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Contributions to the Mechanism of Isobutene Polymerization. III. Effect of Branched Alkenes and Influence of Steric Factors

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Summary

The effect of branched alkenes on the rate (yield) and molecular weight of polyisobutene has been investigated. Monosubstituted branched ethylenes, i.e., 3-methyl-1-butene, 3,3-dimethyl-1-butene, and 4-methyl-1-pentene, were found to be virtually inert and did not affect the polymerization of isobutene under our experimental conditions. 2,2-Disubstituted branched ethylenes, i.e., 2-methyl-1-pentene, 2-ethyl-1-hexene, 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentene, were rate poisons and strong transfer agents. The steric configuration of substituents in the vicinity of allylic hydrogens strongly influences the poison and transfer coefficients of these materials. These coefficients have been discussed quantitatively in terms of the allylic termination theory.

INTRODUCTION

The first two sections in this series presented the basic concept of allylic termination theory and discussed the effect of *n*-alkenes in terms of poison and transfer coefficients on isobutene polymerization (1,2). At this time, we investigated the effect of branched alkenes on the over-all polymerization rate (yield) and molecular weight of polyisobutene. A number of unexpected effects have been discovered and are now explained in the framework of the allylic termination concept. Subtle differences in the steric configuration of branched alkenes have a decisive influence on their poisoning and transfer activity in the polymerization mechanism.

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EXPERIMENTAL

The experimental procedure used was identical to that described previously (1).

RESULTS

The effect of a number of selected branched alkenes on the overall polymerization rate (yield) and molecular weight of isobutene is summarized in Figs. 1 to 4. The poison coefficients and transfer coefficients calculated from Figs. 1 and 2, respectively, by the method described in Ref. (1) are given in Table 1.

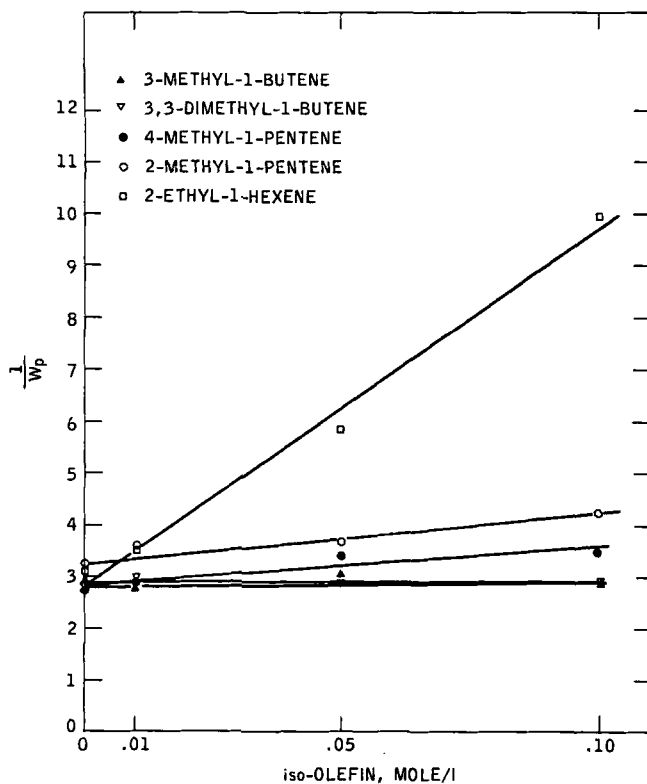


FIG. 1. Effect of isoalkenes on reciprocal polymer yield.

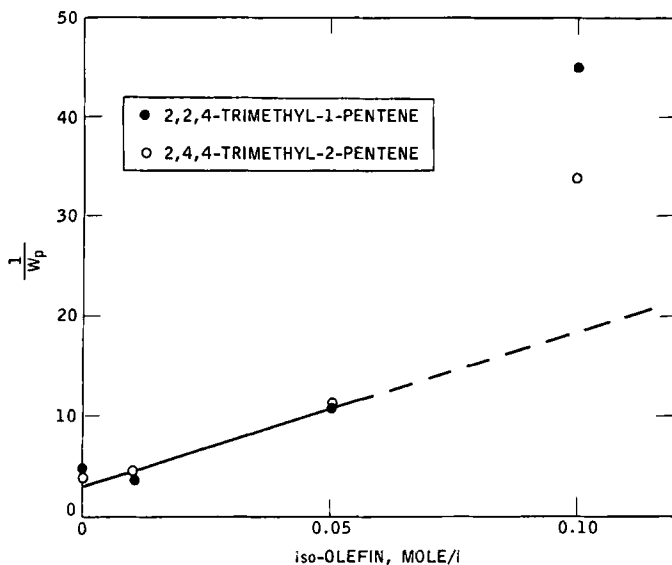


FIG. 2. Effect of isoalkenes on reciprocal polymer yield.

DISCUSSION

The most striking feature of these data lies in their duality. Whereas some of the materials in Table 1 appear to be inert (P.C. and T. C. = 0), others are both powerful poisons and transfer agents under our conditions. From the point of view of the present dis-

TABLE 1

Empirical Poison Coefficients and Transfer Coefficients of Branched Olefins

Isoalkene	Slope ^a	Int. ^a	P.C.	Slope ^b × 10 ⁻⁶	Int. ^b × 10 ⁻⁶	T.C.
3-Methyl-1-butene	0	2.8	0	0	1.0	0
4-Methyl-1-pentene	8	2.8	2.9	0	1.0	0
3,3-Dimethyl-1-butene	0	2.8	0	0	1.0	0
2-Methyl-1-pentene	11.3	3.2	3.5	78	1.45	53.8
2-Ethyl-1-hexene	69	2.8	24.7	360	1.45	248
2,2,4-Trimethyl-1-pentene	200	3.0	66.7 ^c	700	1.0	700 ^c
2,4,4-Trimethyl-2-pentene	200	3.0	66.7 ^c	45	1.3	34.6

^a Calculated from Fig. 1.

^b Calculated from Fig. 2.

^c Became nonlinear at high poison concentrations.

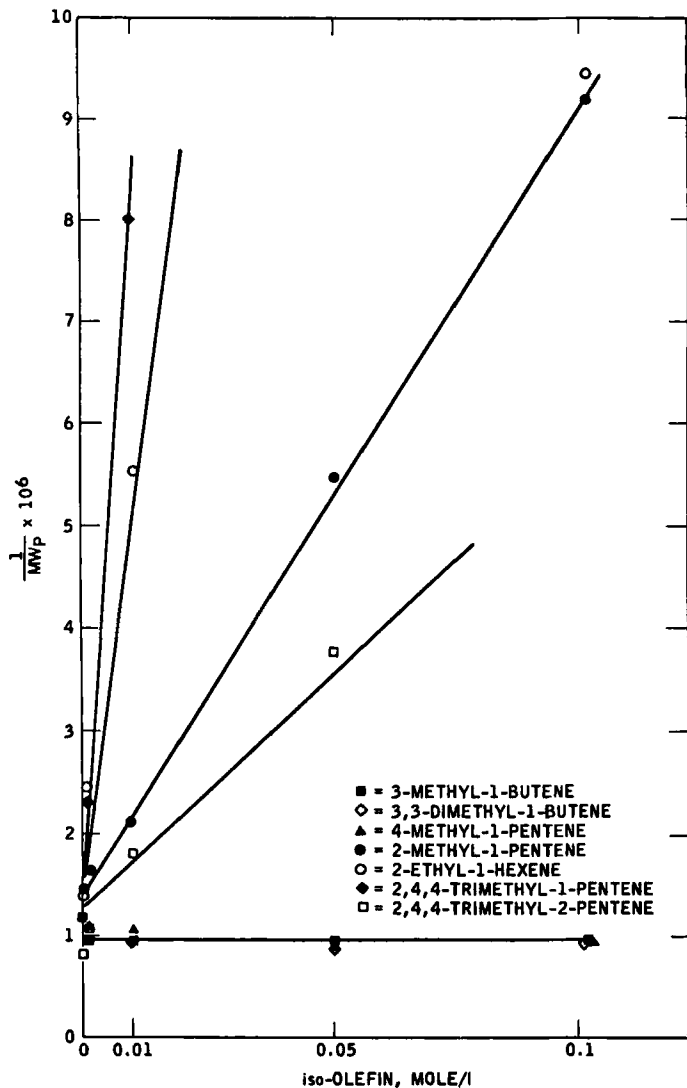


FIG. 3. Effect of isoalkenes on reciprocal molecular weights.

cussion it is best to differentiate between two kinds of branched olefins: monosubstituted ethylenes (the first three compounds in Table 1) and 2,2-disubstituted ethylenes (the rest of the compounds in Table 1).

Monosubstituted ethylenes carrying a branch α to the double

bond behave as inert materials under our experimental conditions. The inertness of 3-methyl-1-butene was unexpected. Since this molecule contains a tertiary allylic hydrogen atom, we anticipated a powerful rate-inhibiting effect on the polymerization of isobutene. Experimentally, however, this material turned out to be "non-

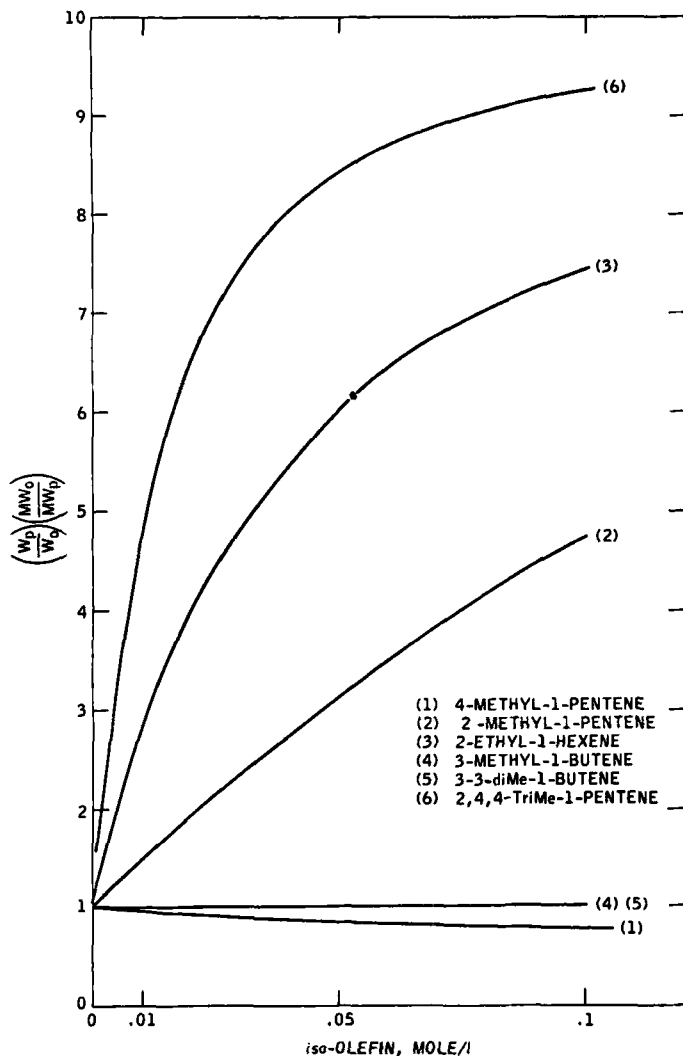
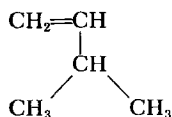
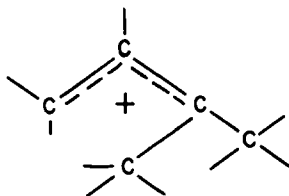


FIG. 4. Effect of isoalkenes on relative number of polymer molecules formed.

poisonous." An explanation is probably that the allylic H is shielded by the vinyl and two methyl groups in the molecule



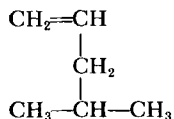
and the attacking carbonium ion cannot react it, so no hydride transfer can occur. Fisher-Briegleb models indicate that about 50% of the available space around the allylic hydrogen is shielded by neighboring groups. These models also suggest that the primary-tertiary 1,1-disubstituted allyl ion obtainable from 3-methyl-1-butene on hydride abstraction is probably sterically hindered, which might considerably decrease its stability; i.e.,



The surprising inertness of this molecule also manifests itself in the zero value of its transfer coefficient.

The situation is similar to vinylcyclohexane, whose P.C. and T.C. are also very low, 3.72 and 6.6, respectively. Vinylcyclohexane and 3-methyl-1-butene are structurally closely related. The reason vinylcyclohexane has a measurable poison coefficient at all is probably because the rotation of the two methylene groups shielding the allylic H is somewhat restricted.

If the shielding groups around the allylic hydrogen are partially removed, poisoning activity reappears. In 4-methyl-1-pentene, for example, the two secondary allylic hydrogens are flanked by a vinyl and an isopropyl group:

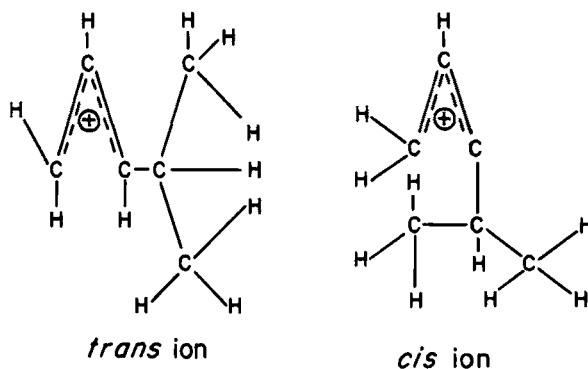


Evidently, steric hindrance toward allylic hydrogen abstraction is not as severe in this case as with 3-methyl-1-butene, and 4-methyl-

1-pentene starts to exert a limited amount of poisoning, P.C. = 2.86, but still does not affect the molecular weights, T.C. = 0. Consequently, we may regard 4-methyl-1-pentene as a weak rate poison.

It is interesting to note that the poisoning activity of 4-methyl-1-pentene carrying secondary allylic hydrogens is somewhat less than that of propene P.C. = 4.9 with primary allylic hydrogens. A possible explanation is that the isopropyl group in 4-methyl-1-pentene exerts some shielding over the allylic hydrogens, which cannot be the case with propene (e.g., 4-methyl-1-pentene can be regarded as a propene molecule in which one of the CH_3 hydrogens is replaced by an isopropyl group). It is expected that by removing farther the steric hindrance from around the allylic hydrogens, i.e., in 6-methyl-1-heptene, for example, the poison and transfer coefficients will approach that of the corresponding straight-chain 1-alkenes. In this context it is important to mention that tertiary hydrogens are apparently inert under our conditions. Isobutane, for example, is a completely inert solvent.

Another factor which might be considered with 4-methyl-1-butene is the stability difference of the geometric isomers of allyl ions derivable from this olefin. In contrast to 3-methyl-1-butene, which can yield only one allylic ion, 4-methyl-1-butene can give a *cis* and *trans* allylic carbonium ion. Models indicate that the *cis* ion is sterically heavily restricted, so its stability is probably low in comparison to the *trans* ion, whose rotation is almost completely free, i.e.,



Conceivably, the poisoning activity might mainly be due to the more stable *trans* ion. If neither of these ions would be restricted, 4-methyl-1-pentene would probably be a more severe poison. Thus

it is anticipated that 5-methyl-1-hexene, in which the allylic hydrogens are less shielded and which would yield less hindered allylic ion isomers, would be a stronger poison than 4-methyl-1-pentene.

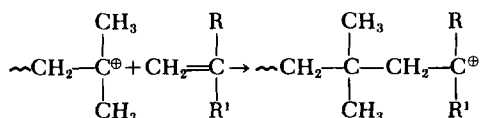
The fact that 3,3-dimethyl-1-butene appears to be completely inert in our polymerization system is to be expected, since no allylic hydrogen atoms are present in this molecule. This finding is strong evidence for the correctness of the basic hypothesis of allylic termination.

Transfer efficiency of various materials presumably involves a reaction in which the particular agent is incorporated into the growing polyisobutene chain. Evidently, if the propensity of the newly formed chain end for proton expulsion is larger than that of the polyisobutene carbonium ion, the H^{\oplus} will be ejected; i.e., chain breaking occurs which will result in lowered molecular weights. However, with monosubstituted ethylenes in general, incorporation in the polyisobutene chain would mean the formation of a secondary carbonium ion. Since the energetics of this reaction would be quite unfavorable (i.e., tertiary \rightarrow secondary ion), it is unlikely that these materials could be incorporated into the polyisobutene chain under conventional experimental conditions. Thus it is not unexpected that 1-alkenes, normal or iso, do not exhibit chain-transfer activity but, nevertheless, might have appreciable poison coefficients.

Turning to 1,1-disubstituted ethylenes, another type of steric effect must be considered. The 1,1-disubstituted ethylenes can be regarded as isobutene homologs and consequently should be susceptible to cationic attack and subsequent polymerization to high polymer. However, this is not the case experimentally and, in fact, even the next simplest higher homolog, 1-methyl-1-ethyl ethylene (or 2-methyl-1-butene), gives low molecular weight products in low yield under conventional cationic polymerization conditions. The most likely explanation for this behavior is that the carbonium ion which is formed from this monomer is a crowded or "buried" one and is impeded from propagating efficiently due to steric hindrance around the growing site. Such sterically hindered carbonium ions most likely stabilize themselves to branched internal olefins by proton elimination. It is known that even the simplest 2,2-disubstituted ethylene, isobutene, requires about 6.7 kcal/mole to overcome steric hindrance to polymerization (3,4). This energy requirement must necessarily be greater and the

crowding around the propagating site more severe with higher homologs, whose substituents are necessarily larger than the methyl group. Consequently, the life time of carbonium ions derived from isobutene homologs will be longer than that derived from isobutene itself, and the bulkier ions will be more apt to stabilize by proton expulsion. Thus lowered rates and/or molecular weights could be expected in the presence of these more sterically hindered materials.

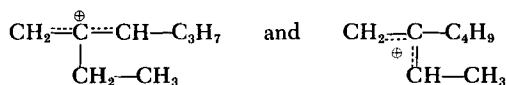
When isobutene is polymerized cationically in the presence of 2,2-disubstituted ethylenes, incorporation of the latter could take place:



This step is exoenergetic, since energy is gained by creating a new C—C bond, and the energy of the new tertiary carbonium ion is probably quite similar (or higher) to that of the original carbonium ion of the *t*-butyl type. With *n*-alkenes or monosubstituted ethylenes, such an incorporation is much less likely to occur, since the new carbonium ion would be a less stable secondary cation.

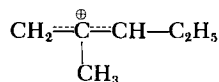
Obviously, then, when isobutene is polymerized in conjunction with isoalkenes steric factors *and* allylic termination might affect the over-all rate and average product molecular weight. Experiments reflect the over-all effect and it is difficult to separate these influences.

It is interesting to examine and compare the results obtained with 2-methyl-1-pentene and 2-ethyl-1-hexene (see Table 1). The allylic termination theory would suggest that 2-ethyl-1-hexene possessing four secondary allylic hydrogens gives two dissimilar but energetically virtually identical end-and-middle-substituted allyl carbonium ions; e.g.,

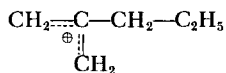


whereas 2-methyl-1-pentene carrying two secondary allylic hydrogens and three primary allylic hydrogens will give preferentially

the more stable

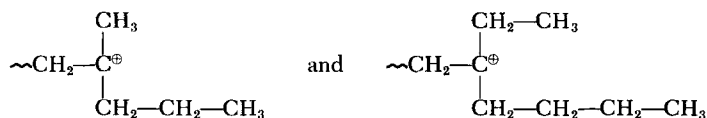


and perhaps some



ions. In other words, 2-ethyl-1-hexene is expected to be a relatively more efficient allylic hydrogen donor than 2-methyl-1-pentene.

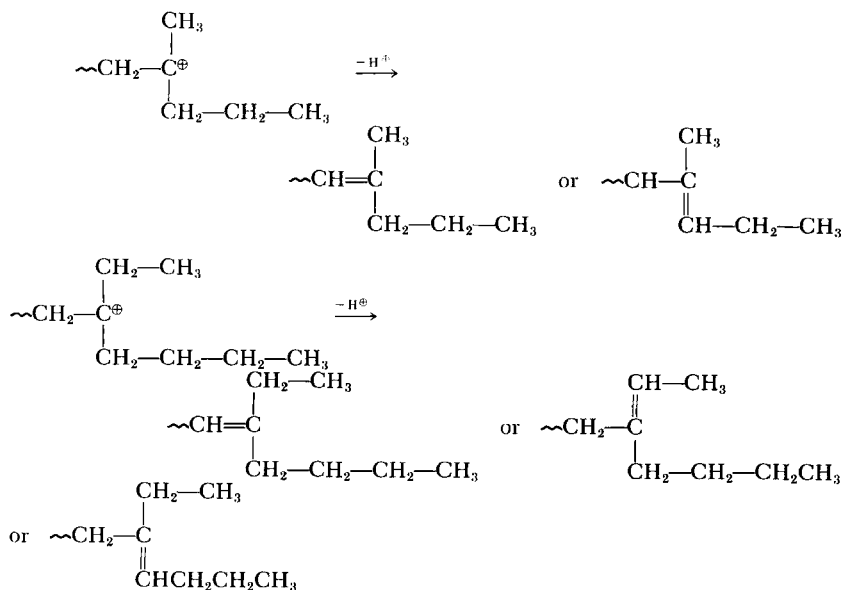
However, it is quite likely that the over-all energetics of propagation, i.e., incorporation of these isoolefins in the polyisobutene chain, is more favorable than that of termination by hydride abstraction and allylic stabilization. Thus it may be assumed that 2-methyl-1-pentene and 2-ethyl-1-hexene would enter the propagating chain, giving the following tertiary carbonium ions:



These ions are "buried" or sterically hindered carbonium ions and as such will conceivably slow down further propagation considerably. Consequently, the poisoning activity of these, and probably similar isoolefins, can be attributed to steric hindrance rather than to simple termination of allylic stabilization. From this it follows that the somewhat larger P.C. of 2-ethyl-1-hexene than that of 2-methyl-1-pentene could be due to the additional $\text{---CH}_2\text{---}$ group around the growing site in the former molecule.

Both isoolefins, 2-methyl-1-pentene and 2-ethyl-1-hexene, have pronounced transfer activity. Whereas the former compound is a mild transfer agent (T.C. = 53.8), 2-ethyl-1-hexene is a stronger transfer agent (T.C. = 248). Transfer activity of these olefins in general and the difference in transfer activities between 2-methyl-1-hexene and 2-ethyl-1-hexene in particular can be explained in terms of carbonium ion lifetimes and stabilization by proton expulsion. Both carbonium ions derivable from these olefins have increased lifetimes (crowded carbonium ions and thus sterically retarded propagation) as compared to the polyisobutene cation and

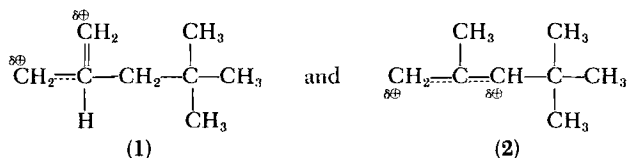
as such are more apt to stabilize by H^{\oplus} elimination. The essential difference between the two isoalkene ions is the number of secondary (expellable) hydrogens α to the electron-deficient carbon; i.e., whereas the incorporated 2-methyl-1-pentene ion has only 4 s -hydrogens and can stabilize to two internal olefins, the incorporated 2-ethyl-1-hexene cation has 6 s -hydrogens and can yield three internal olefin structures by proton elimination:



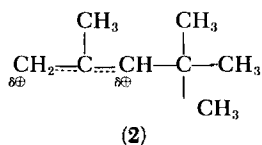
The expelled proton then can protonate a new isobutene monomer molecule initiating a new chain, i.e., reducing the molecular weight. Again it is interesting to note the strong chain-transfer activity, enhancing influence of the two additional secondary hydrogens α to the electron-deficient carbon in the case of 2-ethyl-1-hexene cation.

The case of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene is particularly revealing. The effect of mixtures of these materials on the rate and molecular weight of polyisobutene has been investigated by Thomas et al. (5) and Horrex and Perkins (6). These authors found a severe molecular weight decreasing effect when isobutene was polymerized in the presence of these compounds. Our findings corroborate and expand these observations. The facts

show that 2,4,4-trimethyl-1-pentene is a strong rate poison (P.C. = 66.7) and a strong molecular-weight depressor (T.C. = ~700), whereas the other isomer 2,4,4-trimethyl-2-pentene is a strong rate poison (P.C. = 66.7) but a comparatively mild transfer agent, i.e., molecular weight depressor (T.C. = 34.6). The allylic ions formed by hydride transfer to the growing polyisobutene chain from these isomers are

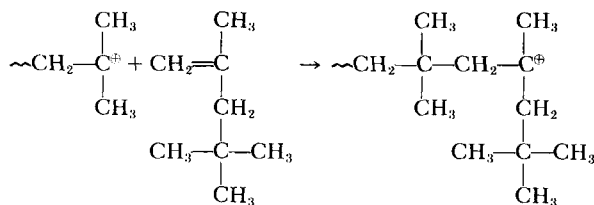


from 2,4,4-trimethyl-1-pentene, and

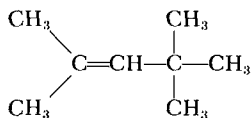


from 2,4,4-trimethyl-2-pentene. Since the di-primary middle-substituted allyl ion (1) is energetically much less favored than the primary-tertiary middle-and-end-disubstituted allyl ion (2), 2,4,4-trimethyl-1-pentene most likely yields the latter on allylic termination, which is the same as that formed from 2,4,4-trimethyl-2-pentene. In other words, the allyl cations resulting from the two isomers could conceivably be identical. Fisher-Briegleb models indicate clearly that the two secondary allylic hydrogens in 2,4,4-trimethyl-1-pentene are relatively unhindered and that there is probably only a small degree of steric hindrance impeding hydride transfer to the growing polyisobutene carbonium ion. Thus termination by allyl hydrogen transfer could explain the fact that these two isomers exhibit similar poison coefficients.

Significantly, however, the 1-pentene isomer strongly depresses molecular weights, whereas the other isomer shows much less of an effect. An explanation could be that 2,4,4-trimethyl-1-pentene can easily be incorporated at the end of a growing isobutene chain:



resulting in a strongly buried carbonium ion. This hindered ion is unable to propagate, has an extended lifetime, and stabilizes itself by proton expulsion; i.e., chain transfer takes place. On the other hand, molecular weights are much less affected with the 2,4,4-trimethyl-2-pentene isomer, which is unable to incorporate into the growing carbonium ion because of its sterically protected unreactive internal double bond:



At this point the question arises whether the molecular weight effect of 1,1-disubstituted ethylenes is due to strong poisoning (row 3c, Fig. 2, Ref. 1) or to a combination of poisoning and transfer activity (row 4, Fig. 2, Ref. 1). Molecular weight depression in these cases cannot be explained with pure transfer activity (row 2, Fig. 2, in Ref. 1) because the poison coefficients are also appreciable. The answer is spelled out in Fig. 3, according to which the n_p/n_0 ratio, i.e., the number of polymer molecules produced, increases strongly with increasing 1,1-disubstituted ethylene concentration. Consequently, these materials are most likely fairly strong transfer agents.

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Zusammenfassung

Der Einfluss von verzweigten Alkenen auf die Geschwindigkeit (Ausbeute) und das Molekulargewicht von Polyisobutylen wurde untersucht. Monosubstituierte, verzweigte Äthylene, z.B. 3-Methyl-1-buten, 3,3-Dimethyl-1-buten, und 4-Methyl-1-penten verhielten sich wie Inertsubstanzen und beeinflussten die Polymerisation von Isobutylen unter den von uns gewählten Bedingungen überhaupt nicht. 2,2-disubstituierte, verzweigte Äthylene wie z.B. 2-Methyl-1-penten, 2-Ethyl-1-hexen, 2,4,4-Trimethyl-1-penten, und 2,4,4-Trimethyl-2-penten verhielten sich als Katalysatorgifte und waren starke Überträger. Die sterische Konfiguration der Substituenten in der Nähe der Allyl-Wasserstoffatome beeinflusst sehr stark die Vergiftungs- und Überträgerkoeffizienten dieser Substanzen. Diese Koeffizienten wurden in quantitativer Weise mit Hilfe der Allyl-abbruch-Theorie diskutiert.

Résumé

On a étudié l'effet des alcènes branches sur la vitesse (rendement) et le poids moléculaire de polyisobutène. On a trouvé que les éthylènes monosubstitués ramifiés c. a. d. le méthyl-3-butène-1, et le méthyl-4-pentène-1 sont pratiquement inerts et n'affectent pas la polymérisation l'isobutène dans nos conditions expérimentales. Les éthylènes branchés disubstitués en positions 2,2 c. a. d. le méthyl-2-pentène-1, l'éthyl-2-hexene-1, le triméthyl-2,4,4-pentène-1, et le triméthyl-2,4,4-pentène-2 sont des poisons de vitesse et des puissants agents de transfert. La configuration stérique des substituants au voisinage des hydrogènes allyliques influencent fortement les coefficients empoisonnants et de transfert de ces substances. On discute ces coefficients quantitativement à l'aide de la théorie allylique de terminaison.