INVITED REVIEW

Synthesis and process development of polyether polyol with high primary hydroxyl content using a new propoxylation catalyst

Toru Miyajima¹, Kenji Nishiyama², Munekazu Satake³ and Takayuki Tsuji²

We have developed a novel class of propylene oxide-based polyether polyol (PPG) with up to 70% higher primary hydroxyl content, which is produced through a Lewis acid-mediated propoxylation reaction using a specific borane catalyst. Conventional PPGs produced via anionic ring-opening polymerization have secondary hydroxyls, resulting in poor reactivity in urethane formation. To overcome the poor reactivity, ethylene oxide (EO) is often added to the terminal hydroxyls of conventional PPGs. However, this modification decreases the humidity resistance of the resulting polymer. In contrast, our new PPG has enhanced primary hydroxyl content with little or no added EO, thereby achieving a good balance between reactivity and hydrophobicity. As a result, the new polyol has important advantages, such as enhanced durability, energy and resource conservation, and environmental load reduction for a broad area of polyurethane applications. In addition, we developed an innovative continuous process that uses tube reactors in combination with film evaporators for by-product removal. This review focuses on key technological innovations in process development and examples of the practical applications of the new PPG. *Polymer Journal* (2015) **47**, 771–778; doi:10.1038/pj.2015.64; published online 26 August 2015

INTRODUCTION

Polyurethanes, which are traditionally and commonly formed by reacting polyisocyanates with polyols, are the most versatile polymer materials and have excellent performance properties for a wide variety of applications, such as in automobiles, furniture and bedding, clothing materials, housing and building materials, and so on.¹ The physical properties of polyurethanes depend on the chemical structure of the original reactants. In particular, the chemical characteristics of the polyols used, namely, the number of hydroxyl groups per molecule (functionality), molecular weight, hydrophilicity and steric character of the terminal hydroxyls directly affect the chemical and physical structure of the final polymers and the performance of the end products.

Propylene oxide (PO)-based polyether polyols (commonly referred to as PPGs) are the most widely used polyols for polyurethane production because they are readily available and offer good structural diversity. Over the past five decades, most PPGs have been produced commercially through base-catalyzed, anionic ring-opening polymerization using strong bases (for example, KOH).² With the conventional KOH-initiated route, a serious problem is the predominant formation of secondary hydroxyls, which exhibit poor reactivity in urethane formation. To obtain more reactive primary hydroxyls, ethylene oxide (EO) is often reacted in the final stage of the polymerization. However, this commonly used modification decreases the humidity resistance of the resulting polymer due to the hydrophilic character of the EO block that is introduced. Consequently, achieving a good balance between reactivity and humidity resistance represents a significant challenge in the polyurethane industry, and the development of a new class of polyols has emerged as an important subject to polyol suppliers.

Recently, we successfully discovered a catalytic propoxylation reaction for synthesizing an innovative PPG in which the primary hydroxyl content was increased up to 70%. This finding presents a solution to the long-standing problem described above. Since our initial work, we have worked to develop an industrial production process and to explore the market potential for this innovative PPG. In this review, we introduce this new PPG and its production technology. Key technological innovations in process development and the superior performance of polyurethane products derived from the new PPG are described in detail.

SELECTIVE PROPOXYLATION REACTION USING A NEW CATALYST

Structural optimization of the Lewis acid catalyst

Generally, the selectivity of PO ring cleavage, namely the ratio of primary to secondary hydroxyls in the product, strongly depends on the polymerization mechanism and the type of catalyst.³ As described above, base catalysts such as KOH predominantly yield secondary hydroxyls with very high selectivity (>95%). In base-catalyzed anionic propoxylation, β -cleavage of the PO ring is strongly favored because it

¹Research Division, SDP Global Co., Ltd., Kyoto, Japan; ²Urethane Raw Materials Research Department, Sanyo Chemical Industries, Ltd., Kyoto, Japan and ³Intellectual Properties Department, Sanyo Chemical Industries, Ltd., Kyoto, Japan

Correspondence: T Miyajima, Research Division, SDP Global Co., Ltd., 11-1, Ikkyo Nomoto-cho, Higashiyama-ku, Kyoto 605-0995, Japan. E-mail: t.miyajima@sdp-g.com

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offers smaller steric hindrance. On the other hand, commonly used Lewis acid catalysts such as boron trifluoride (BF₃) are known to produce primary and secondary hydroxyls in almost equal proportions. In the field of selective organic synthesis, catalysts with designed ligands and sterically regulated spaces have received much attention in recent years. Considering these points, structurally well-designed Lewis acids are promising candidates as catalysts to promote α -cleavage of the PO ring with higher selectivity. We focused on boron compounds because they are easy to handle and have good structural diversity. A detailed study on catalyst optimization in terms of electronic and steric effects revealed that tris(pentafluorophenyl)borane⁴ promotes α -cleavage with a high selectivity of 70% in propoxylation reactions. Scheme 1 shows the basic method for synthesizing an innovative PPG with an increased proportion of primary hydroxyls that we established.⁵

Reaction mechanism and origin of selectivity

Acid-mediated epoxide opening reactions are thought to proceed via a borderline S_N^2 process (that is, bimolecular substitution having considerable S_N^1 character in the transition state).³ The transition state geometry resembles that of a standard S_N^2 reaction, but C–O bond breaking is relatively more advanced compared with carbon-nucleophile bond formation, resulting in a buildup of considerable positive charge on the carbons. In the presence of strong acids, this positive charge buildup is enhanced. Thus, the transition state that has a buildup of positive charge on the carbon that would be the more stable carbocation is favored. Therefore, tris(pentafluorophenyl)



Scheme 1 Selective propoxylation reaction mediated by tris (pentafluorophenyl)borane. A full color version of this scheme is available at *Polymer Journal* online.

borane should favor α -cleavage because it has very strong acidity due to the electron-withdrawing character of the pentafluorophenyl groups. A different hypothesis concerning the selectivity can be proposed from a steric viewpoint. As depicted in Figure 1, β -cleavage should be energetically unfavorable because its transition state has large steric hindrance between the methyl group of PO and the fluorine atom in the ortho position of the ligand. We believe that the electronic and steric effects of the new catalyst work synergistically to promote α -cleavage in the propoxylation reaction.

Features of propoxylation reactions using the new catalyst

The new catalyst affords not only high α -cleavage selectivity in propoxylation reactions but also demonstrates additional advantages over conventional propoxylation catalysts such as KOH, double metal cyanide (DMC) complexes⁶ and BF₃. A comparison of the properties of these catalysts is summarized in Table 1. There are two notable advantages of using the new catalyst:

- Extremely high catalytic activity (2000 times as active as KOH). This property can dramatically reduce catalyst usage to approximately 30 p.p.m., making catalyst removal from the product unnecessary.
- (2) Immediate initiation of the reaction without any pretreatments. Unlike many of the other catalysts, catalyst activation before use is unnecessary and no induction period is observed.

Notably, these advantages play an important role in designing an industrial production process, which is covered in detail in the following section.

INDUSTRIAL PPG PRODUCTION PROCESS USING A NEW CATALYST

General problems involved in using Lewis acid catalysts

Lewis acid catalysts have rarely been used in PPG synthesis, despite their unique reaction characteristics. Their infrequent use is probably



Figure 1 Plausible transition states for propoxylation mediated by tris(pentafluorophenyl)borane.

Table 1 Comparison with commonly used catalytic propoxylation technologies

		Conventional catalysts		New catalyst
	КОН	$Zn_3[Co(CN)_6]_2 \cdot ZnX \cdot L$	BF ₃	$B(C_6F_5)_3$
Mechanism of propoxylation	Anionic	Coordination	Acid mediated	Acid mediated
Primary hydroxyl content	2%	5%	50%	70%
Relative rate of propoxylation	1	300	200	2000
Typical catalyst loading	2000 p.p.m.	100 p.p.m.	300 p.p.m.	30 p.p.m.
Reaction temperature	100–110 °C	130–150 °C	80 °C or lower	80 °C or lower
Pretreatment	Alkoxide formation by water removal	Activation with heat (ligand exchange)	Unnecessary	Unnecessary
Catalyst removal (after treatment)	Neutralization/ adsorption	Unnecessary (difficult to remove)	Removal of free acid (HF)	Unnecessary

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Subsequent reactions

 $\begin{array}{c} \text{H}_{3}\text{CH}_{2}\text{CHO} + \begin{array}{c} R^{1} - \text{OH} \\ R^{2} - \text{OH} \end{array} \xrightarrow{H^{+}} \begin{array}{c} R^{1} - \text{O} \\ Cndensation \end{array} \xrightarrow{R^{1} - \text{O}} \begin{array}{c} R^{1} - \text{O} \\ Ch_{2} + h_{2} \text{O} \\ Ch_{2} + h_{2} \text{C} \end{array} \xrightarrow{Ch_{3}} \begin{array}{c} H^{+} \\ Propoxylation \end{array} \xrightarrow{H^{+}} \begin{array}{c} H^{+} \\ HOCH_{2} + HOCH_{2} \\ CHOH \end{array} \xrightarrow{PO} \begin{array}{c} Propylene \\ Propoxylation \end{array} \xrightarrow{Po} \begin{array}{c} Propylene \\ Propoxylates \end{array} \xrightarrow{Po} \begin{array}{c} Propylene \\ Propyle$

Scheme 2 Acid-promoted isomerization of propylene oxide and subsequent undesirable reactions.

attributed to them being difficult to handle as well as the possibility of side reactions. As shown in Scheme 2, PO readily isomerizes to propionaldehyde in acidic conditions.⁷ In addition, acids promote subsequent reactions in which the aldehyde reacts with 2 mol of alcohol species to produce acetal derivatives. The water formed also reacts with PO to yield short chain diol derivatives. These by-products are undesirable because they negatively affect basic qualities of the PPG, such as functionality and molecular weight distribution. For example, acetal by-products in PPG, which have higher functionality, can cause the viscosity of the PPG to increase and lead to abnormal reaction progress when reacted with polyisocyanates. Furthermore, acetal derivatives in PPGs can be gradually hydrolyzed in humid conditions to release propionaldehyde, which has a strong odor. Short chain diol by-products can degrade the mechanical properties of the resulting polyurethane by forming structural defects in the polyurethane network. These problems constitute a serious obstacle to industrial process development in terms of product quality control.

Basic information on temperature limitations and side reactions with the new catalyst

Unlike many of the other Lewis acids, the new catalyst tris (pentafluorophenyl)borane is known to be an air-stable, water-tolerant and thermally robust compound.⁴ However, our stability studies revealed that it reacts with trace moisture in the reaction mixture during propoxylation at temperatures exceeding 90 °C to form pentafluorobenzene and boric acid. Therefore, the reaction temperature during propoxylation needs to be kept at ~80 °C or lower to reduce its decomposition to a tolerable level. This requirement means that the preferred reaction temperature for the new catalyst is ~30 °C lower than the typical temperatures used with KOH as the catalyst.

Like other Lewis acids, the new catalyst is prone to the side reactions shown in Scheme 2. Fundamental kinetics analysis made the following points clear. A detailed description is omitted here for simplicity.

- Approximately 3–10% of the total amount of PO consumed is converted to propionaldehyde under the typical reaction conditions used for PPG synthesis.
- (2) The ratio of the amount of propionaldehyde produced to PO consumption depends on the hydroxyl concentration of the reaction system but not on the concentration of other components, including the catalyst. Aldehyde formation is promoted in preparing high molecular weight PPG in which the hydroxyl concentration is low.
- (3) The amount of propionaldehyde produced is nearly independent of reaction temperature because the difference in activation energy between propoxylation and aldehyde formation is small.



Figure 2 General batch-type process for conventional polyether polyol production. A full color version of this figure is available at *Polymer Journal* online.

These findings suggest that it is inherently difficult to suppress the formation of propionaldehyde itself and that it would be effective to prevent the subsequent reactions by controlling the concentration of aldehyde that accumulates in the reaction system.

General batch-type process for conventional PPG production

Currently, industrial PPG production using traditional KOH catalysis almost always employs a batch-type process. As shown in Figure 2, this process consists of three basic steps. First, a starter (polyols are most often used) is treated with KOH in a reaction vessel and is converted to the corresponding alkoxide, the actual active species, after removing the water that is formed. Next, PO is slowly charged into the reaction vessel and propoxylation is carried out. In this step, the reaction system is typically maintained at a temperature between 100 and 110 °C during the addition of PO. Heat removal and control over the PO feed rate is of technical importance in this step because propoxylation is highly exothermic. In the last step, the catalyst is removed from the mixture after complete consumption of the PO. In most cases, this step cannot be skipped because alkaline residue in PPG often causes abnormal reaction progress in practical use.

Newly developed continuous process for primary hydroxyl PPG production

As discussed above, propoxylation with the new catalyst involves a reduction in the reaction temperature by ~ 30 °C compared with the conventional process using KOH. To use the new catalyst in the conventional batch process, the PO feed rate, and consequently the production rate, is considerably restricted because of the limited surface area-to-volume ratio of the reaction vessel and the small temperature difference between the reactants and the cooling medium. To solve this problem, we focused on developing a continuous flow process using tube reactors, which are superior in terms of heat removal efficiency. Continuous flow processes have rarely been applied to PPG production with conventional catalysts that require pretreatment and catalyst removal steps. In contrast, it is suitable for propoxylation with the new catalyst that requires neither. Thus, a continuous flow process successfully enhances the strengths and eliminates the weaknesses of the new catalyst



Figure 3 Newly developed continuous process for primary hydroxyl polyether polyol production. A full color version of this figure is available at *Polymer Journal* online.

Next, we worked to find a solution for the by-products problem and finally adopted the process depicted in Figure 3, in which the propionaldehyde produced is continuously removed with film evaporators that are directly attached to the tube reactors. We also established a standard reaction condition in which the concentration of propionaldehyde is controlled below a certain critical level by changing the PO feed concentration, depending on the molecular weight of the starter. On the basis of this standard condition, propoxylation and aldehyde removal are repeated alternately to reach the target molecular weight. Thus, an innovative industrial process for the high-throughput production of high-quality primary hydroxyl PPG was developed.

BASIC PROPERTIES OF PRIMARY HYDROXYL PPG

The new PPG produced by propoxylation with the new catalyst is a novel class of PPG that has an increased primary hydroxyl content of up to 70% and, therefore, exhibits enhanced reactivity toward polyisocyanates. For instance, it is several times more reactive than conventional PPG propoxylated with KOH in urethane formation reactions at approximately room temperature.

As shown in Figure 4, the primary hydroxyl content of the new PPG is further enhanced by adding a small amount of EO. For certain applications, such as highly resilient (HR)-molded polyurethane (PU) foam, reactivity-enhanced EO-modified PPG, which has a primary hydroxyl content ranging from 70 to 85%, is commonly used. In the case of conventional PPG produced with KOH, the EO block required usually ranges from 4 to 8 mol (from 10 to 20% by weight of the polymer chain) per hydroxyl on average to reach a primary hydroxyl content in this range. On the other hand, the new PPG requires less than half or no EO block. Thus, the new PPG can achieve an excellent and ideal balance between reactivity and humidity resistance.⁵

PRACTICAL APPLICATIONS OF PRIMARY HYDROXYL PPG

The aforementioned features of our newly developed PPG provide great opportunities to bring considerable benefits to a wide spectrum of PU applications. Advantages of using the new PPG in flexible PU foams, which have a huge global market, are primarily discussed here.^{8,9}

Flexible PU foams with reduced residual aromatic amines for furniture and bedding

Flexible PU foams have seen increased use in the furniture and bedding market in recent years. In this field, consumers are becoming better informed and would like to understand the safety, health and environment aspects of the materials inside the products that they buy and use.

Among the chemical substances contained in PU foam products, specific aromatic amines that are suspected of being carcinogenic, such as 2,4-toluenediamine (TDA), are recognized as a serious concern in today's furniture and bedding industry. Such amines are derived



Figure 4 Relationship between primary hydroxyl content and the number of ethylene oxide (EO) moles added per hydroxyl (Starter: Mw 3000 triol, EO-capping catalyst: KOH). A full color version of this figure is available at *Polymer Journal* online.

from a portion of raw material polyisocyanates that are not incorporated into the polymer networks during the foaming process. Several voluntary certification systems such as CertiPUR^{10,11} and Oeko-Tex,¹² which are promoted by multiple international industrial associations, set an upper limit on the amount of 2,4-TDA and other specific aromatic amines that can be contained in PU foams for products to be certified as premium grade. For example, CertiPUR limits the amount of 2,4-TDA to no more than 5.0 p.p.m. (mgl⁻¹) in a foam. In addition, IKEA, the world's largest furniture retailer sets a similar standard for its products. However, it is becoming increasingly difficult for PU foam producers to meet the required residual amine standards whereas also satisfying a series of foam physical property specifications.

The most uncomplicated and effective approach in reducing residual amines is to increase the conversion rate of NCO components to urethane bonds. Accordingly, highly reactive PPG, namely our newly developed PPG, fits this purpose. To prove this advantage, we prepared foam samples according to typical TDI (toluene diisocyanate)-based free-foaming formulations with a low NCO index, in which a conventional PPG (2% primary hydroxyl) and the new PPG (70% primary hydroxyl) were used in different proportions. Then, the residual 2,4-TDA content of each sample was measured according to the method defined by CertiPUR. The results are summarized in Figure 5. As expected, the amount of residual 2,4-TDA in the foam is reduced dramatically as the proportion of the new PPG is increased. Thus, the high reactivity of the new PPG clearly has a positive impact on residual amine reduction, providing an effective solution to the issue of satisfying certification requirements.

Flexible PU foams for clothing materials with improved discoloration resistance

One of the few drawbacks of PU materials is discoloration (yellowing) over time. In the field of specialized PU foam applications, such as bra-pads, there is a great need for anti-yellowing foams that remain bright and have a long-lasting clean look.

It is well known that foam discoloration is primarily due to the formation of chromophores, such as azo compounds, which are derived from aromatic amine derivatives. In this regard, the use of a new PPG that is highly reactive toward NCO components would also be effective in improving the anti-yellowing properties of foams. To investigate this advantage of the new PPG, we evaluated yellowing



Figure 5 Relationship between residual 2,4-toluenediamine and polyether polyol (PPG) reactivity (PPG: Mw 3000 triol, NCO index: 85, foam density: $24 \pm 1 \text{ kg m}^{-3}$). A full color version of this figure is available at *Polymer Journal* online.



Figure 6 Color changes of foam samples under daylight (conventional polyether polyol (PPG) vs new PPG).



Figure 7 Wet compression sets depending on foam densities (conventional polyether polyol (PPG) vs new PPG). A full color version of this figure is available at *Polymer Journal* online.

resistance of the foams prepared for the residual 2,4-TDA study described above. The test pieces were placed by a window and exposed to daylight for a week. The degree of discoloration of each test piece was evaluated using a spectrophotometer to calculate the yellow index of the pieces after predetermined time intervals. As shown in Figure 6, foam prepared using the new PPG changes its color slowly compared to the conventional system. Hence, our new technology contributes to improving the anti-yellowing properties of PU foams. Flexible molded PU foams for automotive seats with low density HR flexible molded PU foams are commonly used in automotive seats around the world. In this field, there is a strong and continuing demand to reduce the product weight to improve fuel efficiency. For a long time, reducing the weight of automotive seats has been achieved

by reducing the foam density. However, the density is getting close to

the limit of formulations using conventional raw materials. The biggest problem with reducing the foam density is deteriorating the durability of the foam. This problem is not simply because of a reduction in the proportion of resin in the foam, but rather the increased amount of urea groups in the resin due to the higher dose of water used as a blowing agent also has a role. Urea-rich foams often have insufficient softness, resiliency and durability as a result of aggregation of the highly hydrophilic and hydrogen-bonding urea micro-domains. Moreover, the highly hydrophilic nature of the polyols typically used makes it difficult to maintain the humidity resistance of the foams. In the manufacturing of HR-molded foam, terminal EO-capped, highly reactive PPG with a primary hydroxyl content of ~ 80% has been used as the main polyol to achieve good moldability with the ability to be de-molded in a short period.

This problem can be solved by using our new PPG, which can provide a balance between high reactivity and humidity resistance. To prove this, we prepared foam samples with three different densities using a foaming machine, according to our basic formulation for an automotive seat back. The relationship between wet compression set, which is a generally accepted indicator of long-term foam durability under hot and humid conditions, and foam density is illustrated in Figure 7. As expected, the new PPG has a notable durability-enhancing effect at all densities examine and shows a comparable wet compression set even at 15% reduced density. Other physical properties, including ball rebound, tensile/tear strength and elongation, are comparable to those of the conventional systems. These results demonstrate that the new PPG contributes to density reduction for HR-molded foam applications.

Flexible molded PU foams for automotive seats with a comfortable ride

Ride comfort improvement has recently become one of the most important issues in automotive seat development. Vibration absorbing characteristics, namely the frequency dependence of vibration transmission in PU foams used for cushioning, are the most important indicator of the ride comfort of seat pads. To achieve a comfortable ride, a reduction in transmissibility at ~ 6 Hz is effective because the human stomach is sensitive to vibrations at this frequency range.

As illustrated in Figure 8, there are two approaches to reducing transmissibility at ~6 Hz. One is to shift the resonance frequency (that is, the peak position in Figure 8a) to a lower direction. The other is to lower the maximum transmissibility (that is, the peak height in Figure 8a). The former approach is deeply related to enhancing the elasticity of the resin. As shown in Figure 9, we found that reducing the tan δ of the resin in the foams has a positive impact on the resonance frequency shift in our fundamental studies. The latter approach is related to enhancing the viscosity of the foam by reducing air permeability through the cell structure. Therefore, a combination of these two approaches is effective for improving the vibration characteristics. In particular, the enhancement of elasticity is of great importance in the design of a desired resin composition. As shown in Figure 10, another fundamental study concerning the effect of PPG compositions on the viscoelastic behavior of foams revealed that tan δ of the resin tends to decrease as the primary hydroxyl content of the PPG is increased. We assume that high reactivity and fast viscosity



Figure 8 Conceptual diagram for a comfortable ride based on the vibration characteristics of the foam. (a) Frequency dependence of vibration transmissibility; (b) Voigt model for polyurethane foam. A full color version of this figure is available at Polymer Journal online.



Figure 9 Relationship between resonance frequency and tan δ . (core density: $52 \pm 1 \text{ kg m}^{-3}$, 25% indentation load deflection (ILD): $180 \pm 10 \text{ N}$ per 314 cm², air permeability: $17 \pm 5 \operatorname{cc} \operatorname{cm}^{-2} \operatorname{s}^{-1}$).



Figure 10 Relationship between tan δ and primary hydroxyl content of the PPG (core density: $52 \pm 1 \text{ kg m}^{-3}$, 25% ILD: $180 \pm 10 \text{ N}$ per 314 cm^2 , air permeability: $17 \pm 5 \operatorname{cc} \operatorname{cm}^{-2} \operatorname{s}^{-1}$).

Table 2 Vibration characteristics of 100 mmt foam samples (conventional PPG vs new PPG)

	Conventional PPG	New PPG
Resonance frequency (Hz)	3.62	3.36
Maximum transmissibility	3.50	3.25
Transmissibility at 6 Hz	1.02	0.71

Abbreviation: PPG, polyether polyol. Core density: $60 \pm 1 \text{ kg m}^{-3}$, 25% ILD: 270 $\pm 10 \text{ N}$ per 314 cm², air permeability:

buildup in the foaming process derived from a high primary hydroxyl content contribute to the formation of fine and homogeneous phaseseparated structures of hard segments and enhance the elasticity of the resin.

These findings indicate that the vibration characteristics of the foam can be controlled by using our new PPG. To prove this advantage, we prepared 100 mmt foam samples with a core density of 60 kg m⁻³ according to our basic formulation. The foam vibration characteristics are summarized in Table 2. As expected, the new PPG resulted in the resonance frequency being down-shifted by 0.26 Hz as well as a slight decrease in the maximum transmissibility compared with the conventional PPG, resulting in an ~ 30% reduction in transmissibility at 6 Hz. These results show that the new PPG is effective for improving the ride comfort of seat pads.

Flexible molded PU foams for automotive seats with reduced thickness

In the field of automotive seats, a thinner seat design has become increasingly important in terms of both weight reduction and expanding the space in the car, especially with the popularization of hybrid cars. Accordingly, foam thickness reduction is one of the most important themes in this industry. In general, foam thickness reduction leads to a deterioration in vibration characteristics and ride comfort. Indeed, as the thickness is reduced, resonance frequency typically shifts in the positive direction and the transmissibility at ~6 Hz rises.

This problem can be overcome by using the new PPG. Encouraged by the results described in the previous section, we prepared foam samples in the same manner, except that foam thickness was reduced to 80 mmt using a height tunable mold. The vibration characteristics of the foams were measured, and the relationship between the vibration characteristics and foam thickness is illustrated in Figures 11a and b. As expected, 80 mmt foam prepared using the new PPG shows a sufficiently low level of resonance frequency and transmissibility at 6 Hz, comparable to what is achieved with 100 mmt conventional foam. These results demonstrate that thickness can be reduced by 20% by using our new PPG.

Other application examples

The new PPG has many other technical advantages besides the ones described above for both foam and non-foam (that is, elastomer and sealant) applications. The benefits of using the new PPG in each application are summarized in Table 3.



Figure 11 Vibration characteristics as a function of foam thickness (conventional polyether polyol (PPG) vs new PPG). (a) Resonance frequency; (b) transmissibility at 6 Hz (core density: $60 \pm 1 \text{ kg m}^{-3}$, 25% ILD: $270 \pm 10 \text{ N}$ per 314 cm^2 , air permeability: $10 \pm 5 \text{ cc cm}^{-2} \text{ s}^{-1}$).

Table 3 Summary of advantages by using the new	PP(P	7	'(((((((()	2	2	2	Ē	F	F	F	I	I	ł	1	1)	1	1	ł	ł	ł	1	1	1	ł	ł	ł	ł	ł	ł	ł	ł	1)	,)	J)))))))))	2	-	F	F	I				l	1	V	٨	١	۱	ÿ	e	e	(۱	n	I			•	\$	2	e	6	6	IF	1	1	ŀ	ł	t	1	1	1	ž	g	1	n	r	i	i	5	5	l	ι	I	ľ	٧	b			5	es	g	a	ta	n	aı	lä	١	ł	C	1	а	į		f	D	C	1	1	V	٦	r	a	а	lé	l	1	r	r	n	n	r	ſ	11	ľ
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Application	Advantages
Flexible foams for furniture and bedding	 Reduction in aromatic amines to satisfy certification systems Slow discoloration (yellowing) Consistent physical property distribution in the
	foam • Improvement of tensile/tear/elongation and durability
Flexible molded foams for automotive seats	 Density reduction while maintaining durability Comfortable ride Thickness reduction while maintaining vibration characteristics
Elastomers and sealants	 Prevention of foaming while curing Productivity improvement derived from high reactivity Reduction in harmful heavy metal catalysts Durability and strength enhancement of resulting resin

CONCLUSIONS

The establishment of a Lewis acid-mediated selective propoxylation reaction using a specific borane catalyst enabled the synthesis of a novel class of PPG with an increased primary hydroxyl content of up to 70%. In addition, we developed a high yielding continuous process for producing the new PPG with a low amount of by-products by using tube reactors combined with film evaporators for by-product removal. The pilot plant for this innovative process started running in 2011 and expanded to regular commercial production in 2013. The first step in expanding its production capacity is scheduled to be completed in 2015 in response to increase in demand.

Our newly developed PPG has a high primary hydroxyl content with little or no added EO, resulting in high reactivity toward polyisocyanates while maintaining hydrophobicity. As a result, the new PPG achieves an excellent balance between reactivity and humidity resistance, which has been a long outstanding trade-off problem with conventional PPGs. These unique features of our newly developed PPG translate to considerable benefits in terms of durability enhancement, energy and resource conservation, and environmental load reduction for a wide spectrum of practical PU applications, including flexible foams, elastomers and sealants. The technical advantages of the new PPG have been widely recognized by domestic and overseas customers. We believe that the versatility of our new PPG will be further explored in the future.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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- 11 CertiPUR-US is an extension of the European CertiPUR program and run by Alliance for Flexible Polyurethane Foam, Inc. Available at http://certipur.us/.
- 12 Oeko-Tex Standard 100 is run by the International Association for Research and Testing in the Field of Textile Ecology. Available at https://www.oeko-tex.com/.

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Toru Miyajima received his MS degree in Molecular Engineering from Kyoto University in 2008. In the same year he joined Sanyo Chemical Industries. He was engaged in the process innovation for PPG production and the development of raw materials for flexible PU foam for furniture and bedding (2010–2013). He is currently a unit chief at SDP Global Co, a consolidated subsidiary of Sanyo Chemical Industries. His current research interests focus on superabsorbent polymers. He received the Award of the Society of Polymer Science, Japan (2014) for his work on Primary Hydroxyl Polyether Polyol.



Kenji Nishiyama received his MS degree in Applied Chemistry from the Ritsumeikan University in 1998. In the same year he joined Sanyo Chemical Industries. Since then he has been mainly engaged in the development of raw materials for flexible PU foam for automotive seats. He is currently a unit chief at Urethane Raw Materials Research Department. He received the Kinki Chemical Society Award for Chemical Technology (2007) and the Award of the Society of Polymer Science, Japan (2014) for his work on Primary Hydroxyl Polyether Polyol.



Munekazu Satake received his MS degree in Chemistry from Kyoto University in 1993. In the same year he joined Sanyo Chemical Industries. He was engaged in the development of new catalytic reactions including propoxylation reaction and electronics chemicals. He is currently a manager at Intellectual Properties Department. He received the Kinki Chemical Society Award for Chemical Technology (2007) and the Award of the Society of Polymer Science, Japan (2014) for his work on Primary Hydroxyl Polyether Polyol.



Takayuki Tsuji received his MS degree in Applied Chemistry from Osaka University in 1989. In the same year he joined Sanyo Chemical Industries. Since then he has been mainly engaged in the development of raw materials for flexible PU foams. He is currently a manager at Urethane Raw Materials Research Department. He received the Award of the Society of Polymer Science, Japan (2014) for his work on Primary Hydroxyl Polyether Polyol.