Contributions to the Mechanism of Isobutene Polymerization. V. Effect of Cyclic Olefins

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Contributions to the Mechanism of
Isobutene Polymerization. V. Effect of Cyclic Olefins

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Summary

The effect of various cyclic and bicyclic olefins on the yield (rate) and molecular weight of polyisobutene has been investigated. Cyclic olefins were found to be both rate poisons and transfer agents and the corresponding coefficients appear to be a function of ring size. Alkyl and aryl substitution on the ring increases both the poison and transfer coefficients. With bicyclic olefins, norbornene and norbornadiene both show moderate and similar poison coefficients, but only the former exhibits transfer activity. These coefficients have been discussed in terms of the allylic termination hypothesis and the known geometry and steric effects of the various rings studied.

In previous sections of this series we have attempted to correlate linear and branched olefin structures with the poison coefficient (yield-decreasing effect) and the transfer coefficient (molecular-weight-decreasing effect) of isobutene polymerization (1). We have now investigated the influence of cyclic and bicyclic olefin structures upon the overall polymerization rate (yield) and the molecular weight of polyisobutene. These olefins represent interesting structural problems by virtue of their fixed geometry. The results can be explained by correlating poison and transfer coefficient values with carbonium ion stabilities. A reduction in steric hin-

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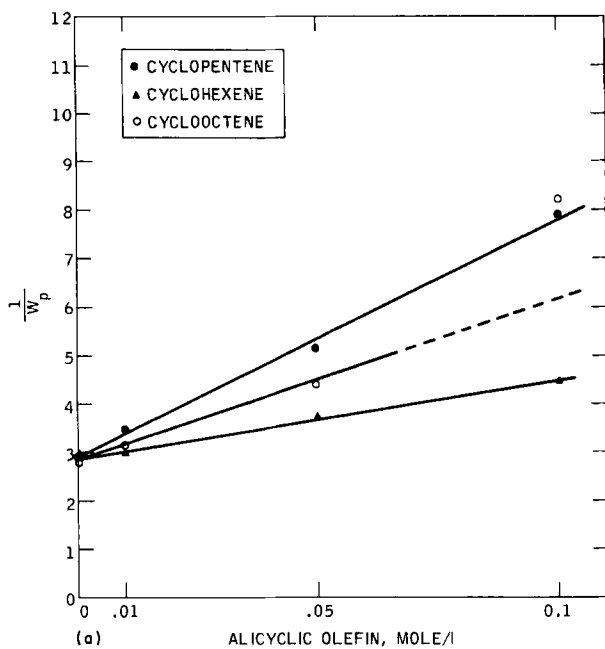
FIG. 1a. Effect of alicyclic olefins on reciprocal polymer yield.
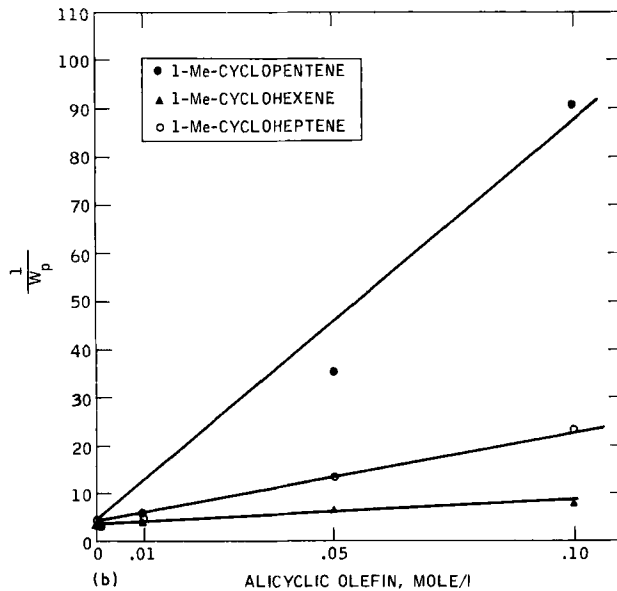
FIG. 1b. Effect of alicyclic olefins on reciprocal polymer yield.
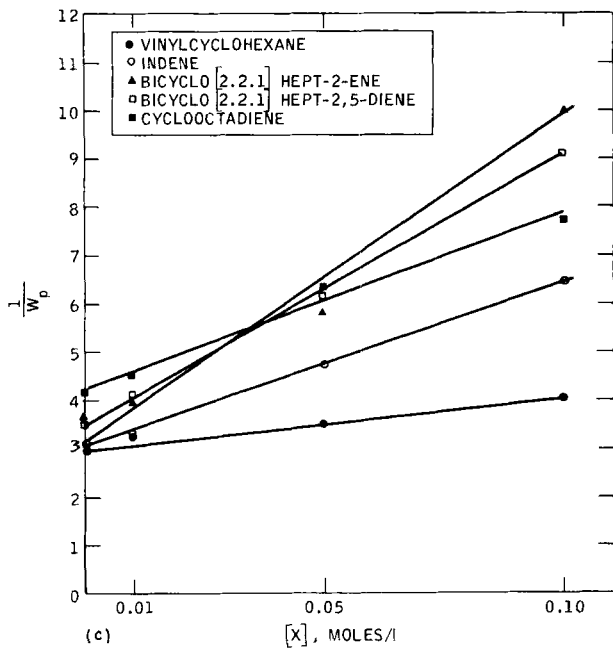
FIG. 1c. Effect of various hydrocarbons on reciprocal polymer yield.
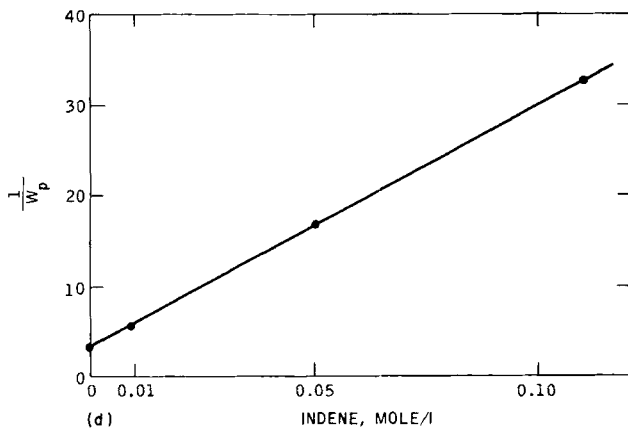
FIG. 1d. Effect of indene on reciprocal polymer yield.

drance and an increase in double-bond strain of the olefin seem to contribute to transfer activity.

EXPERIMENTAL

The experimental procedure has been described in the first paper of this series (1).

RESULTS

The effect of various cyclic olefins on the overall yield (polymerization rate), the molecular weight of polyisobutene, and the number of polymer molecules formed are summarized in Figs. 1a, 1b, 1c, 1d, 2a, 2b, 2c, 3a, 3b, and 3c. The poison and transfer coeffi-
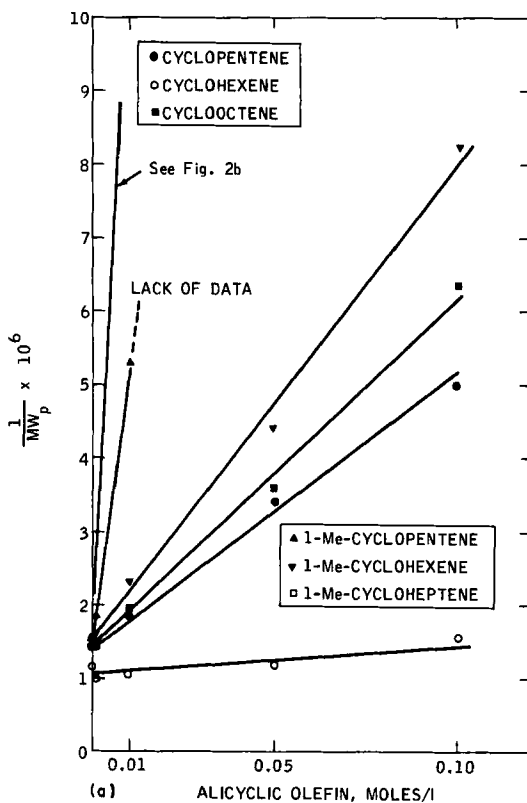
FIG. 2a. Effect of alicyclic olefins on reciprocal molecular weight.
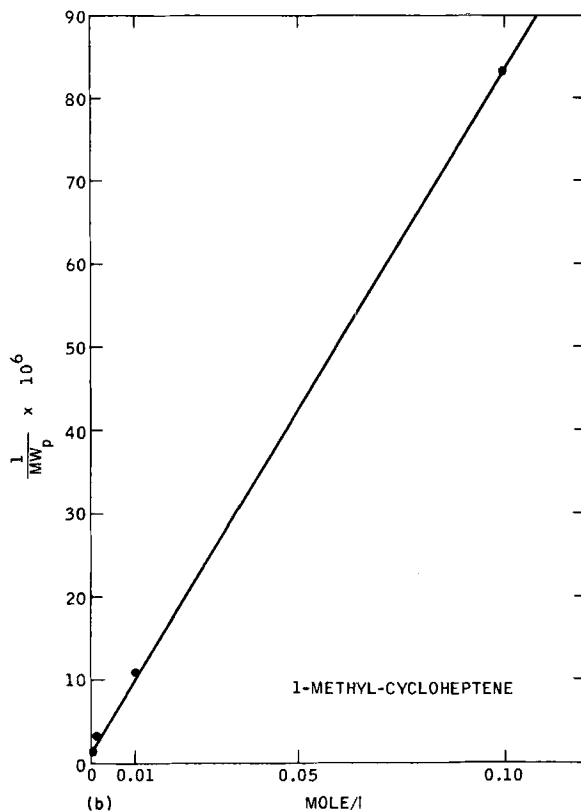
FIG. 2b. Effect of alicyclic olefins on reciprocal molecular weight.

cients calculated by the method described in Ref. *1* are shown in Table 1.

DISCUSSION

Cyclic olefins strongly affect the yield and molecular weight of polyisobutene. The effects of ring size, alkyl and aryl substitution on the ring, and bicyclic structures have been examined and will now be discussed.

The effect of ring size on the yield (rate) of isobutene polymerization is indicated by comparing the poison coefficients in Table 1 for cyclopentene (P.C. = 16.3), cyclohexene (P.C. = 5.3), and cyclooctene (P.C. = 11), where the following order is obtained: $C_5 > C_8 > C_6$. Since an explanation for the poison coefficients arises from the
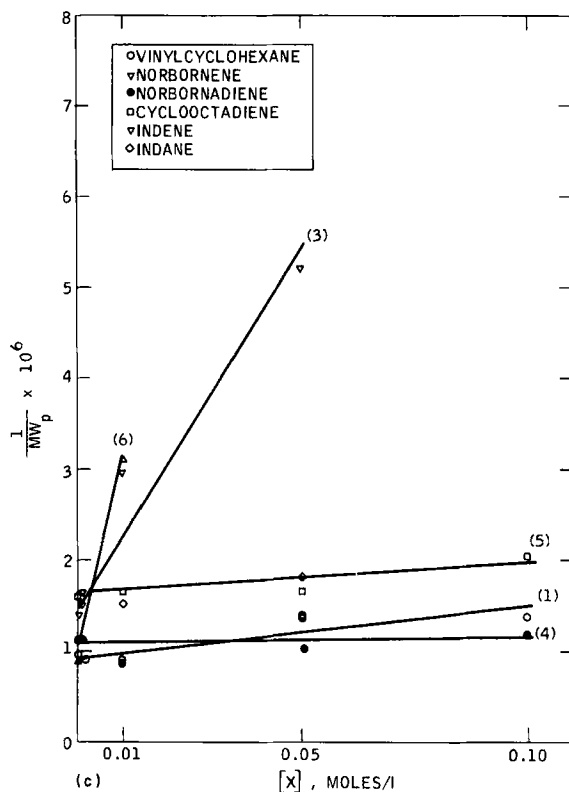
FIG. 2c. Effect of various hydrocarbons on reciprocal molecular weight.

concept of polymerization termination by allylic stabilization, the magnitudes of these coefficients should reflect the stability of the resulting allylic ions. This is substantiated in that the cyclic allylic carbonium ions produced by other means have stability preferences comparable to the observed order. It is known, for example, that cyclopentenyl chloride solvolyzes 600 times faster than cyclohexenyl chloride in ethanol (2), explained by the relief of the hydrogen-hydrogen eclipsing strain in forming the cyclopentenyl carbonium ion in contrast to the increase in strain in forming the cyclohexenyl carbonium ion. Since the eight-membered ring is more strained than the six, the cyclooctenyl carbonium ion should

be more stable than the cyclohexenyl but less stable than the cyclopentenyl carbonium ion, which in fact is observed experimentally.

The chain transfer activity observed in the presence of these compounds is likely the result of hydride abstraction from the cyclic olefin followed by proton expulsion from the resulting allylic ion

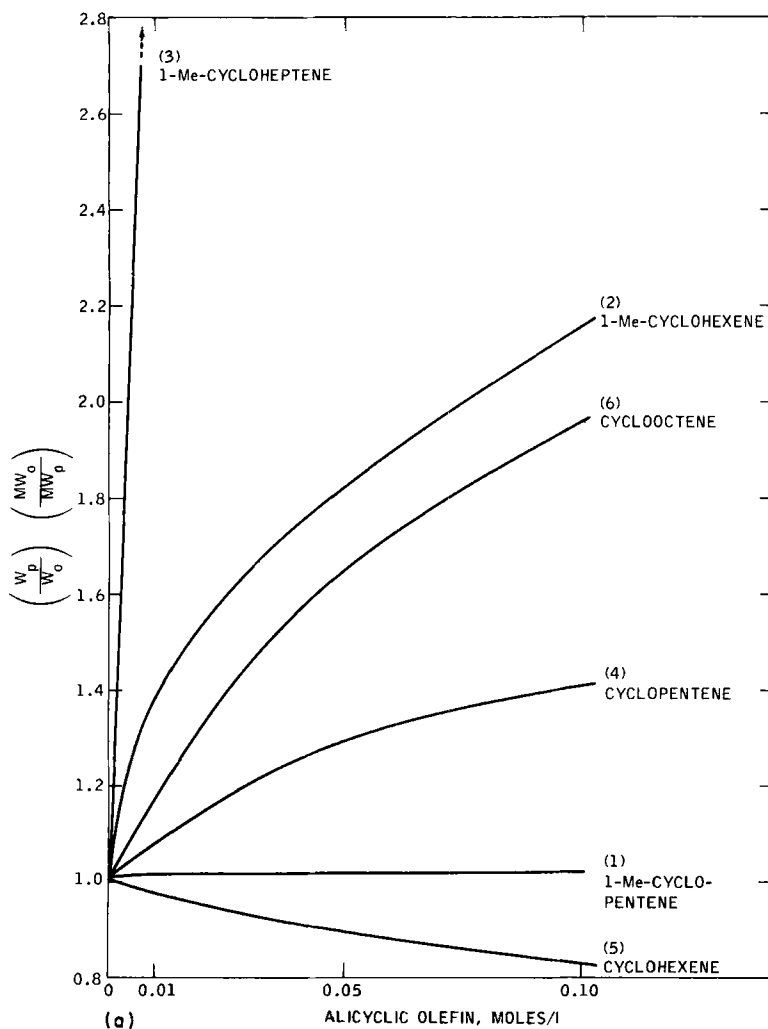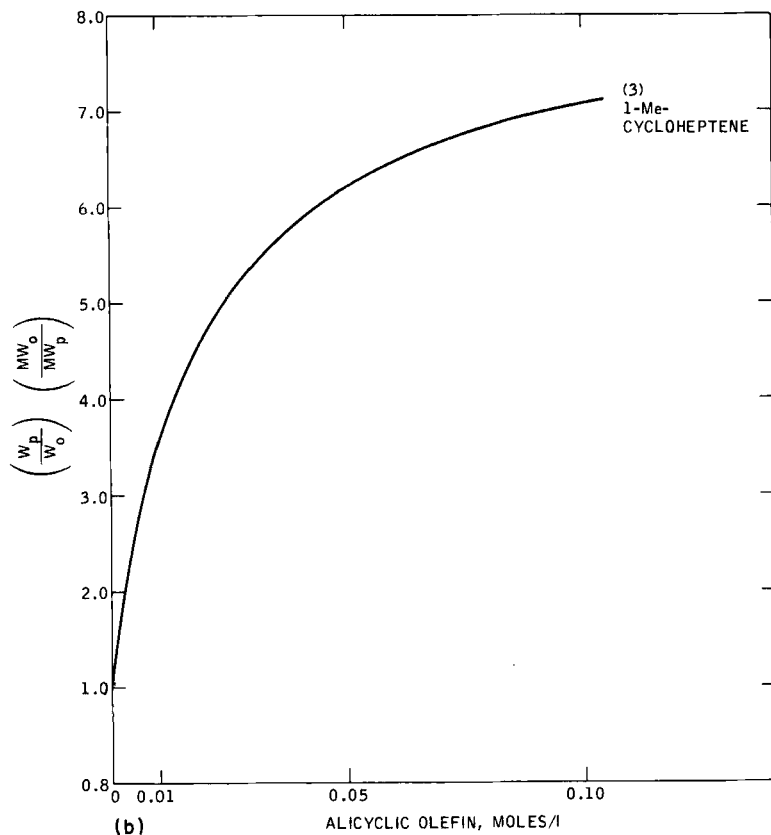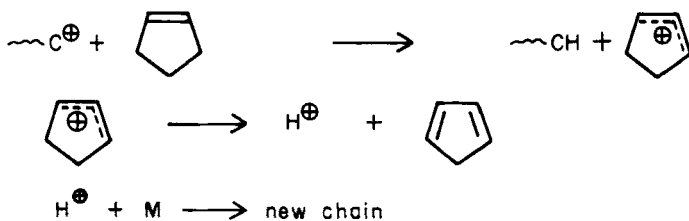**FIG. 3a.** Effect of alicyclic olefins on number of polymer molecules formed.

FIG. 3b. Effect of alicyclic olefins on number of polymer molecules formed.

to form the conjugated diene and a proton which initiates a new chain. For example:

$$H^{\oplus} + M \longrightarrow new\ chain$$

The low transfer coefficient for cyclohexene in contrast to the higher values for cyclopentene and cyclooctene indicate that di-

olefin formation might only be significant when relatively stable diolefins are formed, i.e., cyclopentadiene and cyclooctadiene.

As for nonconjugated diolefins, it is interesting that the poison coefficient for 1,5-cyclooctadiene (P.C. = 9) is very similar to that of cyclooctene (P.C. = 11), suggesting that the two double bonds act independently. This is in contrast with the previously studied conjugated olefins, where, with the exception of butadiene, much higher poison coefficients were obtained (3). This could be explained either by the diolefin failing to isomerize to the conjugated structure under our low-temperature conditions or by the nonplanarity of the cyclooctyl ring, which diminishes the conjugative effect.

On the other hand, the chain transfer coefficient of 1,5-cyclooctadiene (T.C. = 1.8) is considerably lower than that obtained for
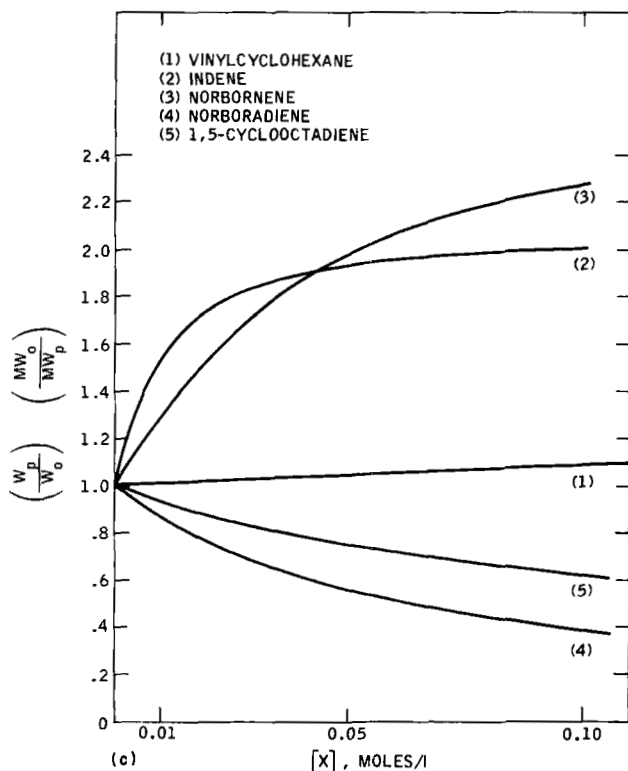

FIG. 3c. Effect of various hydrocarbons on relative number of polymer molecules formed.

cyclooctene (T.C. = 31.2). Chain transfer activity has been ascribed to proton expulsion by the allylic ion to form a polyene. Whereas for the cyclooctenyl allylic cation the product is a diene, the cyclooctadienyl cation gives a triene under corresponding conditions:

$$H^{\oplus} + M \longrightarrow \text{new chain}$$

$$H^{\oplus} + M \longrightarrow \text{new chain}$$
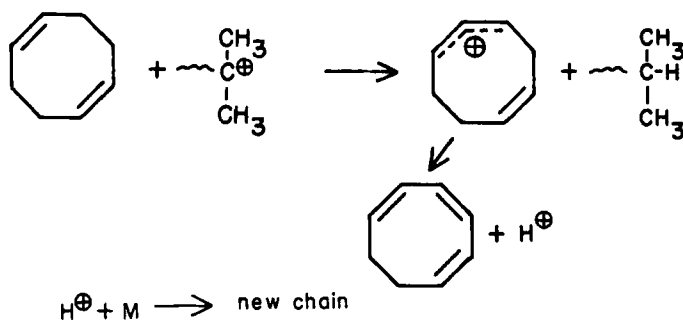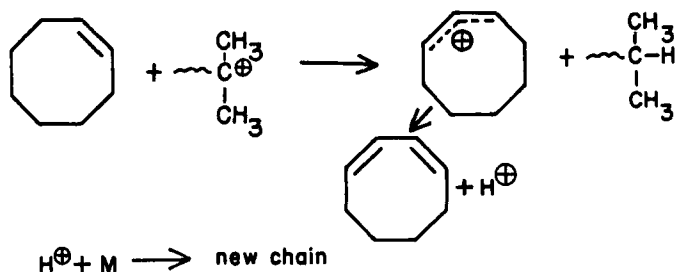
The latter compound, 1,3,5-cyclooctatriene, is probably not very favored, owing to the preferred tub structure of the C_8 ring. Proton loss from the corresponding allylic ion is therefore not favored, which might explain the low chain transfer coefficient of the parent nonconjugated diene.

The effect of alkyl substitution of cyclic olefins was studied by comparing the poison and transfer coefficients of substituted cyclic olefins with those of corresponding unsubstituted compounds. As shown in Table 1, both coefficients are larger for the substituted olefin. As for the poison coefficients, a methyl group on a five-membered ring brings about a 17-fold increase, whereas the same substituent in a six-membered ring brings about a change of about 3-fold. In the medium-sized rings (seven and eight), 6-fold increase

TABLE 1

Empirical Poison Coefficients and Transfer Coefficients of Alicyclic Olefins

Cyclic olefin	Slope[a]	Int.[a]	P.C.	Slope[b] 10^{-6}	Int.[b] 10^{-6}	T.C.
Cyclopentene	49	3.0	16.3	38	1.4	27
Cyclohexene	16	3.0	5.3	3	1.1	2.7
Cyclooctene	33	3.0	11	47	1.5	31.2
1-Methylcyclopentene	840	3.0	280	400	1.4	286
1-Methylcyclohexene	44	3.0	14.7	65	1.5	43.4
1-Methylcycloheptene	200	3.0	66.7	810	1.5	540
Indane	33	3.0	10.8			
Indene	296	3.0	99	210	1.0	210
Norbornene	68	3.5	19.4	80	1.4	57.2
Norbornadiene	56	3.5	16.0	0	1.1	0
1,5-Cyclooctadiene	37	4.1	9.0	3	1.6	1.8
Vinylcyclohexane	11	2.9	3.7	6	0.9	6.7
Benzene			0			0
Toluene			0			0
o-, p-, and m-Xylene			0			0

[a] Calculated from Fig. 1.
[b] Calculated from Fig. 2.

is observed. The increase in the P.C. in the six-membered and medium-sized rings is probably due to the increases in both the number and ease of formation of possible allylic ions:

(1)   (2)   (3)
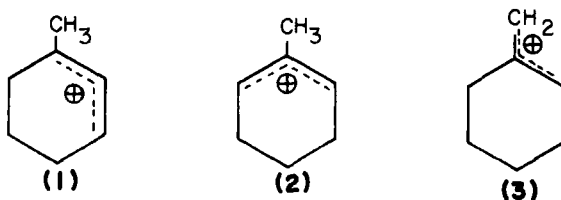
In the case of the five-membered ring, some of the increase is likely due to the addition of the polymer chain to the double bond, resulting in a tertiary carbonium ion. And, since the ion is buried, it resists further addition.
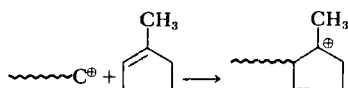
While the addition to internal double bonds is usually not observed in acyclic olefins, addition to the five-membered ring is facilitated because of the favorable steric arrangement of this rigid and planar system. Solvolysis data also indicate high stabilities for tertiary carbonium ions in five-membered ring systems (4).

The transfer coefficients of cyclic olefins also increase upon the introduction of an alkyl group and the order of the effect with ring size is $C_7 > C_5 > C_6$. For the five- and six-membered rings, the methyl substituent increases the T.C. by about one order of magnitude. This effect is in agreement with the increased relative stabilities of the alkyl-substituted ions. 1-Methyl cycloheptene has an unexpectedly large transfer coefficient (T.C. = 540); the reason for this is not apparent.

The effect of aryl substitution on cyclic compounds is more complicated than that of alkyl substitution. It is somewhat surprising that the poison coefficients of indane (P.C. = 10.8) and cyclopentane (P.C. = 16.3) are of the same order of magnitude, since indane has no alicyclic double bonds and both toluene and xylene have poison coefficients of zero. The poisoning activity of indane is probably a result of the formation of a relatively stable secondary benzylic carbonium ion. This ion might in turn deprotonate and convert to indene, which might bring about chain transfer activity. (Unfortunately, the T.C. of indane is not available.)
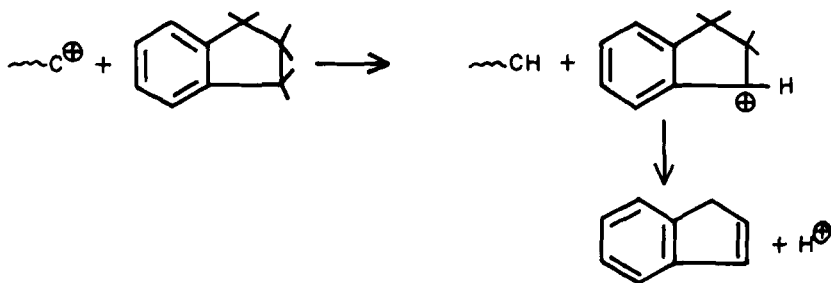

Indene has high poison and transfer coefficients (P.C. = 99 and T.C. = 210). Poisoning could occur by two important paths: allylic abstraction (path A) and addition (path B).
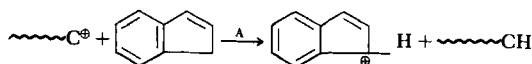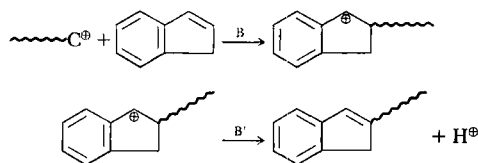
Path A produces an ion stabilized by both allylic and benzylic resonance and path B produces by addition a secondary benzylic carbonium ion. As support for the proposed addition to indene, it is significant that indene itself can be cationically polymerized (5). The high transfer coefficient might be explained by path B', since the alkylated ion might readily form the resonance-stabilized indene system by proton expulsion. The proton would then initiate a new chain, explaining the transfer activity.

Finally, the bicyclic olefins norbornene and norbornadiene have similar and appreciable poison coefficients (P.C. = 19.4 and 16.0, respectively). This terminating activity is probably due to alkylation by the growing polymer chain (paths A and B), since the allylic ion involving the bridgehead atom (path C) is forbidden according to Bredt's rule (6).
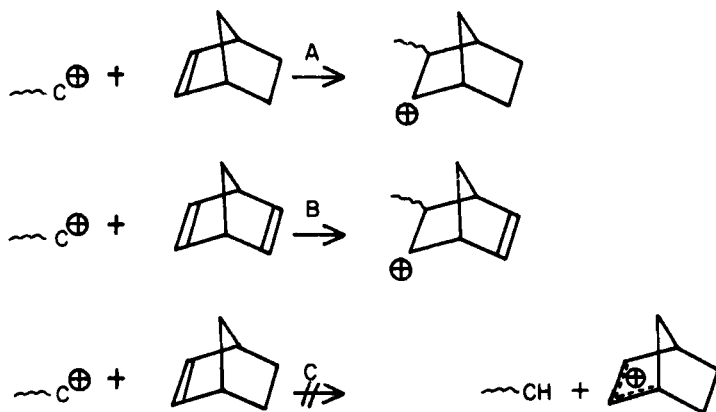
In both bicycloheptyl derivatives, addition is facilitated by severely strained double bonds (7). Similar poison coefficients would be expected since these compounds represent comparable double-bond strains and form secondary carbonium ions of comparable stability.

However, very different transfer coefficients are observed for

these bicyclic olefins (T.C. = 57.2 and 0). The alkylated ion derived from addition to norbornene can undergo a facile rearrangement to give either a nortricyclene (path A) or a bicycloheptene structure and a proton (paths B and C).
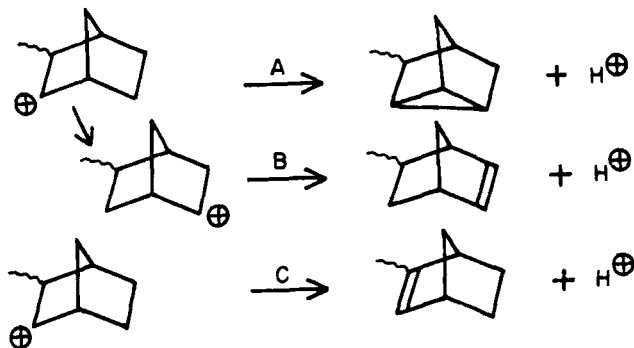
Path A would be expected to dominate, since double-bond formation in these systems is not favored. Thus, with the generation of a proton, norbornene acts as a transfer agent. Norbornadiene, on the other hand, shows no transfer activity. The ion derived from addition probably does not undergo a similar rearrangement:
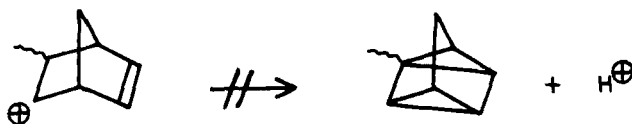
because this process would lead to a highly unfavorable tetracyclic structure. A much more favorable alternative is copolymerization with unreacted isobutene:
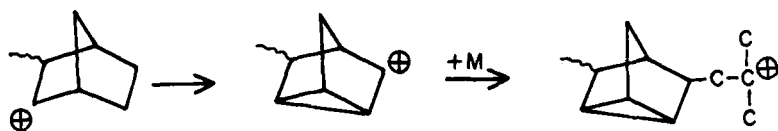
This is supported by the fact that norbornadiene can be readily polymerized cationically (8). With norbornene, owing to the lack of a double bond in the alkylated ion, rearrangement to an ion capable of propagating with monomer is less favorable.

Acknowledgment

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Zusammenfassung

Der Einfluss verschiedener cyclischer und bicyclischer Olefine auf die Ausbeute (Geschwindigkeit) und das Molekulargewicht von Polyisobutylen wurde untersucht. Cyclische Olefine sind sowohl Geschwindigkeitsgifte als auch Übertragungsmittel, wobei die entsprechenden Koeffizienten eine Funktion der Ringgrösse zu sein scheinen. Mit bicyclischen Olefinen zeigen Norbornen als auch Norbornadien mittelmässige und ähnliche Vergiftungskoeffizienten, aber nur die erstere Verbindung zeigt auch Übertragungsaktivität. Diese Koeffizienten werden im Sinne der Allylendgruppen Hypothese und der bekannten Geometrie und auch der sterischen Effekte der verschiedenen Ringe diskutiert.

Résumé

On a étudié l'effet de différentes oléfines, cycliques et bicycliques, sur le rendement (vitesse) et la masse moléculaire de polyisobutène. On a trouvé que les oléfines cycliques sont à la fois des poisons de vitesse et des agents de transfert et que les coëfficients correspondants semblent être une fonction de la taille du cycle. Des substituants alkyl et aryl augmentent les deux coëfficients d'empoisonnement et de transfert. Pour les olefines bicycliques, norbornène et norbornadiène, les deux composés montrent des coëfficients d'empoisonnement modérés et analogues, mais le premier seulement possède une activité de transfert. On discute ces coëfficients en termes de l'hypothèse de terminaison allylique et des effets connus géometriques et stériques de ces différents cycles etudiés.