

Preparation and Characterization of Poly(isobutylene Oxide)

J. BOOR and R. S. BAUER, *Shell Development Company,
Houston, Texas 77001*

Synopsis

High molecular weight poly(isobutylene oxide) has been synthesized and characterized. Two novel catalysts were found: (1) a Zn-S composition made by reacting ZnEt_2 and H_2S in presence of cyclohexylamine and (2) a ternary system consisting of ZnEt_2 , a metal compound (such as ZnO , ZnS , or Zn titanate), plus cyclohexylamine. Products with reduced specific viscosities of 1.5 to 13 dl/g were easily made. Highest yields were obtained at 110°C , but these products had lower molecular weights than products synthesized at 70°C . The activity of the Nippon-Carbide catalyst was increased two to three times by heating it with a small amount of styrene oxide. High molecular weight poly(isobutylene oxide) appears to have an attractive balance of properties which are in the range of many engineering thermoplastics.

INTRODUCTION

Isobutylene oxide has been polymerized earlier in the presence of cationic and coordinative-anionic initiators as well as by radiation techniques. Table I collects the leading references. Cationic and x-ray irradiation-initiated polymerization produce low molecular weight polymers, i.e., $\text{MW} \approx 3000\text{--}10,000$ ($\eta_{sp}/c \approx 0.1$) (Fig. 1). Cationic initiators such as Friedel-Craft compounds (SnCl_4) and aluminum alkyls (AlEt_2Cl) were used. In contrast, metal oxide initiators formed by hydrolysis of zinc alkyls in presence of certain amines produced high molecular weight polymers. High molecular weight poly(isobutylene oxide) was first reported by Nippon-Carbide workers, who used the ternary initiator $\text{ZnEt}_2\text{--H}_2\text{O}$ –cyclohexylamine.⁷ Later, Vandenberg at Hercules reported other initiators that also gave high molecular weight polymers, namely, MgEt_2 plus diethylenetriamine¹⁰ and $\text{MgEt}_2 + \text{NH}_3$.¹² This paper describes several new initiators which we found for synthesis of high molecular weight poly(isobutylene oxide).

Previous work has indicated that high molecular weight poly(isobutylene oxide) was much like isotactic polypropylene. A characterization of the products produced in this study indicates that poly(isobutylene oxide) has an overall balance of properties which are in the range of many engineering thermoplastics.

TABLE I
Earlier Results on Polymerization of IBO

| Year | Authors | Preparation of Catalyst | Polymerization Conditions | | | Polymer | | Melting point, °C | |
|------|------------------------------------|---|---------------------------|-----|--------------------|----------|-------------------|-------------------|---|
| | | | °C | hr | Solvent | Conv., % | Viscosity | | |
| 1947 | Davies and Peacock ¹ | Friedel-Crafts catalysts such as BF ₃ , AlCl ₃ , SnCl ₄ | -78 | <1 | CH ₂ Cl | ca. 40 | waxy solid | 108 | |
| 1961 | Oniwa et al. ² | ZnEt ₂ + H ₂ O (7 mole-%) (reported earlier by Furukawa as catalyst for polymerizing propylene oxide (1957-58)) | 25 | | | 10 | IV = 0.11 | crystalline | |
| 1960 | Ishida ³ | FeCl ₃ or FeCl ₃ ·propylene oxide (5% wt) | 70 | 64 | | 15 | — | — | |
| | | BF ₃ ·Et ₂ O (5%) | 25 | 24 | | — | — | 159-160 | |
| | | TiCl ₄ (3.5% wt) | -78 to 25 | 48 | | 28.5 | — | — | — |
| | | Al(<i>i</i> -PrO) ₃ or Al(<i>i</i> -PrO) ₃ ·ZnCl ₂ | 8 | 144 | | nil | — | — | — |
| | | AlEt ₃ | 25 | 120 | | — | — | 152 | — |
| | | ZnEt ₂ in Et ₂ O | 25 | 96 | | 46.8 | — | 151-152 | |
| | | ZnEt ₂ ·Al ₂ O ₃ | 25 | 480 | | nil | — | — | |
| 1962 | Kambara and Takahashi ⁴ | Acid catalysts (SnCl ₄ , AlEt ₂ Cl, AlEt ₃) | -78 | 24 | hexane | 15-34 | IV = 0.10 to 0.19 | 142-151 | |
| | | AlEt ₃ + H ₂ O | -78 | 24 | hexane | 56 | IV = 0.15 | 154-156 | |
| | | AlEt ₃ + Co (acac) ₃ | -78 | 72 | hexane | 29.8 | IV = 1.28 | 155-158 | |
| | | AlEt ₃ + VO (acac) ₃ | -78 | 72 | hexane | 42.7 | IV = 0.35 | 151-153 | |
| | | AlEt ₃ + Cr (acac) ₃ | -78 | 72 | hexane | 45.3 | — | 148-151 | |

| | | | | | | | | |
|------|------------------------------------|--|---------------------------|----------------|-------------------------------|-----------------|---------------------------------------|---|
| 1963 | Kambara and Takahashi ⁶ | Ni(dmg) ₂ + AlEt ₂ (1:4) Co(dmg) ₂ + AlEt ₃ (1:4) Co(salim) ₂ + AlEt ₃ (1:3) acid catalysts (SnCl ₄ , SbCl ₅ , AlEt ₂ F, AlEt ₂ Cl or Al(<i>i</i> -Bu) ₃ , AlEt ₂ Cl, AlEt ₂ Cl ₂ and AlEt ₂ OEt) | -78 -30 -78 | 48 48 48 | heptane heptane heptane | 8.5 23 32 | IV = 0.1 IV = 0.2 IV = 0.1 | 151-154 154-155 150-152 |
| 1963 | Bauer ⁶ | only low molecular weight products were formed (ca. 3000 to 6000) | | | | | | |
| 1964 | Kamio et al. ⁷ | ZnEt ₂ + H ₂ O + cyclohexylamine (Zn/H ₂ O = 2.5) | 70 | 42 | hexane | 65 | $\eta_{sp}/c = 3.85$ | |
| 1967 | Vandenberg ⁸ | ZnEt ₂ + H ₂ O (Zn/H ₂ O = 2.5) | 70 | 42 | hexane | 62 | $\eta_{sp}/c = 2.3$ | |
| 1967 | Vandenberg ⁹ | Al(<i>i</i> -Bu) ₃ -H ₂ O (2:1) (expt. 11) Al(<i>i</i> -Bu) ₃ -H ₂ O (2:1) | -78 -78 | — 18 | | | | highly purified IBO was used, but molecular weights were still low: reduced specific viscosities of 0.10 to 0.41 dl/g were measured |
| 1968 | Vandenberg ¹⁰ | MgEt ₂ in ether plus diethylenetriamine react at 30° and 90° for 20 and 16 hr, respectively | 30 | 24 | ether | | Reduced specific viscosity = 2.8 dl/g | 170 |
| 1970 | Bauer and Spooner ¹¹ | high-energy x-rays generated from 3 MeV van de Graff generator | -190° to 25°C heat IBO | | | | | high yields were obtained but the products had very low molecular weights $\eta_{sp}/c \cong 0.1$ |
| 1972 | Vandenberg ¹² | MgEt ₂ + NH ₃ | 30 | 45 | | 9.4 | $\eta_{inh} = 2.4$ dl/g | 175 |

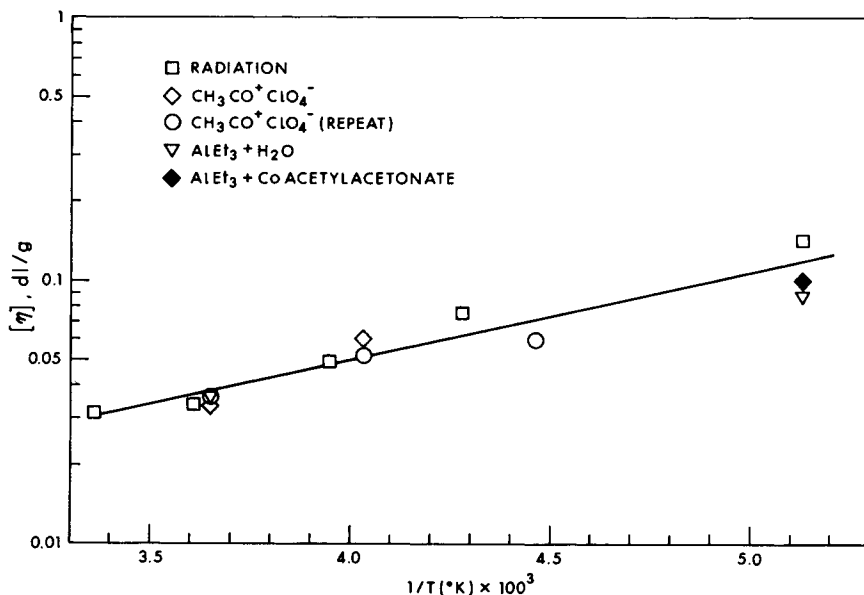


Fig. 1. Dependence of molecular weight of poly(isobutylene oxide) on temperature in cationic polymerizations.

EXPERIMENTAL RESULTS AND DISCUSSION

Polymerization Studies—Synthesis

Figure 2 collects and compares the activities of the different catalysts that were examined at temperatures of 70° to 140°C. A comparison is made with the Nippon-Carbide catalysts (denoted by shaded triangles) which were repeated in the present work.

The polymerization results obtained with these catalysts are described according to the following classification: (1) Nippon-Carbide Catalyst, (2) activation of Nippon-Carbide catalyst by styrene oxide, (3) ZnEt_2 - H_2S -cyclohexylamine catalyst, (4) ZnEt_2 -metal compound-cyclohexylamine catalyst, (5) miscellaneous catalysts, and (6) polymerizations at high temperatures.

Isobutylene oxide is also easily polymerized by cationic initiators which can be prepared by hydrolysis of metal alkyls or reaction of metal alkyls and certain transition metal salts. Such poly(isobutylene oxide) products have very low molecular weights (see Table I) and tend to have higher molecular weights as the temperature of polymerization is decreased (Fig. 1). We believe that the high molecular weight polymers prepared in this investigation involved coordinative-anionic mechanisms of the type discussed by Vandenberg,^{8-10,12} but we do not present experimental evidence for this view.

The Nippon-Carbide Catalyst

As already mentioned above, the Nippon-Carbide patent⁷ was the first disclosure of a catalyst for synthesizing high molecular poly(isobutylene

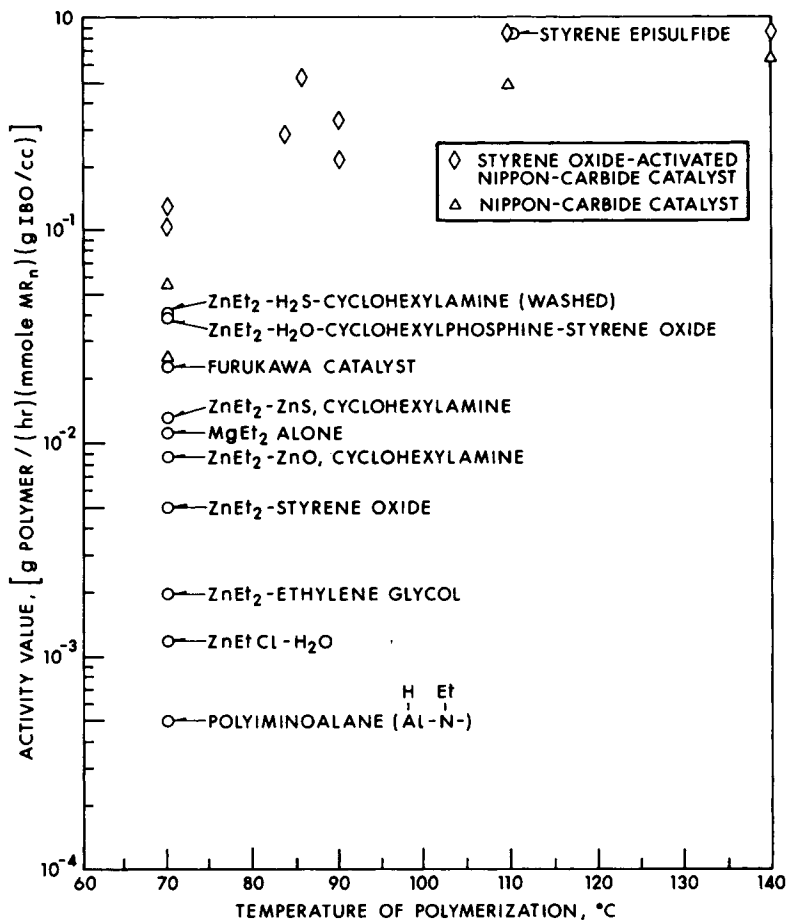


Fig. 2. Activities of experimental catalysts compared.

oxide) (PIBO). This catalyst was made by reacting ZnEt₂, water, and cyclohexylamine at ambient temperatures in molar ratios of about 1:0.39:0.27, respectively. In our hands, a conversion of 81% wt was obtained when 16.5 g IBO was polymerized for 42 hr at 70°C with a charge of 14 mmole ZnEt₂, 5.5 mmole H₂O, and 3.8 mmole cyclohexylamine in 25 cc heptane. The PIBO product had a reduced specific viscosity of 8.2 dl/g. When we left out the cyclohexylamine component, the catalyst was less active (52% wt versus 81% wt conversion), and the polymer which was formed had a lower reduced specific viscosity (3.1 dl/g).

Table II compares these findings with those reported in the Nippon-Carbide patent. We confirmed the claims of this patent that a higher molecular weight PIBO is formed when cyclohexylamine is added to the ZnEt₂-H₂O system. Our experiments also show that the amine also increases the yield from the ZnEt₂-H₂O system (from 52% to 81%) while the patent disclosed 65 to 62% wt conversions in the presence and absence of the amine, respectively.

TABLE II
Polymerization of Isobutylene Oxide with the Nippon-Carbide Catalyst

| Expt. no. | Solvent, cc | ZnEt ₂ , mmole | H ₂ O, cc | CHA, cc | IBO, g | Polymerization ^c | | Polymer | |
|---|-------------|---------------------------|----------------------|---------|--------|-----------------------------|----|----------|-----------------|
| | | | | | | hr | °C | Conv., % | η_{sp}/c^d |
| As Disclosed in Example 1 of GB 972, 898 ^a | | | | | | | | | |
| 1a | hexane, 120 | 70 | 0.38 | 1.3 | 100 | 42 | 70 | 65 | 3.85 |
| 1b | hexane, 120 | 70 | 0.38 | 0 | 100 | 42 | 70 | 62 | 2.30 |
| As Demonstrated in Current Investigation ^b | | | | | | | | | |
| 108-1 | toluene, 25 | 14 | 0.1 | 0 | 16.5 | 42 | 70 | 31 | 2.8 |
| 108-2 | heptane, 25 | 14 | 0.1 | 0 | 16.5 | 42 | 70 | 52 | 3.1 |
| 108-3 | toluene, 25 | 14 | 0.1 | 0.35 | 16.5 | 42 | 70 | 77 | 8.2 |
| 108-4 | heptane, 25 | 14 | 0.1 | 0.35 | 16.5 | 42 | 70 | 81 | 13.5 |

^a Preparation of catalyst: To a mixture of hexane, water, and amine was added a hexane solution ZnEt₂, the mixture was agitated for 30 min, and then IBO was added.

^b Preparation of catalyst: To a solution of ZnEt₂ in heptane was added a solution of 0.35 cc cyclohexylamine (CHA) and 0.1 cc H₂O, the mixture was aged for 2 hr at ambient temperature, and then IBO was added.

^c The catalyst and monomer were charged into 8-ounce bottles and these were rotated in baths which were thermostated at 70°C.

^d Reduced specific viscosities were done in *o*-dichlorobenzene at 150°C (see experimental section).

The ZnEt₂-H₂O system, while disclosed as an example, was not claimed by the patent. This system was first disclosed by Furukawa and his co-workers in 1960 as a polymerization catalyst for propylene oxide but not for IBO. The claimed novelty of the Nippon-Carbide patent is the use of an amine in the Furukawa catalyst to improve the molecular weight of PIBO.

The Nippon-Carbide patent did not disclose how the amine modified the catalyst so that it could produce PIBO having a higher molecular weight. In additional experiments we demonstrated that the amine effect was more pronounced (77% versus 31% wt conversions) when toluene was used as solvent in place of heptane (compare expts. 108-1 and 108-3 in Table II).

We had some difficulty in reproducing consistently the polymerization of IBO with the Nippon-Carbide catalyst. The data shown in expts. 108-3 and 108-4 of Table II represents the most active catalyst that we synthesized.

The order of mixing of the catalyst components did not influence the activity of the Nippon-Carbide catalyst. There is, however, a practical advantage of mixing the components in the order solvent → ZnEt₂ → H₂O + cyclohexylamine (expt. 108-3) rather than solvent → H₂O → cyclohexylamine (Nippon-Carbide patent example). The first order of addition leads to a fine dispersion (in heptane) or a colloidal suspension in toluene. The Nippon-Carbide order led to the formation of large aggregates of the

TABLE III
 Phosphines as Modifiers in the $\text{ZnEt}_2\text{-H}_2\text{O}$ Catalysts^a

| Expt. no. | Phosphine | | Reaction time, hr | Polymer | | |
|-----------|--|-------|-------------------|---------|----------|----------------------|
| | Type | mmole | | g | Conv., % | η_{sp}/c , dl/g |
| 108-1 | none (control) | — | 42 | 5.1 | 31 | 2.8 |
| | (extrapolated conversion at 66 hr = 46%) | | | | | |
| 106-4 | phenylphosphine | 1.0 | 66 | 9.1 | 55 | 3.6 |
| 106-7 | cyclohexylphosphine | 0.8 | 66 | 6.7 | 41 | 3.1 |
| 106-2 | triphenylphosphine | 0.4 | 66 | 5.0 | 30 | 3.5 |
| 106-5 | hexamethylphosphoramide | 0.62 | 66 | 0.6 | 4 | — |
| 106-3 | tricyclohexylphosphine | 0.2 | 66 | 0.2 | 1.2 | — |
| 106-6 | tributylphosphine | 1.0 | 66 | 0.2 | 1.2 | — |

^a Polymerization: 25 cc toluene, 9 cc 1.6 M ZnEt_2 solution, phosphine amount as indicated, 0.1 cc H_2O , then react at 25°C for 2 hours; add 16.5 g IBO and polymerize at 70°C for time shown.

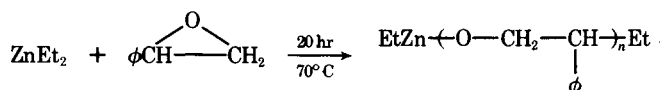
catalyst which adhered tenaciously to the glass walls. Having the catalyst as a colloidal suspension or as a fine dispersion has the advantage that it is more easily handled both in and out of the polymerization reactor.

When cyclohexylamine was replaced by phosphine compounds, catalysts were produced which polymerized IBO but which offered little advantage over the unmodified $\text{ZnEt}_2\text{-H}_2\text{O}$ system (Table III). The PIBO products which were prepared with phenylphosphine, cyclohexylphosphine, and triphenylphosphine had reduced specific viscosities of 3.6, 3.1, and 3.5 dl/g, respectively, compared to a value of 2.8 for the unmodified catalyst. The corresponding conversions were comparable or less when a phosphine was present.

Substitution of cyclohexylamine by N,N,N',N' -tetramethylenediamine (0.3 or 0.6 cc) killed the Nippon-Carbide catalyst when used for polymerizing IBO.

The Styrene Oxide-Activated Catalyst

In the early phase of our exploratory search for novel catalysts, we discovered that an active catalyst for the polymerization of IBO was made by the reaction of ZnEt_2 and styrene oxide. Unlike most epoxides, styrene oxide can be polymerized with ZnEt_2 without the presence of additional coreactants, e.g.,



where n = large number. The driving force for this addition is the ability of the phenyl ring to stabilize a charge on the tertiary carbon in the transition state.

When this apparently soluble polymeric $\text{ZnEt}_2\text{-styrene oxide}$ product was used to polymerize isobutylene oxide, conversions of IBO of about

TABLE IV
 ZnEt₂-Styrene Oxide System^a

| Expt., no. | Solvent, 25 cc | ZnEt ₂ , mmole | Styrene oxide, cc | Age | IBO, cc | Polym., hr | Polymer ^b conv., % |
|---------------|-------------------|------------------------------|----------------------|-----------|------------|---------------|----------------------------------|
| 46-1 | toluene | 14 | 1.8 | 20 hr/70° | 20 | 6 days | 18 |
| 46-2 | toluene | 14 | 1.6 | 20 hr/70° | 20 | 6 days | 34 |
| 46-3 | toluene | 14 | 3.2 | 20 hr/70° | 20 | 4 days | 24 |

^a The polymerizations were done in 8-ounce bottles. The catalyst components, ZnEt₂ + styrene oxide, were reacted at 70°C for 20 hr and then 16.5 g IBO (20 cc) was added. The reaction bottles were rotated in a bath thermostated at 70°C for the indicated times.

^b In separate experiments it was shown that about 0.5 to 1.2 g poly(styrene oxide) was formed in these experiments. The actual per cent conversions of IBO to polymer are about 3% to 8% lower than the shown values.

 TABLE V
 Activation of ZnEt₂-Based Catalysts with Styrene Oxide^a

| Expt. no. | Step 1 | Step 2 | Polymer ^b | | |
|--------------|--|--|----------------------|-------------|---------------|
| | | | Polym., hr | Conv., % | η_{sp}/c |
| 72-1 | 14 mmole ZnEt ₂ + 0.45 cc H ₂ O/CHA solution; age 2 hr at 25°C | 2.4 cc styrene oxide; age 17 hr at 70°C | 18 | 70 | 5.4 |
| 72-2 | 14 mmole ZnEt ₂ + 2.4 cc styrene oxide; age 17 hr at 70°C | 0.45 cc solution of H ₂ O/CHA; age 2 hr at 25°C | 18 | 46 | 8.9 |
| 108-5 | 14 mmole ZnEt ₂ + 0.1 cc H ₂ O | 2.0 cc styrene | 24 | 12 | 1.0 |
| 108-6 | 14 mmole ZnEt ₂ + 0.1 cc H ₂ O | oxide reacted at 70°C for 15 hr | 24 | 20 | 1.4 |
| 108-7 | same as for 108-3 and 108-4 | same as for 108-5 and 108-6 | 24 | 95 | 6.0 |

^a All except 108-6 were done in toluene solvent; heptane was used in 108-6.

^b The polymerizations were done in 8 ounce bottles by the same method described in Table IV. Expts. no. 108-5 and 108-6 were done in toluene and heptane, respectively.

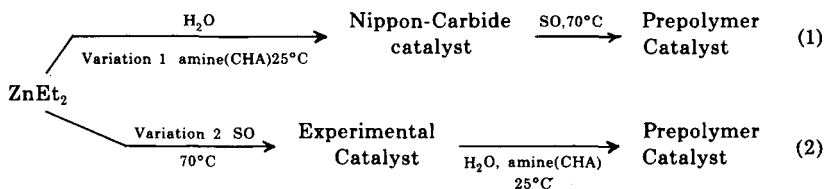
20-30% were obtained (Table IV). Relative to the Nippon-Carbide catalyst, these activities were considerably lower (see Fig. 1).

This finding was applied in two variations in our effort to increase the activity of the Nippon-Carbide catalyst.

Variation 1. The Nippon-Carbide catalyst was reacted with a small amount of styrene oxide (SO) (ZnEt₂/SO = 1/2) in toluene solvent for 17 hr at 70°C. This apparently soluble product was then used to polymerize IBO (expt. 72-1, Table V).

Variation 2. The styrene oxide and ZnEt₂ were first reacted at 70°C for 17 hr, and then a solution of H₂O and cyclohexylamine (CHA) was added, followed by aging for 2 hr at ambient temperatures. This pre-polymer catalyst was also soluble and active for the polymerization of IBO (expt. 72-2, Table V).

The reactions described above can be seen better in the following equation form:



Both prepolymer catalysts were more active than the Nippon-Carbide catalyst and both produced PIBO which had a high molecular weight. Under conditions which led to a 21% conversion with the Nippon-Carbide catalyst, conversions of 70% and 46% were obtained with the prepolymer catalyst prepared according to variations 1 and 2, respectively. Thus, the styrene oxide-modified catalysts were 2 to 3 times more active. Like the PIBO obtained with the Nippon-Carbide catalyst, the PIBO samples synthesized above also had high molecular weights, e.g., reduced specific viscosities above 5 dl/g.

Because we encountered in course of the investigation some variation in activities when polymerizing different lots of IBO, we ran simultaneously in both toluene and heptane solvents the Furukawa, the Nippon-Carbide, and the styrene oxide-activated catalysts. Our previous findings were confirmed, namely, that the styrene oxide-activated catalyst was more active than the Nippon-Carbide catalyst and the latter was more active than the Furukawa catalyst (Tables II and V, compare expts. 108-7, 108-3, 108-4, 108-1, and 108-2).

A substitution or deletion was made in one of the components in the styrene oxide-activated catalyst described above with the goal of improving its activity. As described already, this catalyst was made by combining ZnEt_2 , H_2O , cyclohexylamine, and styrene oxide.

The following was observed:

1. Replacement of styrene oxide by styrene episulfide produced a catalyst of comparable activity. However, no activation was observed when α -methylstyrene oxide was used in place of styrene oxide.

2. If the amine was left out of the catalyst, styrene oxide failed to activate the ZnEt_2 - H_2O catalyst.

3. If ZnEt_2 was replaced by ZnMe_2 , styrene oxide again failed to activate the ZnR_2 - H_2O system. This finding was unexpected because ZnEt_2 and ZnMe_2 formed catalysts of comparable activities when reacted with H_2O and cyclohexylamine, e.g., 20-30% wt conversions were obtained during polymerization of 17-21 hr at 70°C.

4. Replacing the cyclohexylamine component with a phosphine compound produced a less active catalyst (Table VI). The activity of this phosphine-containing catalyst was comparable to that found for the Nippon-Carbide catalyst.

5. When ZnEt_2 was replaced by MgEt_2 , a catalyst was obtained whose activity was comparable to that found with MgEt_2 alone. Substituting

TABLE VII
 Polymerization of Isobutylene Oxide with a ZnS-Type Catalyst Made by Reacting
 ZnEt₂ and H₂S^a

| Expt. no. | Solvent, 25 cc | ZnEt ₂ , mmole | CHA, mmole | H ₂ S, mmole | Age | | Polym., hr | Polymer | |
|--------------|-------------------|------------------------------|---------------|----------------------------|-----|----|---------------|-------------|-------------------------|
| | | | | | hr | °C | | Conv., % | η_{sp}/c , dl/g |
| 170-1 | Toluene | 14 | 0 | 3 | 18 | 25 | 90 | 8 | — |
| 170-2 | Toluene | 14 | 0 | 6 | 18 | 25 | 90 | 3 | — |
| 170-3 | Toluene | 14 | 0 | 12 | 18 | 25 | 90 | 17 | — |
| 65-1 | Heptane | 14 | 0 | 10 | 2 | 25 | 120 | 6 | — |
| 100-4 | Toluene | 14 | 0 | 5.5 | 2 | 25 | 42 | 1 | — |
| 170-4 | Toluene | 14 | 0.35 | 6.0 | 18 | 25 | 90 | 55 | — |
| 170-5 | Toluene | 14 | 0.70 | 6.0 | 18 | 25 | 90 | 61 | — |
| 170-6 | Toluene | 14 | 1.0 | 6.0 | 18 | 25 | 90 | 32 | — |
| 100-1 | Toluene | 14 | 0.35 | 5.5 | 2 | 25 | 42 | 9 | 3.7 |
| 97-1 | Toluene | 14 | 0.35 | 5.5 | 2 | 25 | 66 | 35 | 4.9 |

^a A 1 molar solution of H₂S was made by bubbling H₂S into toluene which was kept at about 0–5°C. This cold solution of H₂S was transferred by a syringing technique to the reaction vessel containing the ZnEt₂ or ZnEt₂ plus cyclohexylamine (if used) in solvent (also cooled to 0–5°C) and then aged. These operations were done under a nitrogen atmosphere. Some H₂S may have been lost through the outlet. This may partly explain our inability to duplicate consistently the activity of these catalysts.

active than were the amine-free ones when used to polymerize IBO. In a 90-hr polymerization at 70°C, conversions of 32% to 61% were obtained, compared to conversions of 3% to 17% with the amine-free catalysts (Table VII).

All of the catalysts used in Table VII were prepared right in the polymerization bottle. Several catalysts were then prepared on a larger scale (two- to eight-fold scale-up) in a separate glass vessel in order that two or more synthesis could be done with each preparation. The ZnEt₂ and H₂S components were reacted in the absence or presence of cyclohexylamine. In both cases, the reaction was fast, and a white powder precipitated. When cyclohexylamine was also present, the formed ZnS powder has a lower bulk density, the apparent volume of the latter catalyst was about three times that of the catalyst prepared in absence of amine.

The solvent was removed from the white solid by a simple decantation (Table VIIIa) or by a decantation after the solid was compacted by centrifuging (Table VIIIb). After the solid was washed with heptane or toluene which contained some ZnEt₂, the separation was repeated. These washed catalysts were examined for polymerization of IBO. Footnotes "a" in Tables VIIIa and VIIIb describe this procedure in more detail.

The highest activity was obtained in experiment 9-2 of Table VIIIa. This catalyst gave a conversion of 39% in 21 hr at 70°C; a conversion of 20–30% was usually obtained with the Nippon-Carbide catalyst under comparable polymerization conditions.

TABLE VIIIa
 Washed ZnEt₂-H₂S Catalysts—Decanting Method

| Expt. no. | Slurry of washed ZnS catalyst ^a | Modification of ZnS catalyst | IBO, cc | Polym. | | Polymer | |
|-----------|--|--------------------------------------|---------|--------|----|----------|----------------------|
| | | | | hr | °C | Conv., % | η_{sp}/c , dl/g |
| 9-2 | 14 mmole ZnS | None | 20 | 21 | 70 | 39 | 1.83 |
| 9-1 | 14 mmole ZnS | 2 cc styrene oxide heat 20 hr/70° | 20 | 21 | 70 | 22 | — |

^a This slurry of ZnS catalyst was prepared by the following procedure: In a 500-cc flask was placed under nitrogen 200 cc heptane, 72 cc ZnEt₂ (1.5*M*), and 3.5 cc pure cyclohexylamine (CHA). The solution was cooled to 0°C, and then 60 mmole H₂S-toluene solution was added while stirring the mixture with a magnetic stirring bar. After the H₂S was completely added, the vessel was closed off and let set overnight. The white ZnS product settled to the bottom of the vessel and the supernatant solution was decanted. Fresh heptane containing some ZnEt₂ (0.5*M*) was added and the procedure was repeated two times. Finally, enough heptane (0.5*M* in ZnEt₂) was added so that 35 cc contained 14 mmole of the ZnS catalyst product.

Unlike the Nippon-Carbide catalyst, the ZnS catalyst was not made more active by heating it with a small amount of styrene oxide (compare expts. 9-1 and 9-2, Table VIIIa).

Active catalysts were also made when the supernatant solution was removed by centrifuging-washing techniques, although these were not as active as the catalyst described in Table VIIIa. Further modification of these washed catalysts revealed the following: (1) addition of ZnEt₂ did not increase their activity, and (2) addition of cyclohexylamine decreased significantly their activity. As already found for unwashed catalysts when cyclohexylamine was left out of the synthesis of the washed ZnS catalysts, the latter had only low activities.

Up to now, only IBO was used to evaluate the activity of the ZnS catalysts. In supplementary experiments, it was found that the unwashed ZnS catalyst was also active for polymerizing propylene oxide and styrene oxide (Table IX). The order of activity was styrene oxide > propylene oxide > isobutylene oxide.

ZnEt₂-Metal Compound-Amine Catalyst

Mixtures of ZnEt₂ and specific metal compounds polymerized isobutylene oxide to high molecular weight products if cyclohexylamine was also present (Table X). Such metal compounds as ZnO, ZnS, zinc titanate, zinc zirconate, zinc molybdate, AlPO₃, Al(*i*-PrO)₃, and ϕ_3 SnOH were effective. Mixtures of cyclohexylamine and the metal compounds were inactive (66 hr at 70°C). In case of ZnO, only when cyclohexylamine was added did the ZnEt₂-ZnO mixture become active. In all cases, the presence of cyclohexylamine enhanced the activities of the corresponding catalysts.

The polymers had high molecular weights (reduced specific viscosities from 2 to 3.5 dl/g) except for the product made with Al(*i*-PrO)₃.

TABLE VIIIb
 Washed $\text{ZnEt}_2\text{-H}_2\text{S}$ Catalysts—Centrifuging Method

| Expt. no. | Washed catalyst, 14 mmole | Additional component ^c | Polym. ^d | | Polymer | |
|-----------|---|-----------------------------------|---------------------|----|----------|----------------------|
| | | | hr | °C | Conv., % | η_{sp}/c , dl/g |
| 195-1 | $\text{ZnEt}_2 + \text{CHA} + \text{H}_2\text{S}$ | None | 66 | 70 | 27 | 0.65 |
| 195-2 | $\text{ZnEt}_2 + \text{CHA} + \text{H}_2\text{S}$ | 0.35 cc CHA | 66 | 70 | 3 | — |
| 199-1 | $\text{ZnEt}_2 + \text{CHA} + \text{H}_2\text{S}$ | 7 mmole ZnEt_2 | 42 | 70 | 33 | 2.79 |
| 199-2 | $\text{ZnEt}_2 + \text{CHA} + \text{H}_2\text{S}$ | None | 42 | 70 | 43 | 1.88 |
| 195-3 | $\text{ZnEt}_2 + \text{H}_2\text{S}^b$ | None | 42 | 70 | 3 | — |
| 195-4 | $\text{ZnEt}_2 + \text{H}_2\text{S}^b$ | 0.35 cc CHA | 42 | 70 | 3 | — |

^a 28 Mmole of a catalyst prepared by the following procedure was used. A solution of 28 mmole ZnEt_2 (1.5M) and 0.7 cc cyclohexylamine (CHA) was made in a centrifuge bottle containing 50 cc toluene. This solution was cooled to ca. 5°C, and then 12 mmole H_2S (as a cold 1 molar toluene solution) was added by a syringe tube. The mixture was kept cold for 30 min and then warmed to ambient temperatures. The serum cap was coated with silicone grease and then covered with a finger cot and the mixture was set aside overnight. The next morning the samples were centrifuged (5 min at 900 rpm) and the supernatant solution was removed. Fresh toluene containing some ZnEt_2 (0.25M) was added and the centrifuging-washing step was repeated. Finally, heptane containing some ZnEt_2 (0.01M) was added to make a slurry to be used in these experiments.

^b The procedure described in "a" was used except that no amine was added.

^c In two experiments, additional cyclohexylamine (CHA) was added to the washed catalysts.

^d The polymerizations were done in 8-ounce bottles. The 35cc of this heptane slurry of the catalyst (14 mmole ZnS) was transferred to the bottle, additional modifier was then added in experiments 195-2 and 195-4, and finally 16.5 g IBO was added. The charge was polymerized for the indicated times and temperatures.

 TABLE IX
 Polymerization of Propylene oxide, Styrene oxide, and Isobutylene Oxide
 with an Unwashed $\text{ZnEt}_2\text{-H}_2\text{S-CHA}$ Catalyst^a

| Expt. no. | Monomer | | Aging | | Polym. ^b | | Polymer conv., % |
|-----------|---------|-------------------|-------|----|---------------------|----|------------------|
| | g | Epoxide | hr | °C | hr | °C | |
| 1 | 17 | propylene oxide | 24 | 25 | 46 | 70 | 80 |
| 2 | 22 | styrene oxide | 24 | 25 | 46 | 70 | 100 |
| 4 | 16.5 | isobutylene oxide | 18 | 25 | 90 | 70 | 61 |

^a Prepared by same procedures described in Table VIIIb. The catalyst components were 14 mmole ZnEt_2 , 0.35 cc cyclohexylamine, and 6 mmole H_2S .

^b Polymerizations were done in 8-ounce bottles.

Other Catalysts Investigated

In addition to the catalysts which were described above, other systems were investigated with the goal of finding very highly active catalysts contained as one of the components a metal alkyl of a group II or group III metal. When the metal alkyl was ZnEt_2 , a number of organic compounds, which were not described in the earlier sections, were examined as coreactants.

TABLE X
 Polymerization of Isobutylene Oxide with Mixtures of Metal Compound, Cyclohexylamine, and ZnEt₂ as Catalysts^a

| Expt. no. | Solvent | | Metal compound | | Cyclohexyl-amine, cc | ZnEt ₂ , mmole | Aging | | Polym., hr | Polymer | |
|-----------|---------|---------|----------------|---|----------------------|---------------------------|-------|----|------------|----------|---------------|
| | cc | Type | g | Type | | | hr | °C | | Conv., % | η_{sp}/c |
| 1 | 10 | toluene | 1.0 | ZnO | 0.2 | 7 | 5 | 25 | 66 | 20 | 3.8 |
| 2 | 25 | toluene | 1.0 | ZnO | 0.2 | 7 | 2 | 75 | 66 | 21 | — |
| 3 | 25 | toluene | 1.0 | ZnO | 0.2 | 7 | 17 | 75 | 66 | 28 | — |
| 4 | 25 | toluene | 1.0 | ZnO | 0 | 7 | 2 | 75 | 66 | — | — |
| 5 | 10 | toluene | 1.0 | ZnS | 0.1 | 7 | 4 | 25 | 66 | 24 | — |
| 6 | 10 | toluene | 1.0 | ZnS | 0.2 | 7 | 4 | 25 | 66 | 32 | 2.0 |
| 7 | 10 | toluene | 1.0 | ZnS | 0.4 | 7 | 4 | 25 | 66 | 38 | — |
| 8 | 10 | toluene | 1.0 | zinc titanate | 0.2 | 7 | 4 | 25 | 66 | 23 | 2.2 |
| 9 | 10 | toluene | 1.0 | zinc zirconate | 0.2 | 7 | 4 | 25 | 66 | 24 | 3.4 |
| 10 | 10 | toluene | 1.0 | zinc molybdate | 0.2 | 7 | 4 | 25 | 66 | 19 | 3.5 |
| 11 | 15 | heptane | 1.0 | AlPO ₃ | 0 | 0 | — | — | 90 | 7 | — |
| 12 | 15 | heptane | 1.0 | AlPO ₃ | 0.2 | 1.5 | 2 | 25 | 90 | 25 | — |
| 13 | 25 | toluene | 1.0 | Al(<i>i</i> -PrO) ₃ | 0.2 | 7 | 2 | 75 | 66 | 20 | — |
| 14 | 25 | toluene | 1.0 | Al(<i>i</i> -PrO) ₃ | 0.2 | 7 | 17 | 75 | 66 | 7 | — |
| 15 | 25 | toluene | 1.0 | Al(<i>i</i> -PrO) ₃ | 0 | 7 | 2 | 75 | 66 | 4 | — |
| 16 | 10 | toluene | 1.4 | Al(<i>i</i> -PrO) ₃ | 0.4 | 7 | 2 | 25 | 66 | 37 | 0.09 |
| 17 | 10 | toluene | 1.4 | Al(<i>i</i> -PrO) ₃ | 0.4 | 7 | 2 | 50 | 66 | 16 | — |
| 18 | 10 | toluene | 2.8 | Al(<i>i</i> -PrO) ₃ | 0.4 | 7 | 2 | 50 | 66 | 23 | — |
| 19 | 10 | toluene | 0.7 | Al(<i>i</i> -PrO) ₃ | 0.4 | 7 | 2 | 50 | 66 | 23 | — |
| 20 | 10 | toluene | 2.6 | $\phi_3\text{SnOH}^b$ | 0 | 7.5 | 2 | 25 | 66 | 32 | — |
| 21 | 10 | toluene | 1.6 | (ϕCH_2) ₃ SnOH | 0 | 7.5 | 2 | 25 | 66 | 8 | — |
| 22 | 10 | heptane | 1.0 | $\phi_3\text{SnOH}$ | 0.4 | 1.5 | 2 | 25 | 66 | 0.8 | — |

^a The polymerizations were done in 8-ounce bottles. The order of mixing was: metal oxide, toluene, cyclohexylamine, and ZnEt₂.

^b Conversions of 0.3%, 2.4% and 1.0% were obtained when Bu₃SnOCH₃, Bu₃SnO₂H, and Bu₃SnBu₃ were examined under comparable conditions.



TABLE XI

Polymerization of Isobutylene Oxide with Mixtures of ZnEt_2 and Organic Compounds^a

| Expt. no. | Coreactant | Amount | Aging cond. | Polymer | | |
|-----------|-------------------------------------|---------|-------------|---------|----|------------------|
| | | | | hr | °C | Conv., % |
| 41-8 | Nippon-Carbide catalyst (reference) | | | 120 | 70 | 85 |
| 40-9 | <i>n</i> -BuOH | 1 cc | 2 hr/25°C | 120 | 70 | 0.6 |
| 40-10 | ethylene glycol | 0.35 cc | 2 hr/25°C | 120 | 70 | 12.7 |
| 40-11 | glycerol | 0.25 cc | 2 hr/25°C | 120 | 70 | 15.2 |
| 49-9 | hexamethyldisilazane | 1.6 cc | 2 hr/25°C | 96 | 70 | 7.5 |
| 49-10 | hexamethyldisilazane | 3.2 cc | 2 hr/25°C | 96 | 70 | 10.3 |
| 48-8 | bisphenol A | 1.0 g | 1 hr/75°C | 96 | 70 | 0 |
| 48-9 | phthalic anhydride | 1.0 g | 1 hr/75°C | 96 | 70 | 0 |
| 48-10 | hexahydrophthalic anhydride | 1.0 g | 1 hr/75°C | 96 | 70 | 0 |
| 48-11 | pivalolactone | 1 cc | 1 hr/75°C | 96 | 70 | 6.0 ^b |
| — | epoxide ^c | 2 cc | 17 hr/70°C | 96 | 70 | ca. 6.0–12.0 |

^a The catalyst was formed by reacting 14 mmole ZnEt_2 and the organic compound followed by aging under conditions shown above.

^b The contribution of the polyester to the weight was not determined.

^c Epoxides such as $\text{H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})\text{OCH}_2$, , $\text{H}_2\text{C}(\text{O})\text{CH}-\text{CH}_2$ — and 2,3-epoxy-

butyrate were used. Comparable results were obtained with AlEt_2 as the metal component.

While many of these systems were found active for the polymerization of IBO, none was very highly active.

Table XI compares the activities of the catalysts which were formed by reacting ZnEt_2 and organic compounds such as *n*-BuOH, ethylene glycol, glycerol, hexamethyldisilazane, epoxides, phthalic anhydride, hexahydrophthalic anhydride, and bisphenol A. Catalysts of low activity were made with ethylene glycol, glycerol, and hexamethyldisilazane (lower than 10% conversions compared to higher than 80% conversions which were obtained with the Nippon-Carbide catalyst). The other systems were inactive.

When ZnEt_2 was replaced by $\text{Zn}\phi_2$ in the $\text{ZnR}_2\text{-H}_2\text{O}$ or in the $\text{ZnR}_2\text{-H}_2\text{O-cyclohexylamine}$ systems, the catalysts became inactive (expts. 38-2 and 38-3 in Table XII). Those based on ZnEtCl were only slightly active (expts. 38-4 and 38-5). MgEt_2 alone was active polymerizing IBO, and reacting it further with H_2O or H_2O plus cyclohexylamine did not increase its activity (expt. 71-1). Comparable catalysts where ZnEt_2 was replaced by AlEt_3 also had low activity (expts. 38-6 and 38-7).

A polyiminoalane having the structure

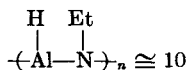


TABLE XII
 Polymerization of Isobutylene Oxide with Catalysts
 Derived from Different Metal Alkyls^a

| Expt. no. | Solvent, 25 cc | Metal alkyl, 14 mmole | Coreactants | | Polymer | | Conv., % |
|-----------|----------------|-----------------------|------------------|---------|---------|----|----------|
| | | | H ₂ O | CHA | hr | °C | |
| 38-2 | toluene | $\phi_2\text{Zn}$ | 0.1 cc | 0.35 cc | 96 | 70 | 0 |
| 38-3 | toluene | $\phi_2\text{Zn}$ | 0.1 cc | none | 96 | 70 | 0 |
| 38-4 | heptane | ZnEtCl | 0.1 cc | 0.35 cc | 96 | 70 | 1.8 |
| 38-5 | heptane | ZnEtCl | 0.1 cc | none | 96 | 70 | 2.4 |
| 38-6 | heptane | AlEt ₃ | 0.1 cc | 0.35 cc | 96 | 70 | 11.5 |
| 38-7 | heptane | AlEt ₃ | 0.1 cc | none | 96 | 70 | 19.1 |
| 71-1 | heptane | MgEt ₂ | none | none | 22 | 70 | 13.3 |
| 68-6 | heptane | MgEt ₂ | 0.1 cc | 0.35 cc | 18 | 70 | 3.6 |

^a The catalysts were prepared in the 8-ounce bottles which were also used to polymerize IBO. The order was solvent → metal alkyl → coreactants. The catalyst mixture was aged at ambient temperatures before IBO was added.

was synthesized¹³ by reaction of EtNH₂HCl and LiAlH₄. The isolated product, which was soluble in toluene, gave only very low conversions (see Fig. 1).

Polymerization Data for Temperatures Above 70°C

The Nippon-Carbide and the styrene oxide-activated modification were examined at 80°, 90°, 110°, and 140°C for activity (Table XIII).

Both became more active up to 100°C but no significant increases in activity was noted on going from 100° to 140°C. Comparing activities at 100° and 70°C, respectively, these catalysts became about 6 to 10 times more active.

There was a corresponding decrease in the molecular weights of the products, e.g., from 5.4–8.2 dl/g to 1.7 dl/g on going from 70° to 110°C and to 0.73 dl/g at 140°C.

In the case of the styrene oxide-activated catalyst, there was found a steady increase in the activity of the catalyst as the temperature of polymerization was increased from 70° to 110°C. This was not the case with the Nippon-Carbide catalyst. Very low conversions (1.8%) were obtained in 4 hr at 90°C (expts. 50-6 and 50-7, Table XIII). Yet the same catalyst at 110°C produced a conversion of 72% in 4 hr. Surprisingly, the same catalyst produced a conversion of 66% at 85° if the polymerization was carried out for 18 hr. The implication of these results was that the activity of the Nippon-Carbide catalyst is increased when this catalyst is aged at a high temperature.

CHARACTERIZATION RESULTS AND DISCUSSION

The high molecular weight poly(isobutylene oxide) obtained in this study was a highly crystalline material, which could readily be fabricated into molded articles or spun into fibers. It is a relatively high-melting, inert

TABLE XIII
 Polymerization of IBO at Temperatures Higher than 70°C

| Expt. no. | Catalyst ^a | Polymerization ^c | | Polymer | | Comments ^e |
|-----------|---|-----------------------------|-----|----------|-----------------------------------|-----------------------|
| | | hr | °C | Conv., % | η_{sp}/c , ^d dl/g | |
| 108-3 | Nippon-Carbide | 42 | 70 | 77 | 8.2 | agitated |
| 72-8 | Nippon-Carbide | 18 | 70 | 21 | — | agitated |
| 43-2 | Nippon-Carbide | 18 | 85 | 66 | — | agitated |
| 50-6 | Nippon-Carbide | 4 | 90 | 1.8 | — | agitated |
| 50-7 | Nippon-Carbide | 4 | 90 | 1.8 | — | not agitated |
| 50-8 | Nippon-Carbide | 4 | 110 | 72 | 1.64 | not agitated |
| 50-9 | Nippon-Carbide | 4 | 140 | 82 | 0.73 | not agitated |
| 72-1 | styrene oxide activated ^b | 18 | 70 | 70 | 5.4 | agitated |
| 50-1 | styrene oxide activated ^b | 3 | 70 | 11 | — | agitated |
| 46-3 | styrene oxide activated ^b | 2 | 84 | 27 | — | agitated |
| 46-4 | styrene oxide activated ^b | 4 | 86 | 68 | — | agitated |
| 46-5 | styrene oxide activated ^a | 6 | 88 | 94 | — | agitated |
| 50-2 | styrene oxide activated ^b | 3 | 90 | 44 | — | agitated |
| 50-3 | styrene oxide activated ^b | 3 | 90 | 30 | 3.67 | not agitated |
| 50-4 | styrene oxide activated ^b | 3 | 110 | 86 | 1.63 | not agitated |
| 50-5 | styrene oxide activated ^b | 3 | 140 | 84 | 0.77 | not agitated |

^a Prepared by adding a solution of water and cyclohexylamine (0.35 cc amine plus 0.1 cc H₂O) to a solution of 14 mmole ZnEt₂ in 25 cc toluene and aging the product for 2 hr at ambient temperature. These were done in 8-ounce bottles as reaction vessels.

^b Prepared by heating the Nippon-Carbide catalyst (see footnote "a") with 2 cc styrene oxide for 17 hr at 70°C.

^c 20 cc IBO (16.5 g) was then added to the reaction vessels; the 8-ounce bottles were capped and then placed in the polymerization bath.

^d Some of these bottles were agitated by rotating them in the polymerization bath. Because the temperatures above about 90°C could not be achieved in this bath, the polymerizations which were done in the 90–140°C range were done in small oil baths which had no agitation. Two control runs were made at 90°C, one with agitation and one without agitation.

^e The reduced specific viscosities were determined in *o*-dichlorobenzene at 150°C.

polymer with an overall balance of properties which appears to put it in the class of the so-called engineering thermoplastics. As can be seen from Table XIV, poly(isobutylene oxide) is clearly superior in physical and mechanical properties to isotactic polypropylene and falls more clearly in the range of thermoplastics, such as chlorinated polyethers and polyacetals.

As is the case for most other polymers, PIBO is affected by ultraviolet light. Unstabilized specimens of PIBO (0.12 in. thick) completely dis-

TABLE XIV
 Summary of Physical and Mechanical Properties of Poly(isobutylene Oxide) versus Some Selected Engineering Thermoplastics^a

| Properties | Poly (isobutylene oxide) | Chlorinated polyether (Penton) | Nylon 6 ^b unmodified | Polyacetal homopolymer | Polycarbonate unfilled | Polypropylene unmodified |
|---|--------------------------------|--------------------------------------|------------------------------------|---------------------------|---------------------------|-----------------------------|
| Density | 1.03 | 1.40 | 1.13-1.15 | 1.42 | 1.2 | 0.902-0.910 |
| Tensile strength, psi | 5700 | 6000 | 11,200 ^a | 10,000 | 9500 | 4300-5500 |
| Elongation at break, % | 9 | 60-160 | 300 ^a | 25 | 100-130 | 200-700 |
| Impact strength (Izod), ft-lb/in., at: | | | | | | |
| 0°C | 1.0 | | | 1.4 | | 0.3 |
| 25°C | 1.2 | 0.4 | 2.5 | 1.4 | 12-18 | 0.7 |
| Heat distortion temp., °F, at: | | | | | | |
| 264 psi | 212 | | 155 | 255 | 265-285 | 125-140 |
| 66 psi | 295 | 285 | 365 | 338 | 270-290 | 200-250 |
| Hardness (Rockwell) | M41, R110 | R100 | R120 | R120 | M73-78, R115-120 | R80-110 |
| Melting point, °C | 174 | 245 | 216 | 175 | | 165 |

^a From ref. 14.

^b After conditioning at 20°C and 50% R.H.

integrated in the accelerated Weatherometer in less than 140 hr—about the same order of UV stability as unstabilized polypropylene. In the only attempt to stabilize the polymer, it was treated with 0.5% Cyasorb UV531, and the loss tensile strength with time was examined. After 250 hr, the tensile strength had dropped to about half of its initial value, and then after 500 hr it had fallen to about 25%. On the basis of this single experiment, it seems certain that further improvement in the UV stability of PIBO is possible.

Thermal Stability

The PIBO sample used for characterization and prepared in these laboratories from the Nippon-Carbide catalyst was thermally stable at its processing temperatures and was readily fabricated into molded articles or spun into fibers. All the specimens used for the mechanical testing described below were prepared in a Van Dorn injection molder at a barrel temperature of 227°C. During this molding process, the inherent viscosity only dropped from 1.0 dl/g to 0.9 dl/g. The sprues and used test specimens were then reground and spun into fibers at a melt temperature of 235°C, which resulted in a fiber with an inherent solution viscosity of 0.80 dl/g. Further evidence of the stability of these polymers was obtained from thermogravimetric analysis, which indicated no appreciable weight loss below 235°C (Fig. 3).

We wish to point out that some of our other samples were less stable at these temperatures, and a decrease in molecular weight was observed during hot milling on a two-roll mill operation. Kamis and co-workers¹⁵ have recently reported that degradation can be decreased by use of a stabilizer mixture consisting of certain phenolic compounds and a metal dithiocarbamate. Since our work preceded the publication of this patent, we had no chance to use this stabilizer.

Mechanical and Thermal Properties

Mechanical properties were obtained on injection-molded specimens prepared as described above, and in specimens that were compression-molded at 200°C and then slowly cooled through the recrystallization temperature (151°C). Essentially no difference was observed in the properties of samples prepared by the two methods. Molded articles from the polymer were white to slightly yellow and were translucent to opaque depending on the thickness, with a hard, smooth surface that has a slippery feel.

Impact and Tensile Strength. The room temperature (73°F), Izod impact strength of the PIBO samples was found to be 1.2 ft-lb/in. and at 0°C it was 1.0 ft-lb/in. PIBO was found to have an elongation, at 73°F, of 8–10% and tensile strength of 5700 psi, with no true yield point.

Heat Distortion Temperature. The heat distortion temperature of PIBO is comparable to, and in several cases better than, that of existing commercial thermoplastics. At 264 psi fiber stress, the heat deflection temper-

TABLE XV
Poly(isobutylene Oxide) Fibers

| Melt temp., °C | Quench temp., °C | Stretch ratio | Tenacity, g/den | Elongation, % |
|-------------------|---------------------|------------------|--------------------|------------------|
| 234 | 82 | 3.5 | 3.4 | 14 |
| 234 | 127 | 3.0 | 2.6 | 30 |
| 231 | 127 | 3.5 | 3.4 | 11 |

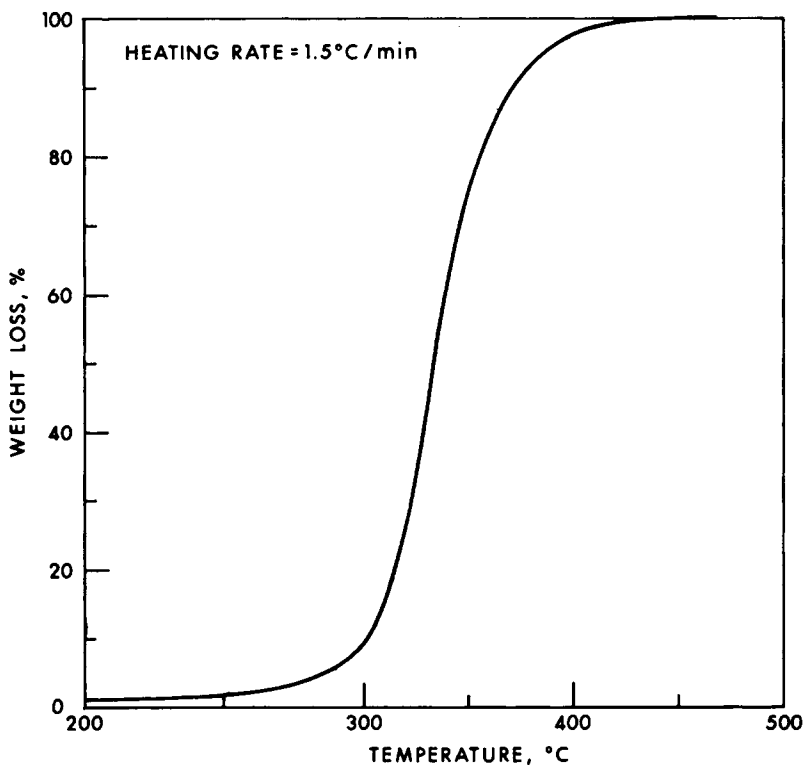


Fig. 3. Thermal stability of poly(isobutylene oxide) under nitrogen.

ature of PIBO was found to be 212°F [100°C and at 66 psi fiber stress 295°F (146°C)].

Fiber Properties. Undrawn fiber was readily obtained on a 1/2-in laboratory extruder from PIBO. Using a four-hole die, spinning conditions were set to give a fiber of about 70 denier (17–18 denier per filament), which has a maximum stretch ratio of 3.5. Table XV summarizes the properties of the fibers obtained and the conditions under which they were prepared. Microscopic investigation of the undrawn fibers under crossed polars indicates a considerable amount of spherulitic structure, which would result in poor stretching characteristics and a poor overall balance of fiber properties. Certainly this could be overcome with higher melt temper-

atures and quench temperatures above the recrystallization temperatures (151°C).

Actually, these particular fibers already have quite a respectable balance of tenacity and elongations; thus, it appears that PIBO has promise as a fiber former.

EXPERIMENTAL

Materials

Isobutylene Oxide. This was initially purchased from Farchan Chemical, Cleveland, Ohio. But because later it was discontinued, we requested Research Organic/Inorganic of Sun Valley, California, to synthesize a 2-kg lot. The monomer was purified by exposing it first to 3A mole sieves for several days, then by treating with CaH_2 . The sample was always distilled within 1 hr of catalyst addition. All operations were done under a nitrogen atmosphere.

Solvents. Toluene was washed with sulfuric acid, distilled water, and Na_2CO_3 , and finally passed through silica gel. It was then mixed with CaH_2 , filtered, and then distilled from fresh CaH_2 , and finally stored over CaH_2 under nitrogen. Heptane was passed through silica gel and distilled from CaH_2 . It was also stored over CaH_2 under N_2 .

Metal Alkyls. These were purchased as 25% wt solutions in hydrocarbon solvents from Texas Alkyls and from Ethyl Corporation.

Other Materials. Distilled water was used to hydrolyze metal alkyls. Cyclohexylamine was distilled before being used.

Procedure

For the screening experiments, 8-ounce hydrogen peroxide-type bottles were used as reaction vessels. These were washed and baked in an oven at 120°C for several days. All components were added under a nitrogen atmosphere. The exact procedures that were used are described on the appropriate tables. At the termination of a polymerization the products were added to excess methanol (ca. five fold), let set overnight, and then filtered. They were dried in a vacuum oven at 60°C.

Analytical Procedure for Determining Molecular Weights

Reduced specific viscosities were determined in *o*-dichlorobenzene at 150°C and at a polymer concentration of 0.3 g/dl. To facilitate the solution of polymer in *o*-dichlorobenzene, it was found indispensable to sprinkle the polymer as a fine powder into hot solvent. Using this procedure, it took about 15 to 20 min to dissolve up to 0.3 g polymer in 100 cc solvent. Adding polymer to solvent in one step resulted in agglomeration and a longer solution time (1 to 3 hr).

This procedure was essential because poly(isobutylene oxide) degrades moderately fast in solution at 150°C. By dissolving the polymer within 20

min and extrapolating the flow times back to zero time, it was possible to determine reproducibly the reduced specific viscosities of our polymers. The reduced specific viscosity values are for analyses which used 0.3 g polymer per 100 cc *o*-dichlorobenzene. Also, an inhibitor such as phenyl- β -naphthylamine (0.3 g per 100 cc) was essential to minimize decomposition in the *o*-dichlorobenzene solution.

Typical results are shown below for two samples ($c = 0.3$ g/dl):

| Sample 1 | | Sample 2 | |
|-----------|---------------|-----------|---------------|
| Time, min | η_{sp}/c | Time, min | η_{sp}/c |
| 28 | 2.87 | 31 | 6.57 |
| 47 | 2.82 | 43 | 5.86 |
| 70 | 2.74 | 59 | 4.89 |
| 91 | 2.69 | 136 | 2.30 |
| 0 | 2.96 | 0 | 7.94 |

Spectroscopic Analysis

Two poly(isobutylene oxide) products were examined by both ^{13}C and ^1H -NMR spectroscopy. (We are grateful to Dr. C. Reilly and Mr. R. Wilson for these measurements and their assistance in the interpretations.)

The ^{13}C spectra showed only three resonance peaks: 23.46 and 23.52 pp (CH_3), 69.21 and 69.26 pp (CH_2), and 74.76 and 74.76 pp (C). The analysis were done in *o*-dichlorobenzene at 120°C with concentrations of polymer at 210 mg/ml and 350 mg/ml. The solvent served as an internal standard. Decoupling power was about 5 watts. Assignments of CH_2 to 69.3 ppm and C to 74.7 ppm resonance signals were made by an additional experiment where, instead of broadband decoupling, off-resonance decoupling was applied. The resonance signal at 69.3 ppm was split into three peaks, whereas the 74.8 ppm signal was unchanged. If impurities of any type were present, they were not visible in these spectra. A Bruker HFX-90 spectrometer was used (Digilab FTS/NMR-35 Data System).

The ^1H -NMR spectra showed only two peaks: 3.28 and 3.31 ppm (CH_2) and 1.14 and 1.20 ppm (CH_3), the peaks being present in a 1:3 ratio. These chemical shift values differ slightly from those reported in reference 12, e.g., $\delta = 1.21$ and 3.41 ppm were found. These were also related to tetramethylsilane. The analysis were done in *o*-dichlorobenzene at 100 and 150°C , respectively, with concentrations of polymers being at 70 mg per 0.4 ml. Tetramethylsilane served as reference material. No other peaks were present. A Varian HR 100 spectrometer was used.

Both PIBO samples were extracted with acetone for 20 hours (Soxhlet extractor) to remove inhibitors and any impurities which may be present. High molecular weight PIBO is not soluble in acetone at the refluxing temperatures of acetone.

References

1. P. Davies, D. K. Peacock, and J. E. Fearey to (Imperial Chemical Industries) Brit. Pat. 582, 266 (1947).
2. S. Oniwa, C. Aso, and S. Akiyoshi, paper presented at the Meeting of the Japanese Chemical Society, April, 1961, and cited as ref. 122, p. 207 of *Polymerization of Aldehydes and Oxides*, Vol. 3 of *Polymer Reviews*, by Furukawa and Saeguessa, Interscience, New York, 1963.
3. S. Ishida, *Bull. Chem. Soc. Japan*, **33**, 924 (1960).
4. S. Kambara and A. Takahashi, *Makromol. Chem.*, **58**, 226 (1962).
5. S. Kambara and A. Takahashi, *Makromol. Chem.*, **63**, 89 (1963).
6. R. S. Bauer, unpublished work, Shell Development Company.
7. K. Kamio, M. Kuwana, and S. Nakada (to Nippon-Carbide Kogyo Kabushiki Kaisha) U.S. Pat. 3,509,074 (April 28, 1970); GB972, 892 (October 21, 1964).
8. E. Vandenberg (to Hercules), U.S. Pat. 3,337,487
9. E. Vandenberg (to Hercules), U.S. Pat. 3,354,097
10. E. Vandenberg (to Hercules), U.S. Pat. 3,374,277
11. R. S. Bauer, and W. W. Spooncer, *J. Polym. Sci.*, **A-1**, 2971 (1970).
12. E. Vandenberg, *J. Polym. Sci.*, **A-1**, 329 (1972).
13. R. Erlich, A. R. Young II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **3**, 628 (1964).
14. *Modern Plastics Encyclopedia*, 1971-1972, pp. 550-568.
15. K. Kamis, and M. Kiawana (to Nippon-Carbide Kogyo Kabushiki Kaisha) U.S. Pat. 3,477,972, (November 11, 1969).

Received March 22, 1974

Revised June 3, 1974