that can be cooled/heated from −150 to +400 °C and fixed the source temperature at about 250 °C. The spectrum was scanned repeatedly to m/z 900 as the probe temperature was raised from an initial value of 5–10 °C to a maximum of 375 °C, under manual control with an eye to keeping the ion beam as nearly constant as possible. The sample temperature may lag the measured probe temperature;[14] the difference between them is uncertain, and, especially at higher temperatures, it may be considerable. Successive scans gave evidence of fractional distillation with increasing probe temperature, although the first scans usually showed inordinate amounts of higher molecular weight components, probably because of volatilization, under the influence of the source temperature, of material clinging to the walls of the glass sample tube near its open end. At masses[15] greater than about 100–150 u, all the spectra are dominated by peaks at mass numbers corresponding to the type formula $C_nH_{2n}^+$, which we attribute to olefin molecular ions. At lower masses, intensities of peaks due clearly to fragment ions, chiefly $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$, generally exceed those of $C_nH_{2n}^+$ peaks, and we assume that the latter are also attributable, at least in part, to fragments derived from larger molecules. We have taken relative intensities of the molecular ion peaks in a spectrum as an approximate measure of relative abundances of the respective oligomers.[16] The assumption of equal response factors for all oligomers probably yields a good approximation to carbon-number distribution over a narrow carbon-number range, although perhaps less so over a wider range. In the bulk our polymer samples are stable at 250 °C; e.g., they can be vacuum stripped at a 250 °C pot temperature without decomposition. For the most part, thermal degradation of the polymers during analysis appears unlikely.

Results

Propylene Polymers. Table II[12] shows the spectrum of the volatile fraction of a propylene polymer. The data indicate that substantial quantities of molecules are present that do not conform to the expected $(C_3H_6)_n$ formula. The components containing 21, 24, and 27 carbons, that is, those for which $n = 7$–9, predominate over their respective neighbors in the carbon-number listing. At carbon numbers both above and below this region, the intensity distribution reveals no memory of the propylene monomer from which the polymer was made.

Lachance and Eastham[3] have observed small amounts of C_{10}, C_{11}, C_{13}, and C_{14} molecules in propylene oligomers. A rough estimate based on the ion intensities of Table II suggests that about half the molecules in our poly(propylene) are not true polymers. The differences between Eastham's and our analyses may be attributable to different polymerization procedures.

1-Butene Polymers. Table III[12] shows the spectrum of the volatile fraction of a 1-butene polymer. Over nearly the entire mass range observed, the true 1-butene polymers, $(C_4H_8)_n$, predominate, but substantial quantities of molecules are also present that cannot be derived from 1-butene by simple polymerization.

***cis*-2-Butene Oligomers.** Table IV[12] gives the mass spectra of a *cis*-2-butene oligomer measured under three different sets of instrumental conditions, which are reflected most clearly in differing extents of volatilization of heavier components. The intensity distributions vary but little among the three spectra, supporting the view that no appreciable thermal decomposition intervened, even under the most severe conditions (spectrum B, reservoir temperature 345 °C).

The spectra show no intensity maxima at the masses corresponding to the true oligomers, $(C_4H_8)_n$. Thus, the distribution reveals no memory of the butene monomer. Some 80% of the molecules have carbon numbers that cannot be accounted for solely by butene polymerization. In the *cis*-2-butene oligomers studied by Lachance and Eastham,[4] the concentration of the true $(C_4H_8)_n$ oligomers was slightly higher than that of the anomalous members of the series. As in the case of propylene, the difference between their and our analyses may be attributable to the different initiators ($BF_3 \cdot CH_3OH$ in their work and $AlCl_3$ in ours) and to the different polymerization temperatures (probably −25 vs. 20 °C).

Isobutylene Polymers. Table V[12] summarizes the data for five different isobutylene polymers. The first two (A and B) were made with $AlCl_3$ initiator, the third (C) with BF_3, the fourth (D) with $BF_3 \cdot H_2O$, and the fifth (E) with $BF_3 \cdot {}^1/_2AcOH$. Comparison of the relative intensities of the true polymers and the anomalous species suggests that the polymers made with $AlCl_3$ (samples A and B) underwent more extensive secondary reactions than those made with BF_3-based initiators (samples C–E).

One of the polymers of Table V was also analyzed with direct probe introduction to the mass spectrometer. This analysis yielded results generally similar to those reported in Table V, but scans made at higher probe temperatures

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[11] Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Marecek, J. F.; Okazaki, H. *J. Am. Chem. Soc.* **1978**, *100*, 4062.

[12] See paragraph at end of paper regarding supplementary material.

[13] Purchased from Masspec, Inc., College Station, TX 77843.

[14] Franklin, W. E. *Anal. Chem.* **1979**, *51*, 992.

[15] Use of the simpler term, "mass", rather than the usual "mass to charge ratio (m/z)" introduces no ambiguity because z is equal to unity throughout this work.

[16] Compare (a) Mead, W. L. *Anal. Chem.* **1968**, *40*, 743. (b) Scheppele, S. E.; Hsu, C. S.; Marriott, T. D.; Benson, P. A.; Detwiler, K. N.; Perreira, N. B. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 335. (c) Schronk, L. R.; Grigsby, R. D.; Scheppele, S. E. *Anal. Chem.* **1982**, *54*, 748. (d) Yoshida, T.; Maekawa, Y.; Shimada, T. *Ibid.* **1982**, *54*, 967.

Table VII. Extent of Deviation from True Polymeric Formulas Found with Different Monomers and Polymerization Variables

monomer	initiator	polymerization temp, °C	extent of deviation,[a] %	rel freq of deviation,[b] %
triptene[c]	70% H_2SO_4	? (heated)	45	13.0
cis-2-butene	$AlCl_3$	20	80	8.9
cis-2-butene[d]	$BF_3\cdot CH_3OH$	-25[d]	49	6.9
propylene			55	1.3
propylene[e]	$BF_3\cdot CH_3OH$	-25	<10	0.4
1-butene	$AlCl_3$	20	46	1.5
isobutylene	$AlCl_3$	17-27	58	2.3
isobutylene	BF_3	0	35	0.8
isobutylene	$BF_3\cdot H_2O$	0-8	51	1.6
isobutylene	$BF_3\cdot AcOH$	0-8	20	1.0

[a] Crude estimates of percent of molecules with anomalous carbon numbers. In working with our own data, we have tried to distinguish between molecular ions, at higher masses, and fragment ions, at lower masses, and we have ignored the latter in deriving estimates of extent of deviation. In other cases we have estimated the extent of deviation from published data. [b] Half of the extent of deviation divided by the degree of polymerization (i.e., $\overline{M}_n$/mol wt of monomer). This definition is based on the assumption that one event leads to anomalous carbon numbers in two molecules. The values of $\overline{M}_n$ for the oligomers referenced in footnotes c, d, and e were not reported; we have estimated them as 170, 200, and 250, respectively, in order to allow a comparison. This estimation introduces additional uncertainty. [c] Reference 1. [d] References 3 and 4. [e] Reference 3.

revealed higher molecular weight components. Table VI[12] shows these data. The last scans of Table VI consist chiefly of these heavier components but also show increasing contributions in the low mass region, with a growing gap between the two regions. In these scans only high molecular weight materials should be observed because the low molecular weight fractions had been removed during the earlier scans. Thermal degradation of the polymer may well have set in at these high probe temperatures. In addition, the lower mass $C_nH_{2n}^+$ yields in these scans probably include progressively increasing contributions from fragment ions. In support of this appraisal, odd-mass fragment-ion peaks ($C_nH_{2n+1}^+$, $C_nH_{2n-1}^+$) extend in high intensity to higher masses in the spectra obtained at higher probe temperatures. For example, in the 250–285 °C scan, the ratio of abundances of $C_8H_{17}^+/C_8H_{16}^+$, $C_{12}H_{25}^+/C_{12}H_{24}^+$, and $C_{16}H_{33}^+/C_{16}H_{32}^+$, respectively, are 6.2, 1.4, and vanishingly small. The higher sample temperatures apparently promote decomposition—largely simply "unzipping" or depolymerization—following, as well as preceding, ionization. Thus, in the higher temperature scans, the more valid data for our purposes are those at higher mass numbers.

Discussion

Field-ionization mass-spectral analyses of the volatile fractions of cationic polymers of propylene, 1-butene, *cis*-2-butene, and isobutylene establish the presence of substantial amounts of molecules with formulas C_nH_{2n} that cannot be derived by simple polymerization. They contain different numbers of carbon atoms than the true polymers, i.e., $(C_3H_6)_n$ in case of poly(propylene)s or $(C_4H_8)_n$ in case of the poly(butylene)s. Thus, the earlier finding for triptene dimers[1] and *cis*-2-butene oligomers[2-4] applies also to the oligomers of propylene and the isomeric butylenes, and it may well be general for cationic olefin polymerizations.

In Table VII we estimate and compare on a molecular basis the extent of anomalous carbon-number products in triptene dimer, *cis*-2-butene oligomers, and low molecular weight polymers of propylene, 1-butene, and isobutylene. The values shown for the extent of deviation are approximate, for reasons described in the footnote to the table, but good enough for orientation purposes. These values vary widely. In a *cis*-2-butene oligomer made at 20 °C with $AlCl_3$ initiator, 80% of the molecules had anomalous carbon numbers; in a propylene polymer made probably at -25 °C[3a] with $BF_3\cdot CH_3OH$ initiator, less than 10% of the molecules had anomalous carbon numbers.

The extent of deviation from the expected polymeric formulas ignores the molecular weight of the polymer and may give a misleading impression of the frequency of the reactions leading to anomalous carbon numbers. Since propagation and the secondary reactions leading to anomalous carbon numbers occur side by side, their relative frequencies would seem to provide a better measure of the importance of the latter. For this reason, Table VII defines and reports the "relative frequency of the deviation". In triptene dimer and *cis*-2-butene oligomers, the relative frequency of these secondary reactions is an order of magnitude greater than in the polymers of propylene, 1-butene, and isobutylene. The data also suggest that the differences are in some measure attributable to the initiator and the polymerization temperature. In particular, aluminum chloride seems to give more anomalous carbon number product than boron trifluoride. A more systematic study would be required to clarify the influence of these variables.

Concerning the nature and mechanism of the reactions leading to anomalous carbon numbers in the polymers, two clear conclusions can be inferred: (1) these reactions must involve carbon–carbon bond fissions, because otherwise the anomalous products could not be accounted for; (2) the reactions must be incorporated into the polymerization chain reaction because the oligomers/polymers, when subjected to similar experimental conditions, do not react.[1,4] For the dimerization of triptene, Whitmore et al. proposed carbonium-ion rearrangements with hydride or methide shifts, followed by β-fissions, as part of the dimerization chain reaction. The proposed β-fissions generate *tert*-butyl cations, which can initiate a new chain by reacting with the monomer. The proposed types of reactions have become well established and accepted.[17,18] For illustration of the types of reactions involved, the scheme below can account for 4,4,5,5-tetramethyl-2-hexene (**3**), one of the many unexpected products from triptene.

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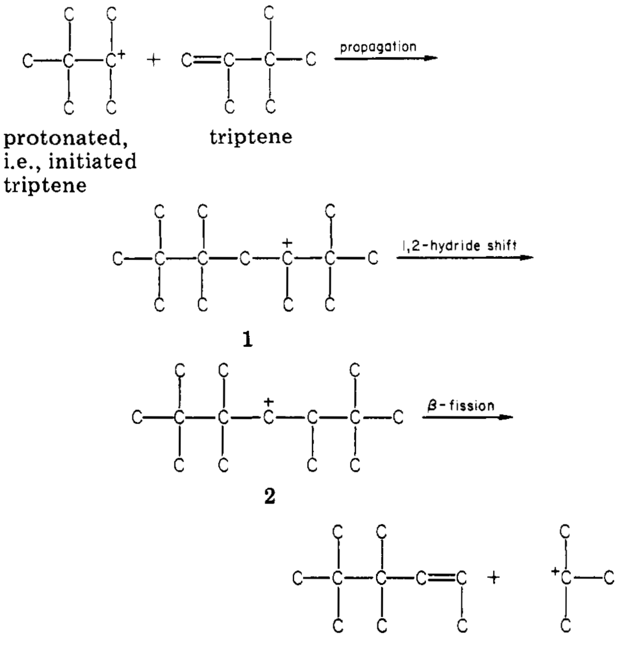
[17] For reviews and leading references, see: "Carbonium Ions"; Olah, G. A.; Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, especially Chapter 13 by Nenitzescu, C. D.; Chapter 14 by Fry, J. L.; Karabatsos, G. J.; and Chapter 15 by Keating, J. T.; Skell, P. S.

[18] Karabatsos, G. J.; Vane, F. M.; Meyerson, S. *J. Am. Chem. Soc.* **1963**, *85*, 733.



protonated, i.e., initiated triptene

triptene

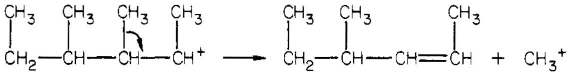
1

2

3

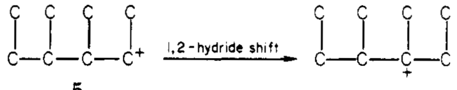
t-Bu cation

In the oligomerization of *cis*-2-butene, Lachance and Eastham[4] have suggested that the anomalous products may arise by transfer of methyl or ethyl cations to the monomer from a growing oligomeric cation, analogous to the proton transfer of the chain-transfer step. These authors, in an elegant study,[4] have separated and identified a large number of C_8 to C_{13} olefins from the products of *cis*-2-butene oligomerization, and they have shown how their mechanism can account in large part for both the skeletal rearrangements and the anomalous carbon-number products observed. Their proposed mechanism, expressed in other terms, involves β-fission of the oligomeric cations but at a methyl or ethyl side chain rather than along the polymer backbone (see illustration), as proposed by Whitmore[1] for triptene. Even though this reaction would generate a nominally primary cation **4**, complexing to a monomer molecule may avoid the formation of a free methyl cation. The methyl group could become attached to the monomer before a free primary methyl ion could form. Although primary carbonium ions have fallen into disrepute as postulated intermediates in alkyl rearrangements,[18] there are reports illustrating the probable involvement of primary carbonium ions in some cases.[19] Thus, the proposal of Lachance and Eastham[4] deserves further consideration and may prove to be valid for *cis*-2-butene oligomerization.



4

While our results do not define the reactions that give rise to products with anomalous carbon numbers, reviewing the available information on the subject can provide some insight. Steric factors in the intermediate polymer cations may play an important role (1) by hindering propagation through steric blocking of the ionic site and (2) by promoting carbon–carbon bond cleavage by β-fission as a means of relieving steric compression. Formulas **1** and **2**, respectively, show the classical and one rearranged dimeric triptene cation. The potential for steric hindrance and for steric blocking of the ionic site can be easily recognized. Formula **5** shows the classical dimeric ion derived from *cis*-2-butene. Here the vicinal methyl substituents create steric crowding. Rearrangement of **5** by 1,2-hydride shift into **6** increases the steric blocking of the ionic site and, hence, should hinder propagation and enhance the chances for carbon–carbon bond fission. In propylene and 1-butene polymers, similar steric blocking of the ionic sites may arise via two sequential 1,2-hydride shifts.[6,20] In the rearranged polymer cations **8** and **9** derived from propylene and **11** and **12** derived from 1-butene, the steric blocking may be sufficient to decrease the chances for propagation, thus increasing the likelihood of either carbon–carbon bond fission or proton loss with double-bond formation.



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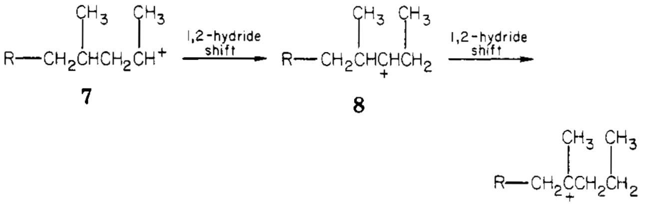

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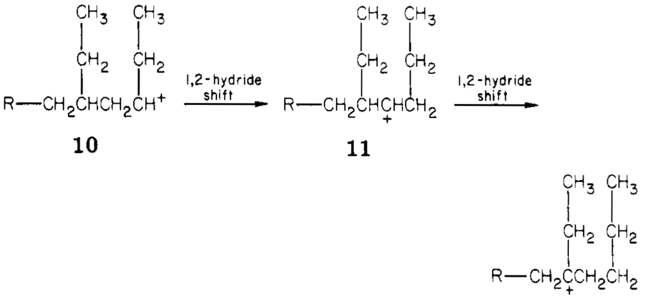
8

6



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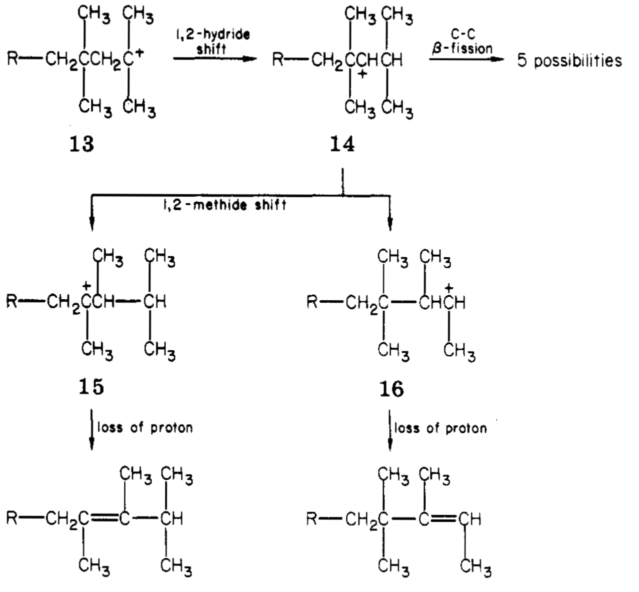
12

The case of isobutylene polymers is somewhat different. The growing polymer cations, **13**, are tertiary, relatively



13

14

15

16

17

18

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[19] (a) McCaulay, D. A. "Primary Carbonium Ions as Intermediates in Paraffin Isomerization"; Paper presented at the Chicago Catalysis Club Symposium, May 10, 1965. (b) Cooper, C. N.; Jenner, P. J.; Perry, N. B.; Russel-King, J.; Storesund, H. J.; Whiting, M. C.; *J. Chem. Soc., Perkin Trans. 2* **1982**, 605.

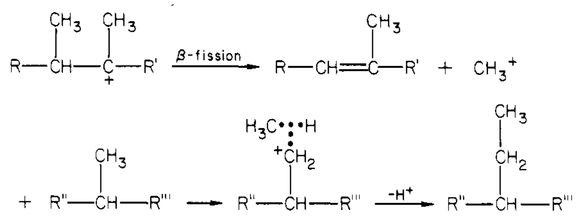
[20] Kelley, A. D.; Harvey, M. G. *J. Org. Chem.* **1961**, *26*, 4649.

stable, yet reactive. These ions, by β-fission, could give only depolymerization but no products with anomalous carbon numbers. However, **13** may rearrange to a less stable secondary cation, **14**. Whitmore has proposed this type of rearrangement,[1] as shown by the sequence from **1** to **2**. The cation **14**, by β-fission, could then lead to products with irregular carbon numbers. Identification of tetrasubstituted olefins[7] and unexpected trisubstituted olefins[7,21] in isobutylene polymers indicates that the cation **14** can further rearrange with 1,2-methide shifts to **15** or **16**, the precursors to the tetrasubstituted olefin **17** and the trisubstituted olefin **18**, respectively. This mechanistic route to the trisubstituted olefin **18** is more plausible than the explanation previously offered.[7]

If we assume that carbocations can cleave only by β-fission, we can derive only primary or secondary, but not tertiary, cations from **5–8**, **10**, **11**, and **14**. While one could derive rearranged structures from these polymeric cations that can give tertiary carbonium ions by β-fission, the rearrangements needed would be complex or would involve controversial reactions. Hence, we are inclined to believe that generation of secondary carbonium ions by β-fission is feasible and occurs during the formation of products with anomalous carbon numbers. The question of the generation of nominally primary cations by β-fission, possibly favored in sterically crowded ions, remains unsettled.

A potentially important consequence of the above-described mechanistic views is that the secondary reactions (rearrangements, carbon–carbon bond fissions, etc.) that occur during cationic polymerizations play a significant role in limiting and determining the polymer molecular weight.[6] In many polymerizations, their role in terminating the polymer growth may be much more important than the classical "chain transfer to monomer" described in polymer textbooks. With many monomers and, in particular in the context of the present work, with *cis*-2-butene, side reactions are so abundant relative to propagation that high polymers can not be synthesized at all. On the other hand, in cationic high molecular weight polymers, such as those prepared from isobutylene at very low temperatures, the contribution of carbon–carbon bond fissions relative to propagation approaches zero. Apparently, these reactions can be eliminated by lowering the polymerization temperature.

While the most likely reaction mechanisms have been discussed above, other, seemingly less probable ones may also be considered. For example, intermolecular methide transfer may occur from a polymer molecule to a polymer cation. Alternatively, free methyl or other small alkyl cations may be generated from sterically crowded polymer cations by β-fission; these ions, instead of reacting with a monomer molecule, could insert into the carbon–hydrogen bond of polymer molecule **19**, giving pentacoordinated carbonium-ion intermediates **20**, which, in turn, could stabilize by losing a proton. Such insertion into a methyl carbon–hydrogen bond would convert a methyl into an ethyl group.



Finally, we return to the question underlying our preliminary thinking as presented in the introduction. Has the failure to recognize the presence of products of anomalous carbon number resulted in any serious misconceptions? Except for carbon–carbon bond cleavages, the reactions leading to these products seem to be part and parcel of the same network of carbonium-ion reactions invoked to account for observed molecular structures differing from those expected from purely classical polymerization processes. Moreover, the data of Table VII suggest that the reactions leading to products of anomalous carbon number are often infrequent relative to the propagation reaction. Hence, lack of consideration of these products in the past has most likely not introduced serious errors in the interpretations of the pertinent spectroscopic analyses. A more precise answer will require separate evaluation for each individual case.

Acknowledgment. We thank A. M. Eastham for the stimulating discussions that triggered this work, D. A. McCaulay for sharing with us his lifetime experience with carbonium ions, E. S. Kuhn for the mass-spectral analyses, and D. H. Meyer for his valuable suggestions.

Registry No. Poly(propylene) (homopolymer), 9003-07-0; poly(1-butene) (homopolymer), 9003-28-5; poly(*cis*-2-butene) (homopolymer), 25989-99-5; poly(isobutylene) (homopolymer), 9003-27-4; aluminum chloride, 7446-70-0; boron trifluoride, 7637-07-2.

Supplementary Material Available: $C_nH_{2n}^+$ ions in field-ionization mass spectrum of polypropylene (Table II), $C_nH_{2n}^+$ ions in field-ionization mass spectrum of poly(1-butene) (Table III), $C_nH_{2n}^+$ ions in field-ionization mass spectrum of poly(*cis*-2-butene) (Table IV), $C_nH_{2n}^+$ ions in field-ionization mass spectra of various isobutylene polymers (Table V), and $C_nH_{2n}^+$ ions in field-ionization mass spectra of an isobutylene polymer distilled from probe (Table VI) (6 pages). Ordering information is given on any current masthead page.

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[21] Note 18 in ref 6.