

有機超強塩基およびその協奏型触媒を用いる 高純度ポリプロピレングリコールの開発

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High Purity Polypropylene Glycol using Organic Superbase and its Cooperative Catalyst

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Polypropylene glycol (PPG) is widely used as raw material for polyurethane (PU)-based products such as flexible foam, rigid foam, coatings, adhesives, sealants, and elastomers. PPG is generally synthesized by using potassium hydroxide (KOH) as base catalyst. However, the unsaturated value (USV) of PPG synthesized by conventional KOH catalysis is relatively high due to the occurrence of side reactions. For example, the USV of a PPG synthesized by KOH is ~ 0.10 meq/g for the OH value (OHV) of 24 mg KOH/g. In addition, high-USV PPG induces low crosslink density in the PU thereof, which sometimes results in undesirable physical properties.

We found that iminophosphazene hydroxide (IPZOH), which is an organic superbase, is an effective base catalyst for the preparation of PPG. Thus, we succeeded in obtaining PPG with an OHV of 24 mg KOH/g by using IPZOH as catalyst. From the corresponding analysis, we found that the USV of the PPG was drastically decreased to less than 0.03 meq/g, which was one third of that of conventional PPG. Moreover, we discovered that the performance of the catalyst for “high purity PPG (low-USV PPG)” could be further enhanced by using a cooperative catalyst based on IPZOH (organic base) and an aluminum compound (Lewis acid). The USV of the PPG (OHV = 24 mg KOH/g) synthesized by the cooperative catalyst (< 0.005 meq/g) was found to be lower than that of any commercial PPG. The flexible PU foams based on this low-USV PPG showed excellent durability and comfort.

1. Introduction

Polypropylene glycol (PPG) is a main raw material for polyurethane (PU). PPG is generally synthesized by using potassium hydroxide (KOH) as base catalyst¹⁾. However, the occurrence of side reactions during

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conventional KOH catalysis renders the unsaturated value (USV) of the PPG relatively high (Fig. 1)^{2), 3)}. Thus, the USV of a PPG synthesized by KOH is ~ 0.10 meq/g for the OH value (OHV) of 24 mg KOH/g⁴⁾.

Since the physical properties of PU are strongly influenced by the USV of the starting PPG, some catalysts for low-USV PPG have been developed in recent years (Table 1). For example, a double metal cyanide complex (DMC) can greatly reduce the USV

of PPG and produce high molecular weight PPG^{5), 6)}. Furthermore, phosphazene (PZN), which is a strong organic base, has also been used as effective catalyst for low-USV PPG⁷⁾. In order to achieve low-USV PPG, we focused on iminophosphazene hydroxide (IPZOH) as catalyst due to its strong basic character and bulky substituents (Fig. 2)^{8), 9)}.

On the other hand, flexible PU foams for automotive seating are required to improve properties such

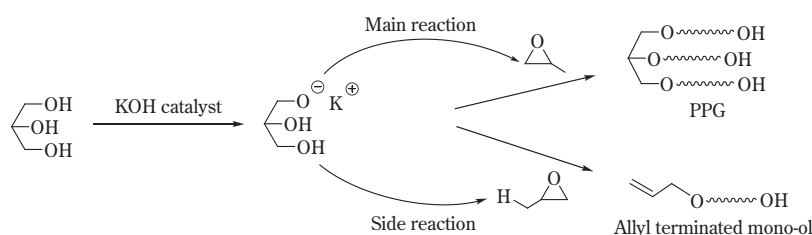


Fig. 1 Main and side reactions at PPG preparation

Table 1 Properties of catalysts for PPG^{a)}

	KOH	DMC	PZN
USV [meq/g]	0.043-0.045	0.006-0.019	0.013-0.017
maximum molecular weight	7,000	>20,000	>20,000

a) T. Hayashi, S. Yamasaki, T. Urakami and T. Nobori, *Catalysts & Catalysis*, 43(7), 532(2001)

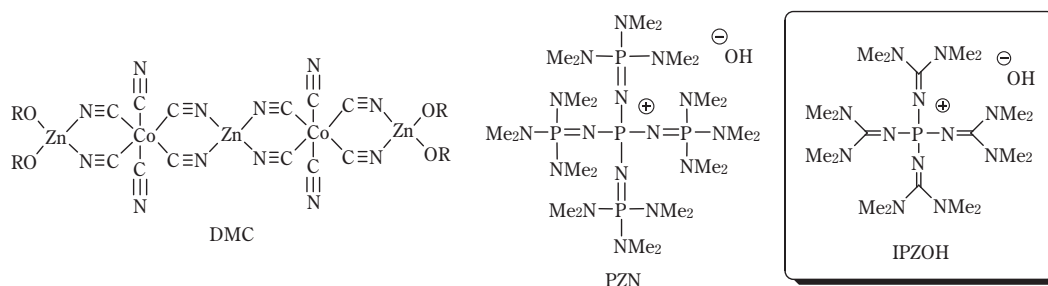


Fig. 2 Structures of catalysts for PPG

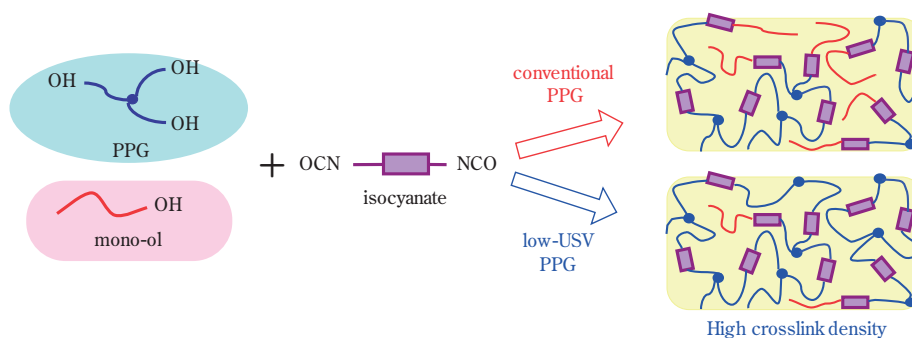


Fig. 3 Influence of the presence of mono-ol on the crosslink density of PU

as weight reduction, riding comfort, durability, incombustibility, and volatile organic compounds (VOC) reduction. In this context, low-USV PPG can afford enhanced riding comfort and durability due to high crosslink density (Fig. 3). This technology can contribute to weight reduction of automotive seating and improvement of fuel efficiency.

2. Experimental

[1] Preparation of PPG

IPZOH and hydroxyl group-containing compound as initiators were added into an autoclave at r.t. and vacuumed. Then, propylene oxide (PO) was added at 90–130 °C under 0.3 MPa. After aging and removal of free PO, crude PPG was obtained, from which clear PPG was obtained after purification.

[2] Analysis of PPG

(1) USV

PPG was dissolved in chloroform-*d* (CDCl₃), and the ¹H-nuclear magnetic resonance spectrum (JNM-E CZ400S/LI by JEOL) was recorded. The amount of mono-ol was calculated from the allyl peak (5.1–5.4 ppm) and the methyl peak (0.8–1.5 ppm).

(2) OHV

PPG was reacted with an acetylating reagent (1.3 mol/L) of acetic anhydride in imidazole pyridine solution (25 mL) at 108 °C for 1 h. Then, the reaction mixture was titrated with sodium hydroxide solution (1.0 mol/L). The OH value was calculated according to JIS K 1557-1.

(3) M_w/M_n

PPG was dissolved in tetrahydrofuran and analyzed via gel permeation chromatography (HLC-8320GPC by Tosoh). The corresponding value of M_w/M_n was calculated by comparison with polystyrene standards.

(4) Aldehydes

PPG was dissolved in acetonitrile and 2,4-dinitrophenylhydrazine (DNPH) reagent was mixed. The obtained solution was analyzed by high performance liquid chromatography (Prominence-i LC-2030 by Shimadzu). Formaldehyde, acetaldehyde and propionaldehyde were calculated by comparison with aldehyde-DNPH standard reagents.

3. Results and discussion

[1] Synthesis of PPG by using IPZOH as catalyst

We investigated (1) the influence of the polymerization temperature, (2) the influence of the molecular weight, and (3) ethylene oxide (EO) copolymerization using IPZOH.

(1) Influence of polymerization temperature

Firstly, the polymerization using a catalytic amount of IPZOH relative to initiator were carried out at 90, 110, and 130 °C. All reactions were successful, and the catalytic activity was high in all cases (500–1300 g/mol·min). The USV of the obtained PPG was in the range from 0.03 to 0.06 meq/g. Fig. 4 shows the catalytic activity at various temperatures (90, 110, and 130 °C). As can be seen, the catalytic activity increased with temperature. Similarly, it was found that the USV also increased with temperature (Fig. 5). We believe

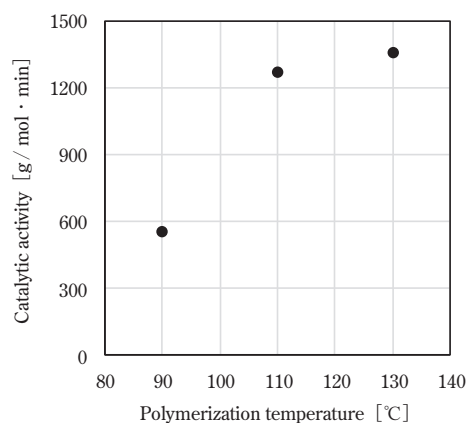


Fig. 4 Polymerization temperature vs catalytic activity

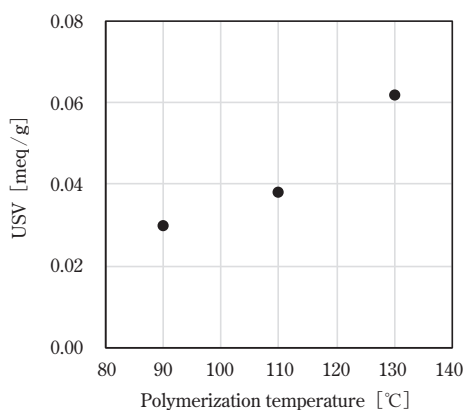


Fig. 5 Polymerization temperature vs USV

that the side reaction that generated the mono-ol was accelerated at high temperature.

(2) Influence of molecular weight

Secondly, we synthesized various PPG of different molecular weights by controlling the ratio PO to initiator. The USV of the obtained PPGs was found to increase slightly with the molecular weight, reaching one third of the value corresponding to the PPG synthesized by KOH catalysis (Fig. 6). The viscosity of the PPGs increased proportionally with the molecular weight, as extracted from Fig. 7.

(3) Copolymerization of PO and EO

Next, we tried the copolymerization of PO and EO

using IPZOH as catalyst. The interest of the PO/EO copolymerization lies on the fact that a high primary OH ratio is necessary to produce flexible PU foam (Fig. 8). In general, although KOH can catalyze the copolymerization of PO and EO, the USV of the obtained copolymers is high. On the other hand, it is known that the DMC can decrease the USV, but block PO/EO copolymers are difficult to achieve under these conditions.

In the reaction using IPZOH, EO was added after the polymerization of PO, and a clear PPG was obtained. Fig. 9 shows the plot of primary OH ratio for various EO/OH ratios. It was found that the primary OH ratio could be controlled by the EO/OH ratio.

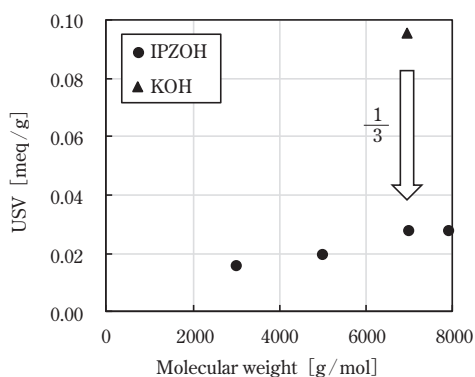


Fig. 6 Molecular weight vs USV

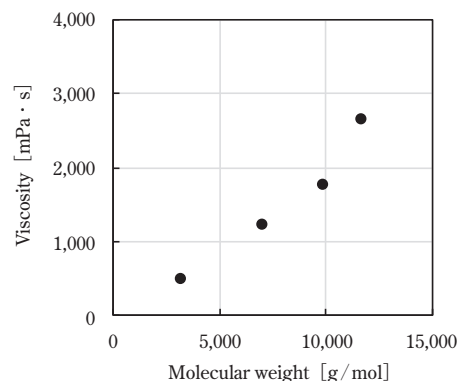


Fig. 7 Molecular weight vs viscosity

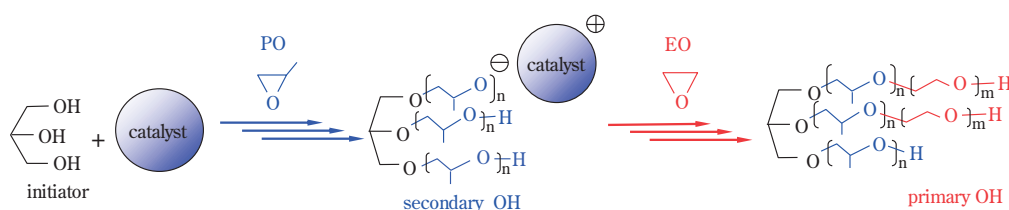


Fig. 8 Copolymerization of PO and EO

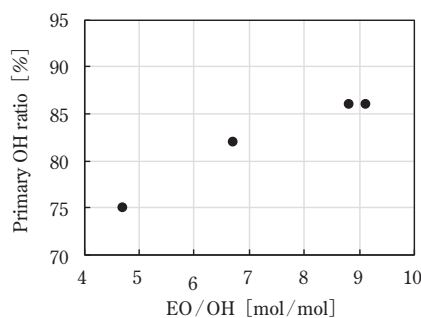


Fig. 9 Amount of EO vs primary OH ratio

[2] Synthesis of PPG by using IPZOH and aluminum as cooperative catalyst

To further reduce the USV, we focused on a cooperative catalyst consisting of an organic base and a Lewis acid^{10) - 12)}. As a result of our investigation, we discovered that IPZOH/aluminum compound constituted an excellent cooperative catalyst for low-USV PPG. We investigated (1) the influence of the catalyst ratio, (2) the influence of the polymerization temperature, (3) the influence of the aluminum compound and, (4) the aldehyde of PPG in the reaction using IPZOH and aluminum compound.

(1) Influence of catalyst ratio

Firstly, we used the cooperative catalyst comprising of IPZOH and triisobutyl aluminum (TiBAL) in a molar ratio IPZOH:TiBAL of 1:1, but the reaction did not proceed (Table 2; Run 1). When we used a 1:2 molar ratio, the reaction proceeded with the same activity as that obtained using IPZOH as catalyst. It was found that the USV of the obtained PPG (OHV = 24 mg KOH/g) was only 0.002 meq/g, which is the lowest level exhibited by commercial PPG (Table 2; Run 2). A similar result was obtained when a 1:3 molar ratio of IPZOH:TiBAL was used (Table 2; Run 3). Incidentally, the reaction did not proceed when using only TiBAL as a catalyst (Table 2; Run 5).

Table 2 Polymerization of PO using IPZOH and TiBAL as catalysts

Run	IPZOH:TiBAL [mol:mol]	activity [g/mol·min]	USV [meq/g]	M_w/M_n
1	1 : 1	0	—	—
2	1 : 2	530	0.002	1.05
3	1 : 3	520	0.002	1.05
4	1 : 0	460	0.028	1.05
5	0 : 1	0	—	—

(2) Influence of polymerization temperature

Then, we investigated the influence of the polymerization temperature on the reaction using the cooperative catalyst. It was found that the catalytic activity increased with temperature (Fig. 10), whereas the USV remained unaltered upon temperature variation (Fig. 11), which contrasts with the result obtained for IPZOH. It seems reasonable to assume that this result

was due to the effect of the aluminum compound. In any case, the synthesis of low-USV PPG could be performed with high catalytic activity at high polymerization temperature.

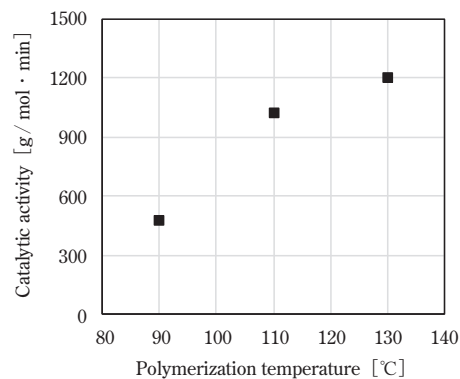


Fig.10 Polymerization temperature vs catalytic activity

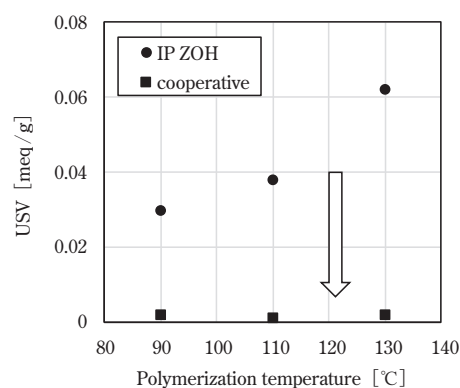


Fig.11 Polymerization temperature vs USV

(3) Influence of aluminum compounds

We also investigated the influence of using different aluminum compounds on the reaction. The polymerization was carried out using TiBAL, triphenyl aluminum (AlPh_3), aluminum tri-isopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$), and aluminum trichloride (AlCl_3). High catalytic activities were obtained in all cases. In addition, the USVs of the obtained PPGs were very low (0.002 meq/g) (Table 3).

Fig. 12 shows the elution curves of gel permeation chromatography (GPC) for the obtained PPGs. Impurity components with low molecular weight were detected in amounts that depended on the aluminum compounds. Thus, when TiBAL or AlPh_3 were used, the amounts of impurities were small. Conversely, when $\text{Al}(\text{O}^i\text{Pr})_3$ or AlCl_3 were used, the impurities were obtained in relatively large amounts.

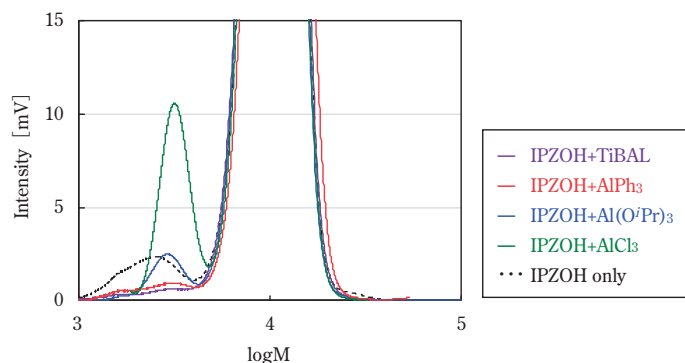


Fig.12 GPC analysis of impurities

Table 3 Properties of the PPG synthesized by IPZOH and aluminum compounds

Run	aluminum compounds	activity [g/mol·min]	USV [meq/g]	impurity ^{a)} [area%]
1	TiBAL	520	0.002	0.8
2	AlPh ₃	480	0.002	1.3
3	Al(O ⁱ Pr) ₃	510	0.002	2.3
4	AlCl ₃	530	0.002	9.0

a) Calculated by GPC.

To identify the structure of the impurities, a sample of the impurity obtained in the synthesis of PPG using IPZOH and Al(OⁱPr)₃ was analyzed with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS). The result is

shown in Fig. 13, in which allyl terminated mono-ol (A), isopropoxy terminated mono-ol (B), and hydroxy terminated diol (C) were detected. We believe that impurity (A) was generated by side reaction, impurity (B) derived from the aluminum compound, and impurity (C) from H₂O.

(4) Aldehydes of PPG

We analyzed aldehydes of PPG synthesized by IPZOH or its cooperative catalyst, because requirement to reduce aldehydes of PU foams for automotive seating have been increasing¹³⁾. The results are shown in Table 4, propionaldehydes of PPG synthesized by IPZOH or IPZOH/TiBAL catalyst were much lower than that of

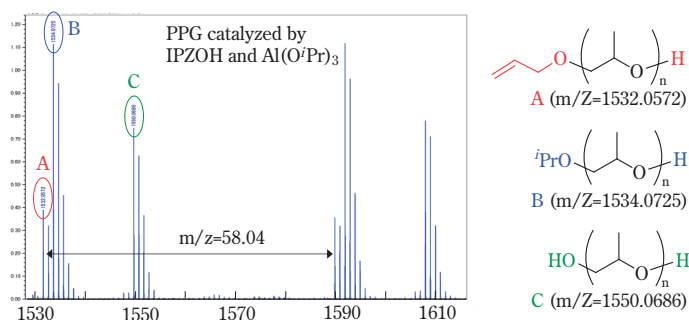


Fig.13 Analysis of impurities with MALDI-TOF/MS

Table 4 Aldehydes of PPG synthesized by various catalyst

Run	catalyst	formaldehyde [ppm]	acetaldehyde [ppm]	propionaldehyde [ppm]
1	IPZOH	1.2	11.1	7.5
2	IPZOH+TiBAL	1.2	1.5	7.9
3	KOH	1.4	5.6	1,590

PPG synthesized by KOH catalyst. Furthermore, an acetaldehyde of PPG synthesized by IPZOH/TiBAL catalyst was lower than that of PPG synthesized by IPZOH catalyst.

[3] Evaluation of flexible foam based on low-USV PPG

(1) Synthesis of PPG for flexible foam

We synthesized a PPG that could be applicable as flexible PU foam. The OHV and USV were 24.1 mg KOH/g and 0.029 meq/g, respectively. It is worth noting that the latter value was only one third of that corresponding to the PPG synthesized by KOH catalysis.

(2) Evaluation of flexible foam

In the evaluation of flexible PU foam (formulation is shown in **Table 5**), we found that the foams based on low-USV PPG showed excellent hysteresis loss, ball rebound, and compression set (CS) in comparison with those based on conventional PPG, which could be attributed to the increase of the crosslink density (**Table 6**).

Table 5 Formulation for flexible foam

Formulation	phr
PPG	75
POP	25
cell opener	4.0
cross linker	2.0
TEDA L33	0.35
TOYOCAT ET	0.08
surfactant	1.0
H ₂ O	4.0

Table 6 Properties of PPG and flexible foam

		low-USV PPG	conventional PPG
PPG	catalyst	IPZOH	KOH
	OHV [mg KOH/g]	24.1	24.0
	USV [meq/g]	0.029	0.091
foam	density [kg/m ³]	45	45
	hardness [N/314cm ²]	252	248
	hysteresis loss [%]	28	31
	ball rebound [%]	63	59
	CS wet [%]	8.6	10.2

4. Conclusions

- [1] We found that IPZOH was an effective base catalyst for the preparation of PPG, which exhibited OHV and USV of 24 mg KOH/g and 0.03meq/g, respectively. Most interestingly, this USV was one third of that of conventional PPG.
- [2] We discovered that a cooperative catalyst of IPZOH and aluminum compound exhibited enhanced, excellent performance in the synthesis of low-USV PPG. The USV of the PPG (OHV = 24 mg KOH/g) was only 0.002 meq/g, which was lower than that of any commercial PPG.
- [3] The flexible PU foams based on this low-USV PPG showed excellent hysteresis loss, ball rebound, and compression set.

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