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Catalysis Today 73 (2002) 29–37

CATALYSIS TODAY

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New industrial process of PTMG catalyzed by solid acid

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Received 9 May 2001; accepted 27 September 2001

Abstract

Polymerization of THF catalyzed by solid acid in the presence of acetic anhydride was studied. A moderate Lewis acid catalyst produces required PTME (PTMG-acetate) having adequate M_n. Zeolitic material is not suitable for this production because very high molecular weight PTME is co-produced. From this aspect, mixed oxide materials show good performance because only these have the required acidic character. Mass-transfer study suggests the importance of pore size of support and the homogeneity of active sites. They affect on the M_n and the M_w/M_n strikingly. The commercial technology has established by utilizing these results. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PTMG; Polymerization; Mass-transfer; Lewis acid; THF; py-IR

1. Introduction

PTMG is one of the useful intermediates for fibers (Spandex, etc.) and thermoplastic elastomers. During several decades, its production demand has been increasing steadily, thus, much effort has been paid to establish an economical process for its production.

Generally, PTMG is obtained by the polymerization of tetrahydrofuran (THF) catalyzed by various kinds of strong acids. The conventional catalysts used in industrial processes are summarized in Table 1.

In the case of homogeneous strong acid systems, anti-corrosive, very expensive materials for reactor vessel and the hydrolysis step of PTMG-ester after polymerization are required [1–3]. Furthermore, the catalysts cannot be reused and a large amount of the waste is generated because the catalysts are neutralized to separate from the reaction mixture. In the case of bleaching earth–acetic anhydride system, the catalysts can be separated from the reaction mixture and reused easily [4]. But it is not so easy to keep the qualities of PTMG constant because the catalyst is prepared from natural minerals and includes various contaminants. In this case, PTME is transformed to PTMG by alcoholysis. In contrast to these two cases, direct polymerization of THF in highly concentrated aqueous solution of heteropolyacids seems to be excellent [5,6]. In this process, reaction proceeds in two liquid phases composed of the catalyst phase and the THF/product phase. Therefore, the catalyst phase can be separated and be reused. However, a trace amount of hereropolyacid dissolves in the THF/product phase, and it is not so easy to remove them completely from the product. Thus, the intrinsic issue of homogeneous catalysis for separation seems to be remained in this process. In all cases, some problems have to be overcome and an establishment of more efficient industrial process has been desired.

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PII: S0920-5861(01)00515-6

Nomenclature

M_n	number average molecular weight
M_w	weight average molecular weight
PTME	polyoxytetramethyleneglycol-diacetoxyester
PTMG	polyoxytetramethyleneglycol or poly-THF

Considering these problems, Mitsubishi Chemical Co., Ltd. has proposed a continuous process with our original heterogeneous catalysis and started PTMG manufacture since August 2000 [7,8].

To the following, we would like to introduce the story for development of this process.

2. Experimental

2.1. Catalysis preparation

MCM-22 and EU-1 were synthesized in laboratory and others were purchased from zeolite suppliers. All proton type zeolites were used as catalyst after treating them at 673 K.

Mixed oxide catalysts are prepared by sol–gel method. Metal nitrates and tetraethoxysilane (TEOS) in ethanol were treated by aqueous NH_3 solution for hydrolysis and the precipitates were filtered and were washed. After drying in oven at 393 K, grinned fine particles were calcined at 873 K.

Mixed oxides on support were prepared by the combination of impregnation and decomposition technique. Metal nitrates, TEOS and urea in ethanol were impregnated on support by using rotary evaporator at 333 K. After drying at 393 K, catalysis was calcined at 873 K.

2.2. Polymerization

A mixture of 60 g of THF and 9.95 g of acetic anhydride were charged in a flat bottom flask with string bar. After pouring catalysis, a flask was sealed and was set in water bath. After reaching reaction temperature, agitation was started. After finishing the reaction, catalysis was separated by filtration. Obtained PTME was analyzed by GPC.

2.3. py-IR

The experiments were done in the similar way according to the method described in literature [9].

3. Results and discussion

3.1. Basic concept of catalyst and process

As a technology for producing commodity chemicals, a continuous process is much more advantageous than batch process from an economical point of view. Furthermore, heterogeneous catalysts such as zeolites are preferable for this process than homogeneous catalysts like heteropoly acids because they can be separated from the reaction mixture and be used repeatedly. Thus, the research for heterogeneous catalyst has started.

Considering the reaction mechanism of PTMG (or PTME) synthesis, it is thought that an oxonium cation is generated by an attack of THF to a strong acid site and it initiates the chain growth, while the termination takes place by an attack of telogen instead of THF to an oxonium cation [10]. Direct PTMG synthesis from THF and water seems to be the most economical way from an industrial point of view. However, the growth rate in this system is very small because the

Table 1
Conventional process for PTMG production

Catalyst	Telogen	Terminal group of polymer	Disadvantages	Reference
FSO_3H	–	FSO_3–, HO–	Catalyst is corrosive; hydrolysis is needed; catalyst is not reused	[1]
$HClO_4$	Ac_2O	AcO–	Catalyst is corrosive; hydrolysis is needed; catalyst is not reused	[2,3]
Tonsil	Ac_2O	AcO–	Catalyst's composition is not constant; alcoholysis is needed	[4]
$H_3PW_{12}O_{40}$	H_2O	HO–	Catalyst contaminates PTMG	[5,6]

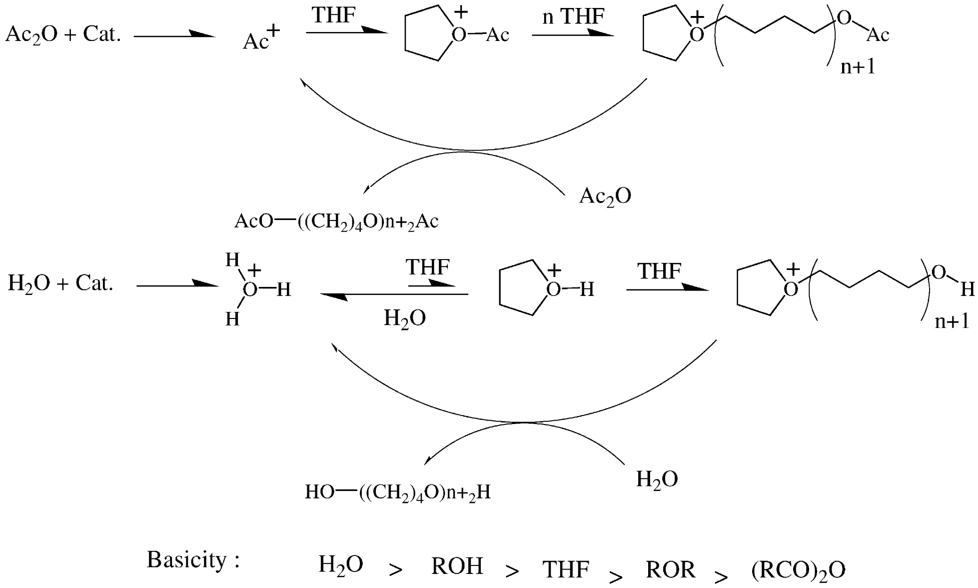


Fig. 1. Reaction mechanism of polymerization of THF in the presence of various telogens.

nucleophilicity of water is much higher than that of THF so that an attack of water to an oxonium cation takes place rapidly, which results in the termination of the chain growth. On the contrary, the catalyst system using acetic anhydride instead of water is expected to show higher growth rate than that using water because its basicity is lower than that of THF and it forms stable product (PTME).

Fig. 1 shows the principle aspect of polymerization of THF in the presence of various telogens.

Additionally, the small molecular ratio of acetic anhydride to THF in PTMG is very important to keep cheaper production cost.

By the reasons above, solid acid catalysts for THF polymerization in the presence of acetic anhydride has been developed.

3.2. Survey of zeolite catalysts

Generally speaking, cation formation at initiation step can be induced by both acid types, Brönsted acid or Lewis acid. It was not clear which type is effective to this reaction. High silica zeolites are known as materials having both acidic characters. To clear this subject, various kinds of zeolites were examined in this reaction and results are shown in Table 2.

Table 2
THF polymerization catalyzed by various zeolites[a]

Catalyst (Si/Al ratio)	Pore structure[b]	M_n ($\times 10^3$)	M_w ($\times 10^3$)	M_w/M_n	Yield (%)
H-beta (25)	3D, 12 m.r.	1.22	4.12	3.4	55
USY (6.1)	3D, 12 m.r.	0.28	0.60	2.2	21
ZSM-5 (30)	3D, 10 m.r.	3.05	98.1	32	13
MCM-22 (40)	1D, 12 m.r.	0.99	2.50	2.5	9.5
EU-1 (27)	1D, 10 m.r.	1.10	3.75	3.4	8.0
MOR (20)	2D, 12 m.r.	2.27	7.00	3.1	2.8

[a] Catalyst, 2.10 g (pretreated at 400 °C in N_2 flow for 3 h); THF, 60.00 g; $(CH_3CO)_2O$, 9.95 g, 40 °C, 5 h.

[b] 1D, 2D and 3D; dimension of the pore; m.r., membered-ring.

Table 3
Effect of various treatments on activity

Si/Al ratio	M_n ($\times 10^3$)	M_w ($\times 10^3$)	M_w/M_n	Yield (%)
Si/Al ratio[a]				
25	1.22	4.12	3.4	55
50	0.76	3213	4.2	21
100	0.61	14.4	24	34

Temperature (°C)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	M_w/M_n	Yield (%)
Influence of hydrothermal conditions[b]				
760	0.94	2.18	2.3	48
900	0.77	1.26	1.6	51
1000	0.86	1.50	1.8	8
Calcination temperature[c]				
400	0.98	3.32	3.4	54
900	0.70	1.29	1.8	48
1000	0.75	1.13	1.5	45

[a] H-beta, 2.10 g (pretreated at 400 °C in N_2 flow for 3 h); THF, 60.00 g; $(CH_3CO)_2O$, 9.95 g, 40 °C, 5 h.

[b] H-beta (Si/Al = 25), 2.10 g (treated in hydrothermal conditions for 3 h); THF, 60.00 g; $(CH_3CO)_2O$, 9.95 g, 40 °C, 5 h.

[c] H-beta (Si/Al = 25), 2.10 g (pretreated in N_2 flow for 3 h); THF, 60.00 g; $(CH_3CO)_2O$, 9.95 g, 40 °C, 5 h.

Many kinds of zeolites showed catalytic activity. Among them, zeolite β was chosen and modified in several ways in order to gain a desirable M_n and molecular weight distribution (M_w/M_n). The target values of M_n and M_w/M_n were achieved by changing Si/Al ratio, calcination temperature, dealumination treatment (acid treatment, steaming, etc.). Table 3 summarizes the effect of various treatments on activity.

At the same time, trace amount of high molecular weight PTMG whose M_n is around 50,000 was observed.

In order to clarify the relationship between acid properties and catalytic performances, the effects of various kinds of modification of zeolites on the molecular weight of PTMG was examined by means of pyridine-absorbed infrared spectroscopy, which gives useful information to assign the acidic properties of zeolites as shown in Fig. 2.

It suggested that there are three kinds of acid sites independently and each acid site produces PTMG having different molecular weight. Fig. 3 shows the schematic image of this relationship [10].

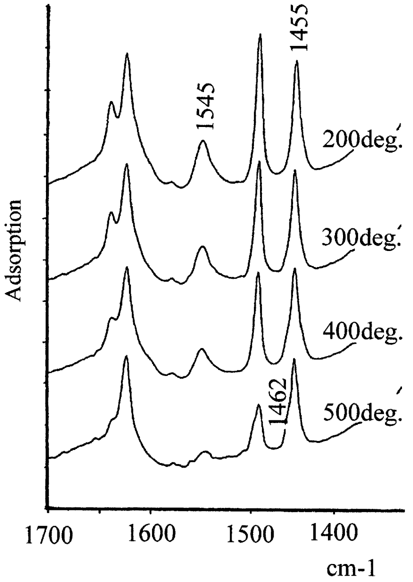


Fig. 2. Py-IR spectra of beta-zeolite calcined at 560 °C.

(a) Brönsted acid site producing oligomer–PTMG (M_n: <700).
(b) Lewis acid site producing desired molecular weight PTMG.
(c) Superacid site producing high molecular weight PTMG (M_n: >50,000).

Oligomer–PTMG can be removed easily by means of the thin-film distillation, although high molecular weight PTMG is very hard to remove. The amount

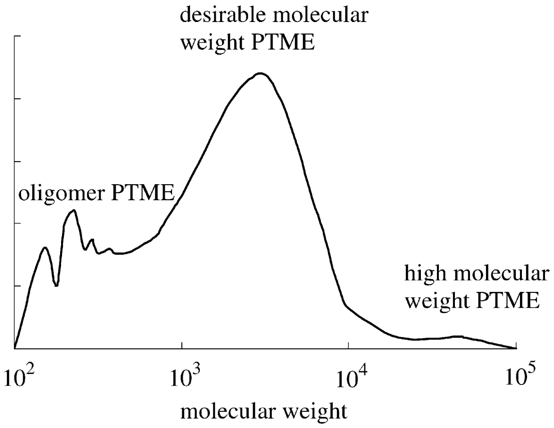


Fig. 3. A sketch of GPC profile of PTME produced by beta-zeolite.

of high molecular weight, PTMG in the products can be reduced to the some degree by means of various modifications of zeolite. However, it is very difficult to reduce high molecular weight PTMG to the negligible concentration. Due to these reasons, we could focus our target to develop solid acid catalysts having desired acidic character alone.

3.3. Survey of mixed oxide

The investigation of zeolites proved that zeolite β calcined at >900 °C showed sufficient catalytic activity, in which significant number of Brönsted acid site should transform to Lewis acid site. Therefore, the Lewis acidic catalyst which does not have super Lewis acid sites existing on some kinds of zeolite are expected to produce moderate molecular weight PTMG and not to produce high molecular weight PTMG. For this purpose, many kinds of mixed oxide were prepared and their catalytic performances were examined. Most of the catalysts were prepared by sol–gel method with TEOS and the various metal salts in alcoholic solvent.

As shown in Table 4, SnO_2, ZrO_2, HfO_2, Fe_2O_3, TiO_2, Ga_2O_3 and Al_2O_3 combined to SiO_2 were active. These results indicated that the stronger Lewis acid sites exist on the catalyst, the lower molecular weight PTMG is produced. SnO_2/SiO_2 shows the best catalytic activity among them although Sn does not form a stable mixed oxide and dissolves under the reaction condition. From this point of view, ZrO_2/SiO_2 and HfO_2/SiO_2 are especially stable. On the other hand, it can be possible to control the molecular weight of PTMG by choosing suitable combination of mixed oxides.

Table 4
THF polymerization catalyzed by various mixed oxides[a]

Catalyst (5% MO_x-SiO_2)	M_n ($\times10^3$)	M_w ($\times10^3$)	M_w/M_n	Yield (%)
SnO_2/SiO_2	1.94	4.98	2.6	45
ZrO_2/SiO_2	1.94	4.21	2.2	40
HfO_2/SiO_2	1.78	3.61	2.0	34
Al_2O_3/SiO_2	0.94	1.65	1.7	24
Ga_2O_3/SiO_2	0.92	1.81	2.0	10
Fe_2O_3/SiO_2	3.10	6.61	2.1	9
TiO_2/SiO_2	1.83	5.98	3.3	1

[a] Catalyst, 2.10 g (pretreated at 600 °C except SnO_2/SiO_2 (at 800 °C)); THF, 30.00 g; $(CH_3CO)_2O$, 4.98 g, 40 °C, 5 h.

3.4. Selection of support

The catalyst that can be manufactured easily and has constant qualities of the various lots, etc. is required on the industrial manufacturing viewpoint. On the other hand, it became clear that active components should disperse homogeneously on the support to perform high activity. The degree of dispersion of the active components should greatly affect on M_n and M_w/M_n of PTMG in this system because the diffusion rates of reactants and products in the pores are quite different (we will discuss this subject later).

On this respect, mesoporous silica having relatively large pore was thought to be an attractive candidate as a support. Furthermore, another experimental result suggested that the catalytic activity is almost proportional to the surface area of support. Thus, we have checked the performance of mesoporous material. As shown in Fig. 4, the reaction deactivated drastically and M_w/M_n increased after several hours in the continuous reaction although they showed good performance in the batch reaction. It suggests that one direction channel of examined material disturbs the diffusion of relatively large PTME molecules and

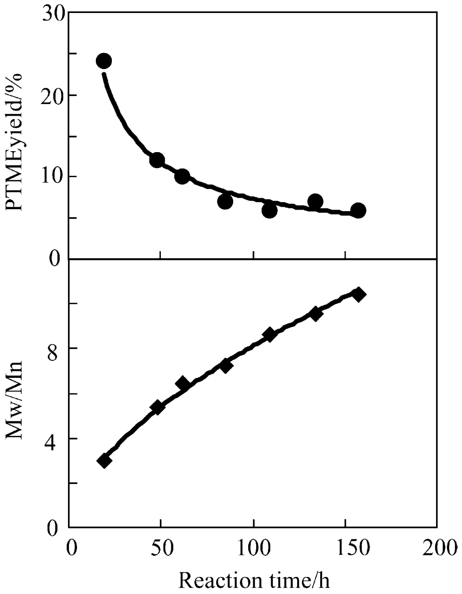


Fig. 4. The courses of PTME yield and M_n using MO_x-MCM-41 in a fixed-bed reactor.

Table 5
Effect of the properties of supports of 5 mol% ZrO_2/SiO_2 on the reaction behavior

Support	S.A.[a] ($m^2 g^{-1}$)	P.D.[b] (nm)	M_n ($\times 10^3$)	M_w/M_n	Yield (%)
5 mol% ZrO_2/extruded SiO_2					
CARiACT Q-10[c]	300	10	2.10	2.0	27
CARiACT Q-15[c]	200	15	2.51	2.0	20
CARiACT Q-30[c]	100	30	2.47	2.1	20
CARiACT Q-50[c]	80	50	2.51	2.1	17
D-150-120A[d]	390	12	1.74	1.9	21
Sairisia430[d]	300	17	1.47	2.0	22

[a] S.A.: surface area.
[b] P.D.: pore diameter.
[c] Catalyst, 1.0 g; THF, 30 g; $(CH_3CO)_2O$, 1.5 g, 40 °C, 5 h.
[d] Catalyst, 1.1 g; THF, 30 g; $(CH_3CO)_2O$, 5.0 g, 40 °C, 5 h.

its intrinsic structure is very fragile in the presence of trace water and acetic acid. The material looses its crystallinity during reaction according to the profile of XRD.

In order to investigate the influence of pore diameter on catalytic activities, the silica materials whose diameter are >10 nm were examined. As shown in Table 5, SiO_2 with relatively large diameter (>15 nm) shows good performance. At the same time, it is also required to keep a quite sharp distribution of pore size in order to avoid the negative effect of smaller pore for diffusion of PTME.

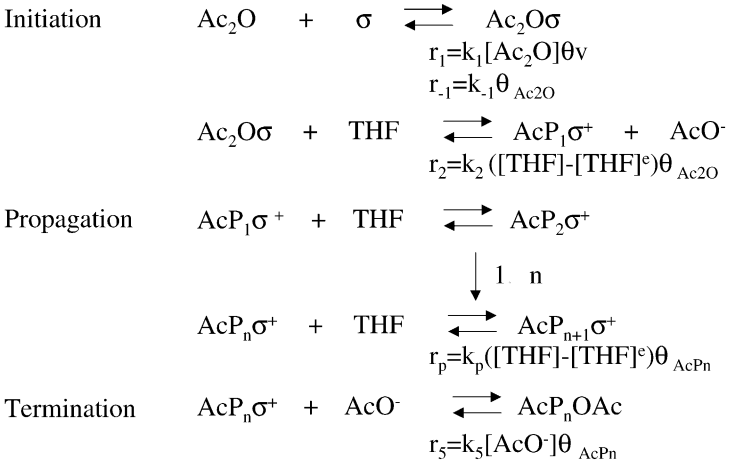
3.5. Study of reaction mechanism by simulation

In the case of polymerization of ethylene or propylene, the molecular weight of polyolefine reaches several million. Polymerization proceeds on the active site and the influence of diffusion to chain propagation can be neglected.

On the other hand, as mentioned above, the pore distribution of support has a great influence on the catalytic performance in the polymerization of THF in which molecular weight of the product is not high and the rate of termination is comparable to that of propagation. Therefore, it is very worthwhile to investigate the reaction kinetic simulation, especially paying attention to mass-transfer phenomena in order to control the properties of PTMG.

In this simulation, it is supposed that:

(a) The catalyst particle is like a ball and all substrates and products move in the radius direction freely.
(b) Their moving are controlled by the individual diffusion constant.
(c) The reaction is initiated by the formation of an oxonium cation.
(d) The chain propagation takes place with a constant probability.
(e) The termination is caused by the attack of acetic anhydride to an oxonium cation and PTMG-ester desorbs.



(σ;active site on the catalyst, P_n;n-mer of cyclic ether, r;reaction rate, k;rate constant, θ;coverage of active site(θv=1-θ)).

Scheme 1.

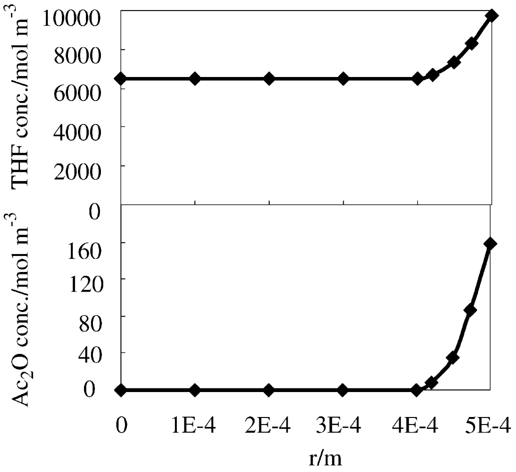


Fig. 5. Concentrations of THF and Ac_2O in the catalyst (r: radius of the catalyst particle).

As a formula, these premises are represented in Scheme 1.

According to the simulation data:

(1) The concentrations of THF and acetic anhydride decrease drastically near the surface of the ball, and high molecular weight PTME will be generated easily in the bulk due to the lack of acetic anhydride as shown in Fig. 5.

(2) M_n is a function determined by the ratio of THF and acetic anhydride. The diffusion of THF, acetic anhydride and PTME affect on M_w/M_n. M_w/M_n becomes the minimum if there is not any limitation of diffusion, and the larger value is obtained in the real system determined by the properties of supports. Fig. 6 shows the relationship between M_n and the corresponding idealized M_w/M_n.

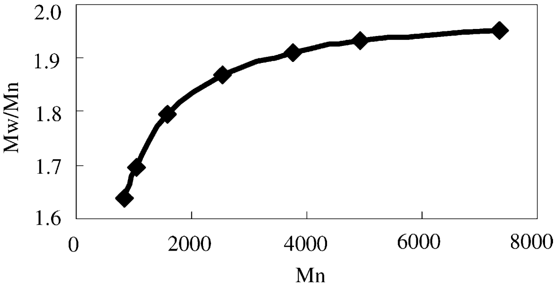


Fig. 6. M_w/M_n vs. M_n calculated from the simulation.

(3) In order to obtain lower M_w/M_n, it is necessary to disperse catalytic species on the surface of the support as thin as possible with keeping unity. M_w/M_n becomes bigger when active species are dispersed thickly even if they are uniformly dispersed. Moreover, M_w/M_n increases if the concentration of active sites differs between outside and inside of the support.

Fig. 7 shows the relationship between M_w/M_n and the distribution of catalytic site along the thickness of sphere particle.

Experimental results agreed well with these simulations, and the effect of the diffusion can be predicted to some degree. These simulations are used in the plants to control the quality of the product.

3.6. Decision of the process

Considering the simulation described in the earlier sections, small particles of SiO_2 was adopted as the support of the mixed oxide. It becomes easy to disperse active species and obtain catalysts with

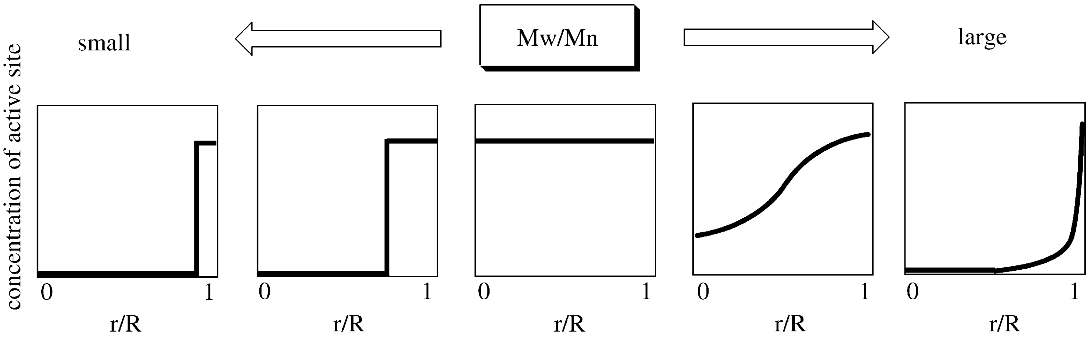


Fig. 7. The effect of the dispersion of the active species of M_w/M_n.

Table 6
Comparison of the reactors

	Fixed-bed	Slurry
Particle size of catalyst	Large	Small
Equipment	Simple	Complicated
STY	Small	Large
Control of the production	Difficult	Easy
M_n	Relatively small; reaction condition has to be changed to keep M_n constant	Relatively large; catalyst deactivation does not have to be considered
M_w/M_n	Changeable	Constant

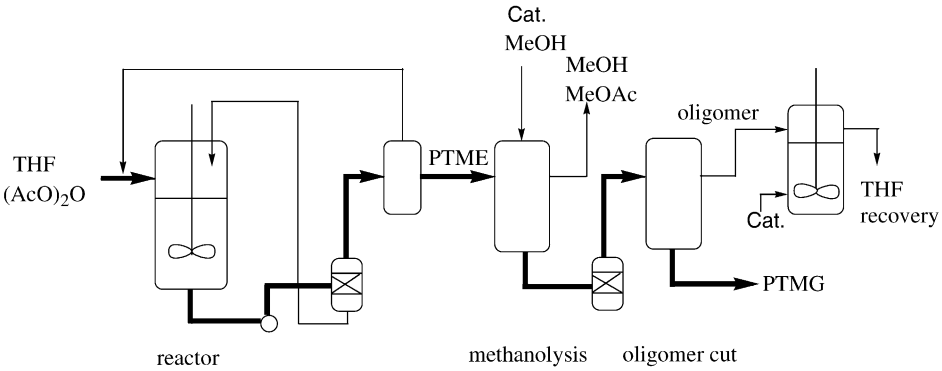


Fig. 8. Flow diagram for PTMG synthesis.

constant performance as a practical manufacturing technology.

It is possible to use a fixed-bed flow reactor because the heat generation of this reaction is not so large. However, the catalytic activity decreases gradually even if the concentration of water is reduced carefully because the Lewis acid catalyst is very sensitive to existence of water. Thus, the fixed-bed reactor is not suitable to control the quality of PTME constantly at adjusted conditions. On the contrary, a slurry process has many advantages. The loss of activity can be compensated easily by adding fresh catalysts, There is no need of consideration to remove reaction heat. The great stirring power is not required because the viscosity of the solution is low due to the relatively low concentration of PTME in the reaction mixture. As a result, we could control the productivity and the quality of PTME easily by adopting continuous stirring flow reactor (CSTR), which resulted in the reduction of the construction cost by 40% compared to the conventional process.

Furthermore, the calcination of catalyst at high temperature (>700 °C) in order to obtain sufficient Lewis acid strength improved the physical strength of the catalyst. Table 6 summarizes the various advantages of our adopted process.

Fig. 8 shows the brief process flow of industrial technology, in which >20,000 tonnes of PTMG can be produced annually.

4. Conclusion

Polymerization of THF catalyzed by solid acid in the presence of acetic anhydride was studied. A moderate Lewis acid catalysis produces desired PTME having adequate M_n. Zeolitic material is not suitable for this production because very high molecular weight PTME is co-produced. From this aspect, mixed oxide materials show good performances because only these have the desired acidic characters. Mass-transfer study suggests the importance of pore size of support and the homogeneity of active sites. They affect on the M_n and the M_w/M_n strikingly. The commercial technology has established by utilizing these results.

Acknowledgements

We thank the permission to exhibit this work by Mitsubishi Chemical Co., Ltd. and giving us the opportunity to show it at ABC IV by the corresponding office.

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