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Effect of Aging on the Nature of the Wichterle-Marek-Trekoval Catalyst

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Summary

The effect of aging on the Wichterle-Marek-Trekoval (WMT) solid cationic catalyst for isobutene polymerization has been investigated. It was confirmed that this complex catalyst gives high molecular weight polyisobutenes at high rates at relatively high temperatures. Aging for various times and temperatures the $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3$ component and the $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3/TiCl_4$ final catalyst strongly depresses rates of polymerization but only slightly affects the molecular weights produced. Fastest rates and molecular weights are obtained with freshly prepared catalyst whose Ti/Al ratio is ~ 0.3 at about 30% conversions. Rates and polyisobutene molecular weights obtained by the present authors were higher than those reported by the Czechoslovakian workers. These results are discussed in terms of cationic polymerization mechanism, and an explanation for the reduced rates and molecular weights produced with aged WMT catalysts is proposed.

INTRODUCTION

First in 1959 (*1*) and later in 1961 (*2*) Wichterle et al. described an unusual solid catalyst which produced unusually high molecular weight polyisobutenes at high rates. The catalyst was prepared by mixing a secondary butyl aluminum alcoholate with gaseous boron trifluoride in hexane diluent and adding titanium tetrachloride to

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activate the complex precipitate. In the course of our fundamental studies on cationic polymerization, it appeared of interest to further investigate this Wichterle-Marek-Trekoval catalyst (WMT catalyst) and to study the effect of aging of the active solid on the rate of polymerization and molecular weight of polyisobutenes. We repeated, confirmed, and extended the results of the Czechoslovakian workers and were able to elucidate some of the peculiarities of this curious catalyst.

EXPERIMENTAL

Material: Isobutene (Phillips, research grade) was used. The monomer was dried by passing through KOH and condensed into a buret at −78°C. *n*-Hexane (guaranteed reagent) was shaken with concentrated sulfuric acid, water, sodium hydroxide solution, alkaline potassium permanganate solution, and water, dried over calcium chloride, and distilled from metallic sodium. Commercial secondary butyl aluminum alcoholate (Kawakami Research Institute) was used without further purification. Titanium tetrachloride was distilled into a small ampoule. Boron trifluoride was prepared by heating sodium borofluoride with concentrated sulfuric acid. It was directly introduced into *n*-hexane solution of secondary butyl aluminum alcoholate to synthesize the WMT catalyst.

Procedures: The WMT catalyst was prepared by the method of Wichterle et al. (*1*). All polymerizations were carried out in *n*-hexane solution in glass equipment as described by Wichterle et al. (*1*). Conversions were determined by withdrawing aliquots from the reactor, quenching the reaction mixture into methanol, and drying the solid polymer. The catalyst was aged by storing the suspension at selected temperatures for various times. In polymerizations at −20°C which went to completion, the temperature rose to −15°C.

Intrinsic viscosities were determined in toluene at 30°C.

Further experimental details will be given when necessary.

RESULTS AND DISCUSSION

According to Wichterle et al. (2), the solid Al alcoholate/BF_3 complex can be stored "for several weeks" at ambient temperatures without loss of catalytic activity; however, the catalyst rapidly deteriorates after $TiCl_4$ has been added. According to our results, both the age of the Al alcoholate/BF_3 complex precipitate and even more so the age of the final active Al alcoholate/BF_3/$TiCl_4$ species are of decisive importance in determining catalyst quality as judged by rate of polymerization and product molecular weights.

Effect of Aging the $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3/TiCl_4$ Catalyst

First we studied the effect of aging on the complete Al alcoholate/BF_3/$TiCl_4$ system. In a series of experiments we bubbled BF_3 gas into various aluminum *s*-butyl alcoholate in *n*-hexane solutions at room temperature and stored the $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3$ solution at 0°C for 2 days and added the final $TiCl_4$ component at various temperatures. Subsequently the system was aged at various temperatures for various times and used in polymerization experiments

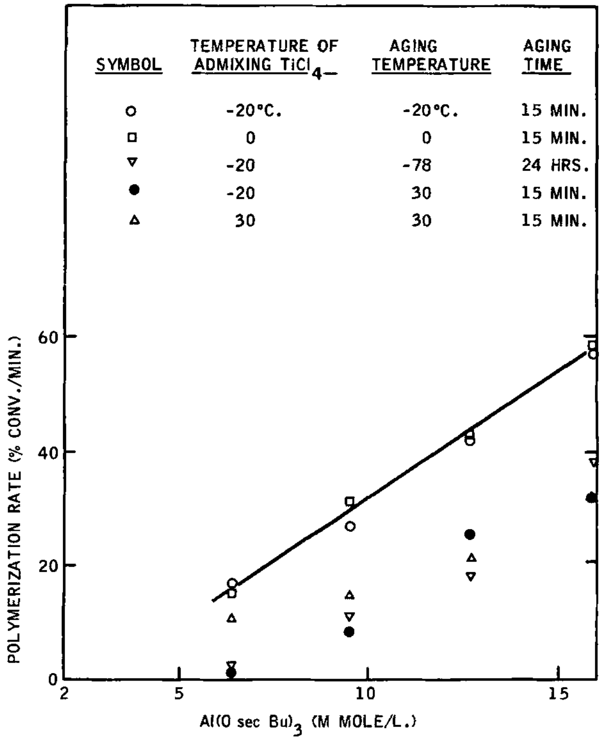


FIG. 1. Effect of catalyst aging temperature and time on the rate of isobutene polymerization at −20°C. (Ti/Al = 0.2), [M] = 8 vol. %.

at −20°C. Figure 1 shows the results. The highest polymerization rates were obtained when the catalyst was aged for 15 min at −20 or 0°C. On longer aging, even at low temperatures (24 hr at −78°C) or shorter aging at higher temperatures (15 min at 30°C), catalyst activity dropped sharply.

These results are amplified by the data shown in Fig. 2, where we plotted the effect of aging time at 0°C on the rate of isobutene

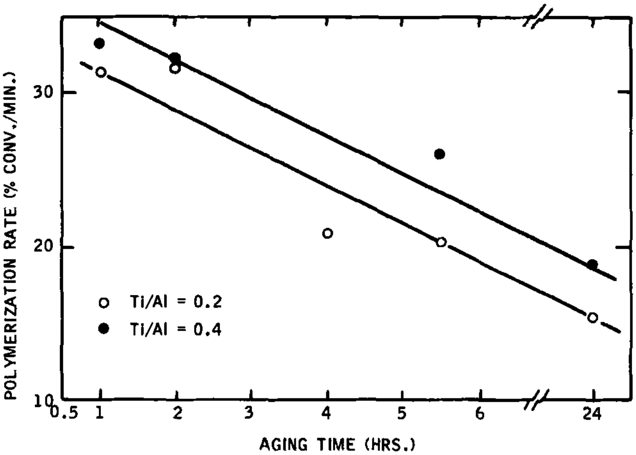


FIG. 2. Effect of catalyst aging time at 0°C on the rate of isobutene polymerization at −20°C

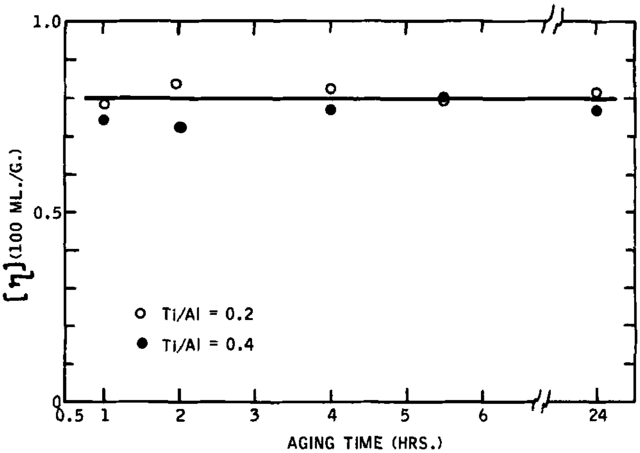
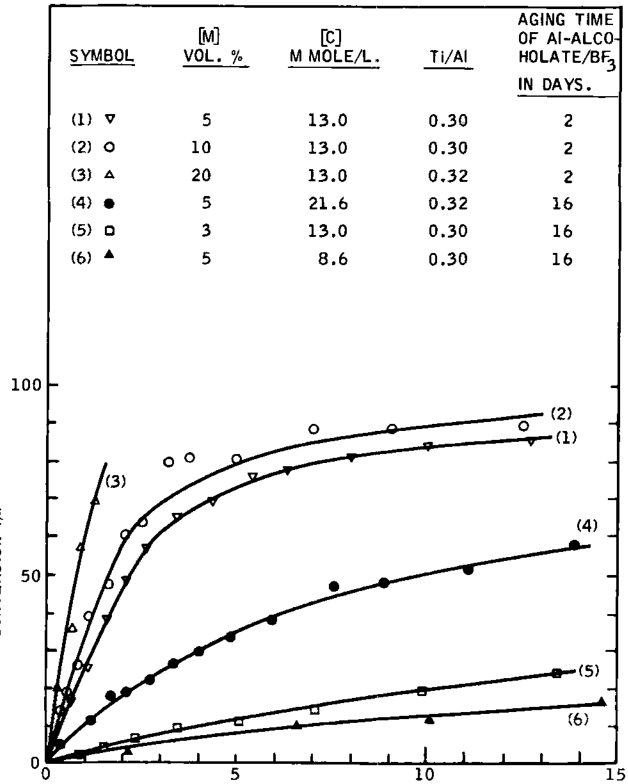


FIG. 3. Effect of catalyst aging time at 0°C on the viscosity of polyisobutene obtained at −20°C.

polymerization for two catalyst preparations. Apparently highest rates are obtained with freshly prepared catalyst, and the polymerization rate decreases monotonically with time. The molecular weights, however, do not seem to be affected by the age of the catalyst. This is shown in Fig. 3, where we plotted [η] versus catalyst aging time at 0°C.

Effect of Aging the Al(O-*s*-$C_4H_9)_3$/BF_3 Component

Next we turned our attention to the effect of aging of the Al alcoholate/BF_3 solid precipitate on the rate and molecular weight. In this series of experiments the Al alcoholate/BF_3 complex was prepared at room temperature and stored for 2 and 16 days at 0°C be-



SYMBOL	[M] VOL. %	[C] M MOLE/L.	Ti/Al	AGING TIME OF Al-ALCOHOLATE/BF_3 IN DAYS.
(1) ▽	5	13.0	0.30	2
(2) ○	10	13.0	0.30	2
(3) △	20	13.0	0.32	2
(4) ●	5	21.6	0.32	16
(5) □	3	13.0	0.30	16
(6) ▲	5	8.6	0.30	16

FIG. 4. Effect of aging the Al alcoholate/BF_3 catalyst component on the rate of polymerization of isobutene at −20°C.

fore mixing it with $TiCl_4$ at 0°C to obtain the active catalyst. Our results show (Fig. 4) that substantially lowered rates of polymerization were obtained with 16-day-old Al alcoholate/BF_3 complexes as compared to 2-day-old complexes.

Although the experiments are not strictly comparable, the over-all or fundamental effect of aging is clearly recognizable. All the runs with "fresh" (2 days old) Al alcoholate/BF_3 complexes gave higher rates than those with "old" (16 days old) solid complex. This is particularly apparent comparing run 1 (5 vol.% isobutene, 13.0 mmoles Al alcoholate/liter) with run 4 (5 vol.% isobutene, 21.6 mmoles Al alcoholate/liter). Thus a relatively fresh but low amount of catalyst gives much higher polymerization rates than a run with old but large amounts of catalyst. Similarly, the deleterious effect of aging the Al alcoholate/BF_3 complex is also apparent, comparing run 1 with run 5, in which the amounts of relatively fresh and old catalysts were the same and the difference in monomer concentrations (5 vs. 3 vol.%) is certainly not sufficient to explain the large differences in rates.

Subsequently, experiments have been conducted at various catalyst concentrations (i.e., initial Al alcoholate concentrations) using relatively fresh and aged Al alcoholate/BF_3 complexes to polymerize isobutene at −20°C. Figure 5 shows the over-all rate constants *k* as a function of catalyst concentration in these comparative experiments.

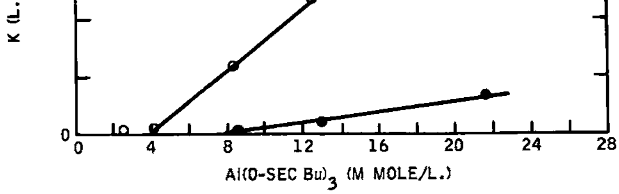


FIG. 5. Effect of aging of the Al alcoholate/BF_3 complex on the over-all rate constant of isobutene polymerization at −20°C. Polymerization conditions: [M] = 10 vol.%, Ti/Al = 0.33.

In the next series of comparative experiments, the effect of the Ti/Al ratio on the over-all rate constant was investigated using the relatively fresh and aged Al alcoholate/BF_3 complex catalyst component at identical monomer concentrations. Figure 6 shows the results. With fresh catalyst the rate constant rapidly rises until a Ti/Al ratio of about 0.3 is reached, after which the rate of increase becomes much slower. The situation is quite similar with aged catalyst also, except the values are much lower.

These experiments together with those shown in Fig. 5 clearly demonstrate the deleterious effect of aging of the Al alcoholate/BF_3 complex on the rate of isobutene polymerization.

A possible explanation for the rate-decreasing effect of aging could be a diminished number of active surface sites as a consequence of deteriorating surface morphology, e.g., decreased surface area and particle aggregation. Catalyst aging is visually noticeable by the appearance of a fine precipitate, indicating particle agglomeration. According to the results shown in Fig. 6, polymerization activity increases rapidly with increasing amounts of $TiCl_4$ added until Ti/Al = 0.3 is reached. Beyond this Ti/Al ratio, catalyst activity increases more slowly, indicating that perhaps at Ti/Al = 0.3 the most active surface has been obtained. Further amounts of $TiCl_4$ would only increase the amount of uncomplexed or free $TiCl_4$, whose catalytic activity is much inferior to that of the solid complex.

In this respect our data are in disagreement with those of Wich-

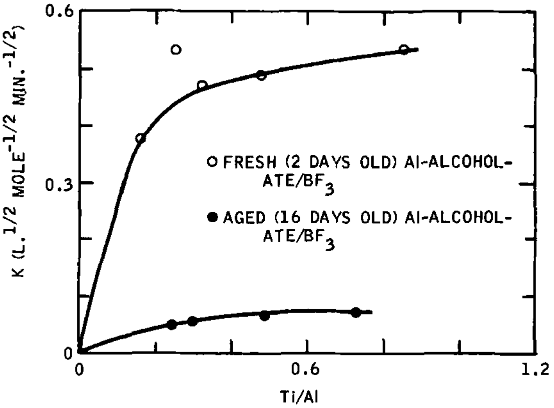
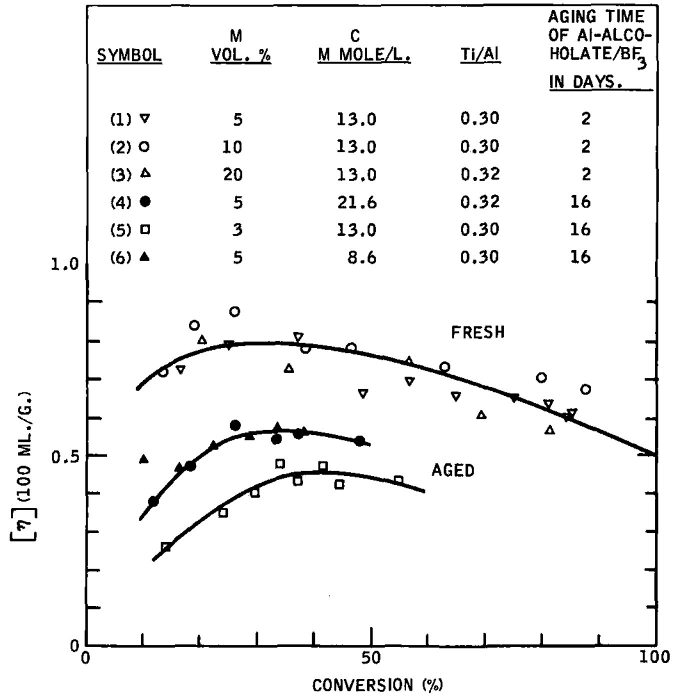


FIG. 6. Effect of Ti/Al ratio on the over-all rate constants [M] = 10 vol.%, $Al(O\text{-}s\text{-}C_4H_9)_3$ = 12.6 mmoles/liter.

terle et al. (2), who found (Fig. 1, Ref. 2) that at 0°C increased amounts of $TiCl_4$ enhanced the rate of polymerization until about Ti/Al = 0.25, but beyond this Ti/Al ratio further amounts of $TiCl_4$ did not result in increased polymerization rates and the rate curve became horizontal. (At this point it should be mentioned that Fig. 1 in Ref. 2 contains an error; the correct $TiCl_4$ concentration on the horizontal axis should be $[TiCl_4] \times 10^3$ and not $[TiCl_4] \times 10^2$.) However, it could be that these data are misleading, since Wichterle et al. carried out the polymerizations at 0°C, at which temperature level only low molecular weight oligomers can be formed, and they might have lost certain amounts of product by the conventional way of polymer recovery. Since the complex catalyst produces higher molecular weights than the uncomplexed $TiCl_4$, lower molecular weight polymer (oligomers) might have formed at high Ti/Al ratios and might have been lost during polymer recovery. Had this oligomer fraction been included and weighed with the higher molecular weight fraction, the curve might have shown a break about Ti/Al = 0.25; however, it would not have become horizontal but would have increased with a diminished slope. In contrast, our polymerizations were carried out at −20°C, at which temperature level higher molecular weight (i.e., methanol-insoluble) products were formed which contributed to the total yield and led to slowly increasing conversions, even beyond about Ti/Al = 0.3.

Simultaneously with the conversion-time plots shown in Fig. 6, we have also determined the intrinsic viscosities of the products (Fig. 7). According to the data, highest molecular weights (intrinsic viscosities) were obtained at relatively low conversions (~30%). Both the fresh and the aged Al alcoholate/BF_3 complex show this phenomenon, except the absolute values obtained with the aged catalyst are somewhat lower than those produced by the fresh one, while the aging of $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3/TiCl_4$ catalyst did not affect the polymer molecular weight (see Fig. 3). It could be that the ascending part of the molecular weight curve is due to the gradual scavenging of chain-breaking impurities or to a longer lifetime of growing species. The descending part of the curve could be due to (1) gradual decreasing monomer concenerations or (2) to an increasing degree of coating of the solid catalyst surface with layers of macromolecules through which monomer penetration is impeded (diffusion control), leading to decreased rates of initiation and prop-

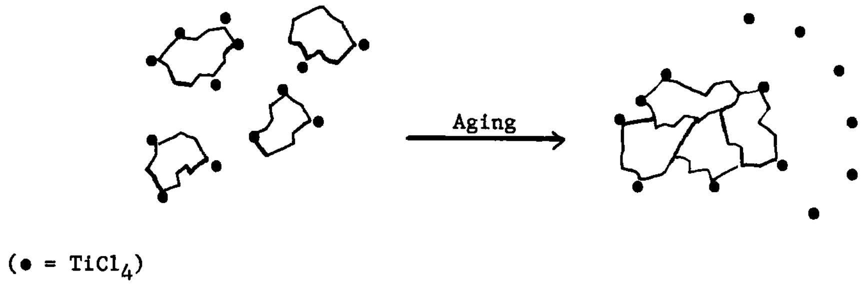


SYMBOL	M VOL. %	C M MOLE/L.	Ti/Al	AGING TIME OF Al-ALCO-HOLATE/BF$_3$ IN DAYS.
(1) ▽	5	13.0	0.30	2
(2) ○	10	13.0	0.30	2
(3) △	20	13.0	0.32	2
(4) ●	5	21.6	0.32	16
(5) □	3	13.0	0.30	16
(6) ▲	5	8.6	0.30	16

FIG. 7. Effect of conversion on the intrinsic viscosities of polyisobutenes obtained with fresh and aged Al alcoholate/BF$_3$ complexes.

agation coupled with unaffected rates of unimolecular termination. Difficulties in dissipating the heat of polymerization at the coated catalyst surface could also contribute to a higher rate of termination or chain breaking.

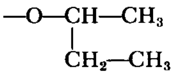
The effect of aging the Al alcoholate/BF$_3$ complex on the molecular weight is also noteworthy (Fig. 7). Apparently the fresh catalyst gives higher molecular weights than the aged one under identical conditions and at identical conversion levels. This phenomenon might be explained by assuming that during aging TiCl$_4$ is gradually released ("uncomplexed") from the solid catalyst whose morphology is changing. The effective surface area of the catalyst could decrease by the gradual loss of surface irregularities, crystallization, and/or particle aggregation. During this process TiCl$_4$ could be released in the solution:



Uncomplexed $TiCl_4$ then independently produces lower molecular weight product and consequently decreases the averages.

The effect of catalyst composition, i.e., Al/Ti ratio on the molecular weights, also provides some valuable information. Figure 8 shows the results of a series of experiments in which the molecular weights of polyisobutenes as a function of various Al/Ti ratios using fresh and aged Al alcoholate/BF_3 complex have been determined. Since the molecular weight is affected by conversion (cf. Fig. 7) the maximum molecular weights obtained in these systems have been used, i.e., those obtained at ~30% conversion with fresh Al alcoholate/BF_3 complex and that obtained at ~60% conversion with the aged complex.

According to the data there is evidence for decreased molecular weights at higher Ti/Al ratios using the fresh Al alcoholate/BF_3 complex. Increasing molecular weights in the 0 to 0.3 Ti/Al range could be due to the gradual formation of the best Al alcoholate/BF_3/$TiCl_4$ system. Perhaps the Al alcoholate/BF_3 complex contains some free —OH or


$$—O—\underset{\underset{CH_2—CH_3}{|}}{C}H—CH_3$$

groups which might be chain breakers. Increasing amounts of $TiCl_4$ might react with or shield these groups, leading to a better catalyst. Also impurities, e.g., moisture, might be present in the system, which could reduce the molecular weight. Once the best ternary Al alcoholate/BF_3/$TiCl_4$ catalyst system is formed, additional amounts of $TiCl_4$ could become deleterious. As mentioned before, free $TiCl_4$ produces low molecular weight polyisobutenes at −20°C; consequently low molecular weight species are formed at increasing Ti/Al ratios. Since intrinsic viscosities are not particularly sensitive for low molecular weight species, the effect observed is expectedly small. Number average molecular weight determinations or molecular weight distribution experiments could shed some more light on this problem.

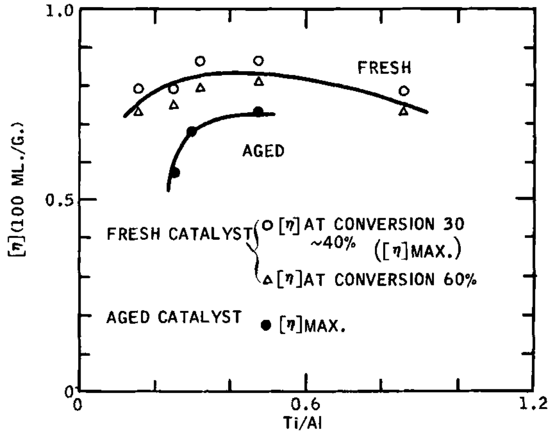


FIG. 8. Effect of Ti/Al ratio on the intrinsic viscosities of polyisobutenes obtained with fresh and aged Al alcoholate/BF_3 complexes. [M] = 10 vol.%, [C] = 12.6 mmoles/liter.

Only a few experiments have been carried out with aged Al alcoholate/BF_3 complexes in this context (Fig. 8). There might be a slight decrease in polymer intrinsic viscosities obtained with this catalyst as compared to those produced by the fresh material. The explanation of this effect could also be an abundance of uncomplexed $TiCl_4$, as discussed above.

Up to this point the effects of aging of the Al alcoholate/BF_3 complex or Al alcoholate/BF_3/$TiCl_4$ catalyst on the polymerization rate and the polyisobutene molecular weight have been explained in terms of morphological changes occurring on the catalyst surface. However, changes in the chemical nature of the catalyst surface during aging might also affect the observed changes in catalyst activity. Further investigation is planned to elucidate aspects of this problem.

COMPARATIVE RESULTS AND CONCLUSIONS

Polymerization rates and product molecular weights obtained in the course of the present work were compared to those reported by Wichterle et al. (*1*,*2*). Thus Fig. 9 shows a comparison of rates

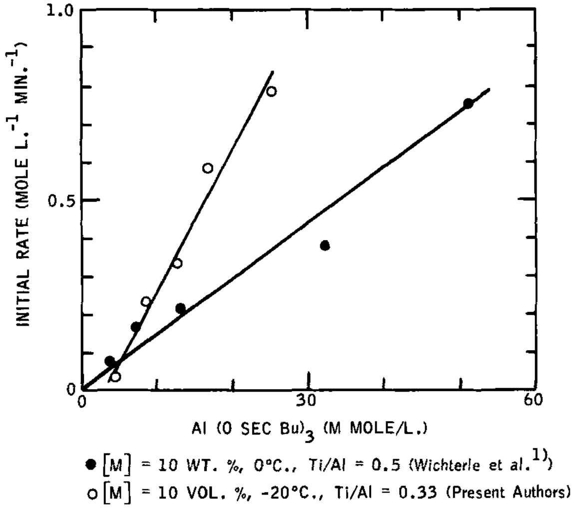


FIG. 9. Comparison of initial rates of isobutene polymerizations.

of isobutene polymerizations and Table 1 a comparison of molecular weights as given by the Czechoslovakian authors and obtained in the present investigations under essentially identical conditions. According to the data in Fig. 9, the rates of polymerization were found to be significantly larger than those observed by Wichterle et al. (2). By Table 1 this is also true for the molecular weights obtained. In the light of the foregoing experimental evidence and discussion, these findings suggest that the catalyst used by Wichterle et al. was more an aged one than that employed by the present authors.

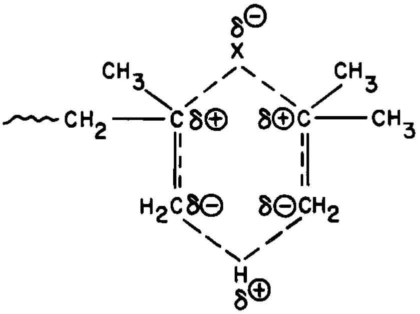
TABLE 1

Comparison of Molecular Weights Obtained at −20° in *n*-Hexane

Wichterle et al. (2)[a]		Present work[b]	
[M]	Mol. wt.	[M]	Mol. wt.
10 wt.%	180,000	10 vol.%	264,000
5 wt.%	130,000	5 vol.%	238,000

[a] [C] = 3.2 mmoles/liter, Ti/Al = 0.5.
[b] [C] = 13.0 mmoles/liter, Ti/Al = 0.3.

One of the important questions to consider is why the Al alcoholate/BF_3/$TiCl_4$ catalyst gives such high molecular weight polyisobutenes at comparatively high temperatures and high polymerization rates. The increase of both polymerization rates and molecular weights might be due to either an increase in propagation rates or to a decrease of termination or transfer rates. Various reasons could explain increased propagation rates: (1) an increase of local monomer concentration on the catalyst surface by adsorption, (2) an activation of adsorbed monomers, (3) propagation by electron migration (without material transport) as a consequence of suitable orientation of adsorbed polarized monomers, etc. Increased molecular weights could be due to suppressed monomer-transfer reactions. Monomer transfer involving the following six-membered transition state has been postulated as the most important chain-breaking event in isobutene polymerization with conventional homogeneous Friedel-Crafts halide catalysts (*3*,*4*):



where $X^{\ominus}$ stands for the gegenion. In isobutene polymerization with the WMT catalyst, the gegenion is probably a bulky structure in the solid phase. Consequently it will be sterically difficult to establish the transition state, particularly if one is to assume a coplanar six-membered ring structure including the gegenion in a separate phase. Thus monomer transfer will be relatively slow and high molecular weight polyisobutenes will be produced.

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Zusammenfassung

Die Folge der Alterung des festen Wichterle-Marek-Trekoval (WMT) anionischen Katalysators für die Isobutylenpolymerisation wurde untersucht. Es konnte bestätigt werden, dass dieser Katalysator bei relativ hoher Temperatur mit grosser Reaktionsgeschwindigkeit hochmolekulare Polyisobutylene ergibt. Alterung der $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3$ Komponente und des $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3/TiCl_4$ Katalysators bei verschiedenen Temperaturen über verschiedene Zeitbereiche reduziert sehr stark die Polymerisationsgeschwindigkeit, beeinflusst aber die sich ergebenden Molekulargewichte nur geringfügig. Höchste Reaktionsgeschwindigkeiten und Molekulargewichte werden mit frisch hergestelltem Katalysator erzielt dessen Ti/Al Verhältnis ≈ 0.3 ist, wobei der Umsatz ungefähr 30% beträgt. Die von diesen Autoren ermittelten Geschwindigkeiten und Molekulargewichte des Polyisobutylens waren höher als jene von den tschechoslovakischen Autoren veröffentlichten. Die vorliegenden Ergebnisse werden unter Heranziehung kationischer Reaktionsmechanismen diskutiert und eine Erklärung für die verminderten Reaktionsgeschwindigkeiten und Molekulargewichte von mit gealtertem WMT Katalysator erhaltenen Produkten wird gegeben.

Résumé

On a étudié l'effet de vieillissement sur le catalyseur solide cationique de Wichterle-Marek-Trekova (WMT) dans la polymérisation d'isobutène. On a confirmé le fait que ce catalyseur complex donne des polyisobutènes de hauts poids moléculaires à des vitesses et températures relativement élevées. Vieillisant à des periodes et températures différentes, le composant $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3$ et le catalyseur final $Al(O\text{-}s\text{-}C_4H_9)_3/BF_3/TiCl_4$ baissent fortement les vitesses de polymérisation mais n'influencent que faiblement les masses moléculaires produites. Les vitesses et les masses moléculaires maxima sont obtenues avec un catalyseur fraichement preparé, dont le taux Ti/Al est ≈ 0.3 aux conversions de 30% environ. Les vitesses et les masses moléculaires obtenues par les auteurs etaient superieures à celles rapportées par des chercheurs de Tchécoslovaquie. On discute ces résultats du point de vue du mécanisme de la polymérisation cationique et on offre une raison de vitesses et masses moléculaires réduites obtenues avec les catalyseurs WTM agés.