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Contributions to the Mechanism of Isobutene Polymerization. VII. Effect of HCl and Chloroethyl Benzene and a Brief Summary of the Data

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Summary

The effect of HCl and chloroethyl benzene on the yield and molecular weight of polyisobutene has been investigated. For these compounds no meaningful poison and transfer coefficients could be derived because HCl appeared as a yield promoter and the effect of chloroethyl benzene was a rather complex one. The molecular weights of polyisobutene decreased in the presence of increasing amounts of these halides. It was postulated that HCl functions as a promoter/transfer agent.

The data obtained in this series of investigations have been compiled by plotting the poison coefficients of individual compounds against the transfer coefficients. Most of the materials investigated exhibit dual character, possessing both poisoning and transfer activity and only few materials are pure (or almost pure) poisons or transfer agents. It is emphasized that these characteristics are purely empirical and the findings should be generalized only with the greatest of care.

Proton-donating substances have often been proposed as cocatalysts in cationic polymerizations (*1*). Quite recently, it has been found that $AlBr_3$-catalyzed polymerization of isobutene does not need the presence of cocatalysts and, moreover, that the rate of polymerization is decreased in the presence of water (*2*). Since $AlBr_3$ and $AlCl_3$ are quite dissimilar materials, results obtained

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with $AlBr_3$ should not be generalized to $AlCl_3$. In this context it appeared of particular interest to us to investigate the effect of HCl on the overall yields and molecular weights of polyisobutene.

Although we still do not know whether or not $AlCl_3$ requires the presence of a cocatalyst to initiate the polymerization of isobutene and only a direct experiment can furnish the final answer, our results indicate that HCl is a rate promotor for this polymerization.

In the course of our fundamental studies on the mechanism of isobutene polymerization, we also studied the effect of chloroethyl benzene on the yield and molecular weights. This aromatic compound easily undergoes cationic polycondensation even at very low temperatures (*3*) and releases HCl during this process. Consequently we anticipated similar results using HCl and chloroethyl benzene in our system; however, the experimental findings have only partially borne out our expectations.

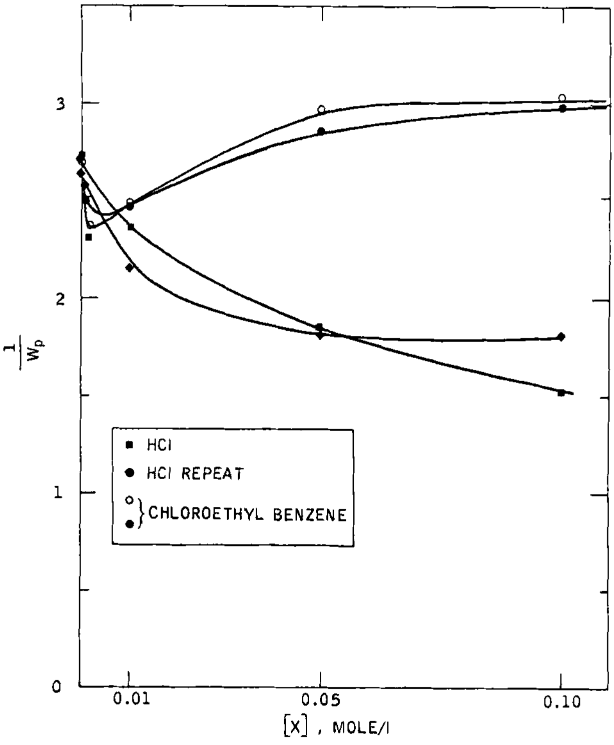


FIG. 1. $1/W_p$ versus [X] plots for HCl and chloroethyl benzene.

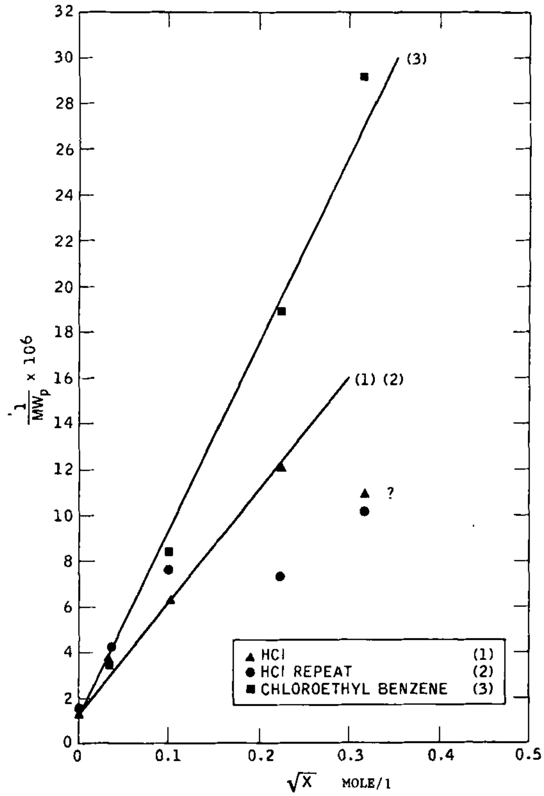


FIG. 2. $1/MW_p$ versus $\sqrt{X}$ plots for HCl and chloroethyl benzene.

EXPERIMENTAL

The experimental technique and procedures were identical to those described previously (*4*). The HCl solutions were prepared by absorbing the required amount of gaseous HCl in the system at −78°C.

RESULTS

The effect of HCl and chloroethyl benzene on overall yields and molecular weights of polyisobutene is shown in Figs. 1 and 2, respectively. Significantly, the HCl experiments in Fig. 1 indicate that more polymer has formed in the presence of HCl than in unaffected control runs. Consequently, HCl differs from all previously discussed materials (*4*) in that it acts as a promoter, increasing instead of depressing polymer yield. Figure 2 shows that product molecular weights are depressed in the presence of HCl. As was found for the other halides studied (*4*), the ordinate is a square-root function in these plots.

DISCUSSION

Qualitatively, these results could be explained by assuming that HCl has a dual function: It is a cocatalyst and transfer agent. In all previous cases it was implied that the initial number of active catalyst species was, at constant experimental conditions, a constant independent of the concentration of other ingredients in the systems. HCl may be cocatalytically active in the present system so that the concentration of active catalyst species is increased by HCl addition, giving increased polyisobutene yields.

Our results also suggest that most of the catalyst must react instantaneously with the HCl to provide the active initiator before polymerization has taken place because independent experiments showed that when HCl (or H_2O) was introduced to a "dead" system after polymerization to low conversions, no polymerization resumption occurred.

Sometimes the role of cocatalyst has been visualized by the following generalized equations:

$$MeX_n + HX \rightarrow H^{\oplus}MeX_{n+1}^{\ominus}$$

$$H^{\oplus}MeX_{n+1}^{\ominus} + \text{monomer} \rightarrow H\text{—monomer}^{\oplus}X_{n+1}^{\ominus}$$

$$\sim\!\!\sim C^{\oplus} + MeX_{n+1}^{\ominus} \rightarrow \sim\!\!\sim CX + MeX_n$$

The MeX_n formed in the last reaction can then reinitiate the chain, provided cocatalyst is available. However, for the system under investigation, this mechanism cannot hold true, because cocatalyst introduced after polymerization did not result in increased yields. Consequently, the MeX_n catalyst species introduced into the system and the MeX_n species formed by termination must be different entities in the case of $AlCl_3$. However, the nature of the difference between these species is obscure at the present.

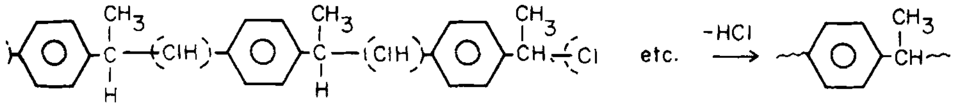
The molecular-weight-depressing effect of HCl can be explained by assuming chain transfer to the monomer, i.e.,

$$\sim\!\!\sim C^{\oplus}Cat^{\ominus} + H^{\oplus}Cl^{\ominus} \rightarrow \sim\!\!\sim C\text{—}Cl + H^{\oplus}Cat^{\ominus}\ ,$$

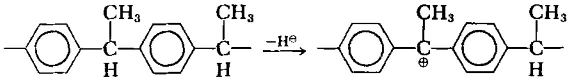
$$H^{\oplus}Cat^{\ominus} + \text{monomer} \rightarrow H\text{—monomer}^{\oplus}Cat^{\ominus}$$

Consequently, on HCl addition, increased amounts of low molecular weight products can be expected, which is in agreement with the experimentally observed facts. While the effect of HCl is qualitatively understood, a quantitative correlation of the data would require a much more complex model than presently proposed.

Chloroethyl benzene has a very peculiar effect on the overall yield (cf. Fig. 1). In the presence of very small amounts of chloroethyl benzene, the overall yields apparently increase, but in the presence of increasing concentrations of this aromatic halide the yields decrease. In other words, chloroethyl benzene at low concentrations appears to act as a promoter, increasing the yield, while at higher concentrations it inhibits the reaction and decreases the yield. It has been shown earlier in our laboratories (3) that chloroethyl benzene and benzyl halides in general in the presence of $AlCl_3$ at low temperatures polycondense according to the following scheme:



In the course of this reaction, HCl is formed. Consequently, it is conceivable that this HCl may act as a cocatalyst, promoting the formation of additional active catalyst species, therefore increasing the yield. The yield-inhibiting effect at high concentrations may be due to the poisoning effect of the ethyl benzene itself, which at higher concentrations more than counterbalances the effect of the HCl. Also the polymer of this aromatic halide may be a suitable hydride source:



stopping the growing polyisobutene chain by hydride capture. The newly formed carbonium ion cannot reinitiate the polymerization of fresh monomer, probably because of the stability of the new cation and severe steric hindrance around the electrophilic site (buried carbonium ion).

Obviously in these instances no meaningful poison coefficients can be derived.

Figure 2 shows the effect of HCl and chloroethyl benzene on the overall molecular weights of polyisobutenes by plotting $1/MW_p$

(reciprocal molecular weights in the presence of poison) versus the square root of halide concentration. In both cases, the molecular weights decrease with increasing halide concentration. The datum points for HCl are rather scattered, but for chloroethyl benzene they satisfactorily define a straight line. However, owing to the complexity of the effect of HCl on the polymerization mechanism, no transfer coefficients have been calculated. It is nonetheless noteworthy that the linear $1/MW_p$ vs. $[X]^{1/2}$ plot, i.e., the plot whose general significance for halides has been demonstrated in Section VI of this series, is also valid for chloroethyl benzene.

BRIEF SUMMARY OF THE DATA

The poison coefficients and transfer coefficients calculated in the course of these studies are summarized in Table 1 and in Fig. 3. In this figure, in which P.C. is plotted against T.C., a "pure" poison would lie along the ordinate, while a "pure" transfer agent

TABLE 1

Empirical Poison Coefficients and Transfer Coefficients

Material	P.C.	T.C.
Propylene	4.9	0
1-Butene	6.2	0
1-Pentene	9.7	0
1-Hexene	11.9	0
2-Octene	20.8	12.1
Butadiene	7.6	2.0
2,5-Dimethyl-2,4-hexadiene	26.7	15.2
2,3-Dimethyl-1,3-butadiene	107	3.6
Cyclohexadiene	103	48
Isoprene	140	60
Piperylene	170	327
Cyclopentadiene	900	
2-Methylcyclopentadiene	685	
Cyclohexene	5.3	2.7
Cyclooctene	11	31.2
Cyclopentene	16.3	27
1-Methylcyclohexene	14.7	43.4
1-Methylcycloheptene	66.7	540
1-Methylcyclopentene	280	286
2-Methyl-1-pentene	3.5	53.8
2-Ethyl-1-hexene	24.7	248

TABLE 1 (*Continued*)

Material	P.C.	T.C.
2,4,4-Trimethyl-1-pentene	66.7	700
2,2,4-Trimethyl-2-pentene	66.7	34.6
3-Methyl-1-butene	0	0
4-Methyl-1-pentene	2.9	0
3,3-Dimethyl-1-butene	0	0
Benzene	0	0
Toluene	0	0
o-, *p*-, and *m*-Xylene	0	0
Vinylcyclohexene	3.7	6.7
Indane	10.8	
Indene	99	210
Norbornene	19.4	57.2
Norbornadiene	16	0
1,5-Cyclooctadiene	9	1.8
Allyl chloride	0	6.2
Methallyl chloride	1.6	6.9
3-Chlorobutene	6.6	24.5
Crotyl chloride	11.2	27.5
Isopropyl chloride	0	0
Isobutyl chloride	12.5	13.4
t-Butyl chloride	4.4	75.7
Isopropyl bromide	0	0
Isobutyl bromide	1.8	15
t-Butyl bromide	3.5	71.4

would lie against the abscissa. Thus norbornadiene (#32) or simple α-olefins (#1–4) behave as pure poisons, whereas allyl chloride (#34) appears as a pure transfer agent. Most of the compounds investigated show a dual character; they are both poisons and transfer agents. Usually, however, one or the other effect predominates. For example, 2,3-dimethyl-1,3-butadiene is an almost pure poison with very little transfer activity, or the two tertiary butyl halides are almost pure transfer agents with very little poison character.

All the poison and transfer characteristics, and particularly their quantitative (coefficient) form, are purely empirical values and should be generalized only with great care. The overall poison/transfer mix exhibited by a particular compound may be due to a number of completely unrelated factors and may have quite different origins. Every compound class and within it every compound

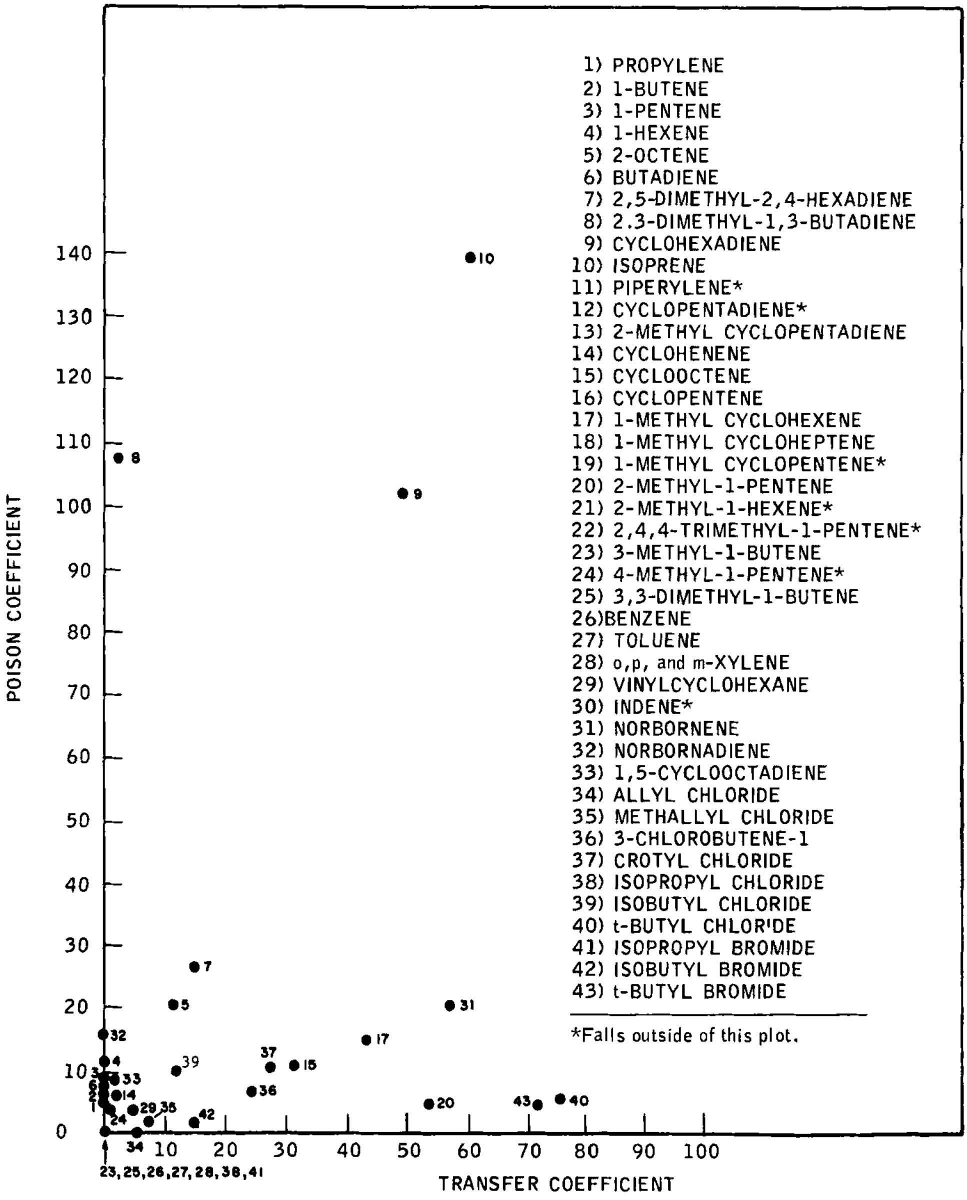


FIG. 3. Poison coefficients vs. transfer coefficients II.

should be considered individually, and there remains very little room for generalization. It should once again be emphasized that a comparison of the relative molecular weight inhibition of a hydrocarbon and a chloride must be based on a comparison of $(\text{T.C.})_{\text{hydrocarbon}}X$ and $(\text{T.C.})_{\text{halide}}X^{1/2}$, not on merely a comparison of $(\text{T.C.})_{\text{hydrocarbon}}$ vs. $(\text{T.C.})_{\text{halide}}$.

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Zusammenfassung

Der Einfluss von HCl und Chloräthylbenzol auf die Ausbeute und das Molekulargewicht von Polyisobutylen wurde untersucht. Es konnten keine sinnvollen Vergiftungs-und Übetrträgerkoeffizienten abgeleitet werden da HCl als ausbeuteverbessernder Promotor wirkte und der Einfluss des Chloräthylbenzols sich als sehr komplex erwies. Die Molekulargewichte der Polyisobutylene waren geringer, je grösser die Menge der vorhandenen Halogenverbindungen war. Es wird postuliert, dass HCl als Promotor und Überträger wirkt.

Die in dieser Untersuchungsreihe erhaltenen Ergebnisse wurden durch Auftragung des Vergiftungskoeffizienten jeder Verbindung gegen den Übertragungskoeffizienten dargestellt. Die meisten der untersuchten Verbindungen sind sowohl Gifte als auch Überträger, nur wenige sind reine (oder fast reine) Gifte oder Uberträger. Es wird betont, dass diese Eigenschaften rein empirisch sind und dass diese Ergebnisse nur mit grösster Vorsicht verallgemeinert werden dürfen.

Résumé

On a examiné l'effect d'HCl et du chloroéthylbenzène sur le rendement et la masse moléculaire de polyisobutène. Pour ces composés on n'a pu obtenir de coëfficients d'empoisonnement et de transfert plausibles comme HCl apparait être un promoteur du rendement et l'effet du chloroethylbenzene etait plutot compliqué. La masse moléculaire de polyisobutène diminue en présence des quantités croissantes de ces halogènes. On a postulé que le HCl fonctionne comme agent promoteur/transfert.

On a obtenu les données dans ces series d'examens en traçant les coëfficients d'empoisonnement de chaque composé envers les coëfficients de

transfert. La plupart de matériaux etudiés exhibent un caractère doublė, possèdant à la fois des activités d'empoisonnement et de transfert, peu d'entre eux sont des agents purement (ou prèsque purement) du poison et du transfert. On a souligné que ces caractéristiques sont uniquement empiriques et qu'on doit exercer un très grand soin dans la géneralisation de ces résultats.

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