

Cationic Oligomerization of α -Methylstyrene by Binary Metal Oxides¹

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ABSTRACT: The cationic polymerization of α -methylstyrene by binary metal oxides at 30°C gave oligomers, especially dimers and trimers, as major products. These dimers [Y. Kawakami *et al.*, *Chem. Lett.*, 13 (1980)] and trimers were separated and identified. A reaction scheme has been proposed on the basis of a study of the effects of water, and pyridine as a poisoning base on catalytic activity, product distribution, and isomer distribution of the dimers and trimers. It seems that there are at least two different active sites which give olefin oligomers and indan ring containing oligomers, respectively.

KEY WORDS Styrene Derivatives / Binary Metal Oxide / Dimerization / Trimerization / Reaction Scheme / Acid Strength / Cocatalyst /

Cationic polymerization, especially the initiation reaction, of styrene by acid clay has been studied extensively.²⁻⁶ We have been interested in obtaining highly active solid catalysts for cationic polymerization. Initially, we chose binary metal oxide systems known for their strong acidity, such as Al₂O₃-TiO₂, SiO₂-Al₂O₃ systems, and studied the polymerization of α -methylstyrene using these catalyst systems. When α -methylstyrene was reacted with 5 wt% of these binary metal oxides at 30°C, oligomers were formed. The selective dimer formation was possible through the proper choice of a binary metal oxide system.⁷ In this paper, other binary metal oxide systems such as TiO₂-ZrO₂, which shows weaker acidity than either the Al₂O₃-TiO₂ or SiO₂-Al₂O₃ system, were also tested in order to study the effect of acid strength on product distribution and selectivity of the isomers of dimers and trimers of α -methylstyrene. For reference, acid clay, PdSO₄, BF₃OEt₂, and CF₃SO₃H were also used as initiators. Based on the results, the catalytic activity of binary metal oxides as initiators in the polymerization of α -methylstyrene and the reaction scheme were considered in relation to acid strength, acid amount, and the method of preparation of

solid acids.

EXPERIMENTAL

Reaction Procedure

Binary metal oxides were prepared by calcining, at 500°C for 4 h under a nitrogen stream, binary metal hydroxides obtained by two different methods: 1) the hydrolysis of mixed metal chlorides with conc. ammonia and 2) the hydrolysis of binary metal alkoxides with water. The acid strength and amount were determined by titrating with *N*/10 *n*-butylamine in benzene using Hammett indicators (*pKa*'s of indicators: 4-Benzeneazodiphenylamine +1.5, Diccinnamalacetone -3.0, Benzalacetophenone -5.6, Anthraquinone -8.2).⁸ In order to study the effect of the calcination temperature on catalytic activity, binary metal oxides from the mixed metal chlorides were calcined at three different temperatures, 300, 500, and 700°C. Acid clay was heated at 500°C for 4 h. Polymerizations were generally carried out at 30°C under nitrogen in bulk. In order to investigate the effect of the amount of water on catalytic activity, reactions of α -methylstyrene were carried out under three different anhydrous conditions.

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A: α -Methylstyrene, dried over CaH₂, was po-

lymerized under nitrogen (general procedure).

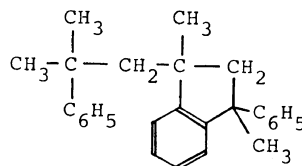
B: α -Methylstyrene, dried over CaH_2 , was polymerized in a high vacuum (10^{-5} mmHg) by an initiator evacuated (10^{-5} mmHg) at 100°C for 1 h after calcination.

C: α -Methylstyrene, dried over CaH_2 followed by drying over sodium mirror, was polymerized within a high vacuum (10^{-5} mmHg) by an initiator evacuated (10^{-5} mmHg) at 100°C for 1 h after calcination.

Separation and Identification of Oligomers

The dimers and trimers of α -methylstyrene were separated by preparative GLC and GPC, respectively, and analyzed by MS, NMR, IR, and elemental analysis. The analysis of the dimers has been reported.⁷ The trimers were further purified by the column chromatography on silica gel using *n*-hexane as the eluent and were identified as the terminal (HT-1) and inner (HT-2) olefin, and indan (INDT) type trimers by ^1H - and ^{13}C -NMR. In the column chromatography, HT-2 was eluted first, and HT-1 and INDT had almost the same elution time. So, in separating INDT by trifluoromethanesulfonic acid which is known to give indan dimer (IND) almost

exclusively in dimer fraction,^{7,9} the product mixture was oxidized by potassium permanganate to remove terminal olefin oligomers before the chromatography. The inner olefin trimer HT-2 was separated from the reaction mixture by acid clay following a similar procedure. The terminal olefin trimer HT-1 was separated from the reaction mixture by titanium deposited alumina which gave terminal olefin dimer predominantly in the dimer fraction.⁹



The ^1H NMR spectra of IND and INDT are shown in Figure 1. As can be seen from the structure, the indan type trimer INDT is a diastereoisomeric mixture. The signals at δ (CDCl_3) 0.97, 1.14, 1.27, and 1.60 can be assigned to four methyl groups. Those at δ 1.34, 1.40, 1.56, 1.57, 1.77, 1.80, 1.99, 2.06, 2.18, 2.30, 2.41, 2.50, and 2.73 can be assigned to the four ring and non-ring methylene protons. The Dreiding model study of the compound in-

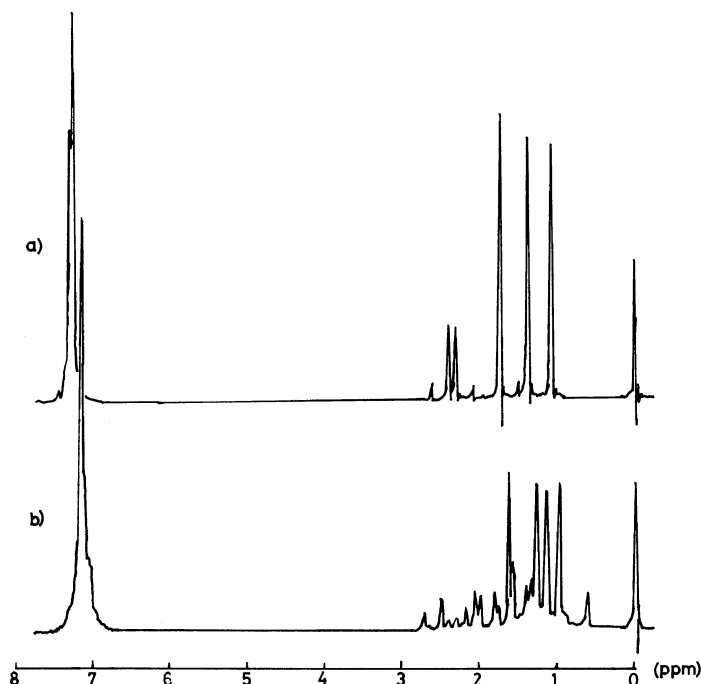
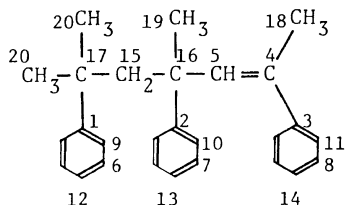


Figure 1. The ^1H NMR spectra of indan type dimer (IND) and trimer (INDT) of α -methylstyrene. a) IND and b) INDT measured in CDCl_3 (10%) using TMS as internal standard.

dicates that both ring and non-ring methylene protons appear as two types of AB quartets. This means that the four methylene protons may show a maximum of sixteen absorption signals. The exact assignment of each signal to a specific proton could not be made.

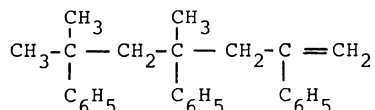
2,4,6-Triphenyl-4,6-dimethylhept-2-ene (HT-2)



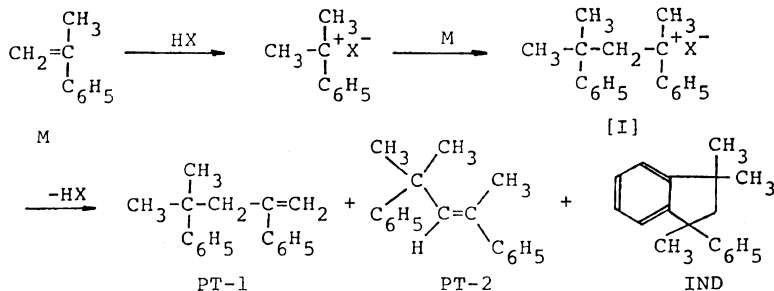
$^1\text{H NMR } \delta(\text{CDCl}_3)$ 1.06 (s, 6H, CH_3), 1.18 (s, 6H, CH_3), 2.72 (s, 2H, CH_2), 5.55 (s, 1H, $\text{CH}=\text{C}$), 6.45–6.75, 6.75–7.10, and 7.10–7.33 ppm (m, 15H, aromatic protons).

$^{13}\text{C NMR } \delta(\text{CDCl}_3)$ 151.4, 149.0, 142.3, 137.6 [C(1), C(2), C(3), C(4)], 140.8 [C(5)], 128.9, 127.7, 127.0, 126.1, 126.0, 125.8, 125.2, 125.0 [C(6), C(7), C(8), C(9), C(10), C(11), C(12), C(13), C(14)], 56.1 [C(15)], 40.2, 39.2 [C(16), C(17)], 31.1, and 29.5 ppm [C(18), C(19), C(20)].

2,4,6-Triphenyl-4,6-dimethylhept-1-ene (HT-1)



$^1\text{H NMR } \delta(\text{CDCl}_3)$ 0.73 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.25 (s, 2H, CH_2), 2.69 (s, 2H, $\text{CH}_2\text{C}=\text{C}$), 4.63 (d, 1H, $\text{C}=\text{CH}$, $J=2$ Hz with allyl coupling), 4.95 (d, 1H, $\text{C}=\text{CH}$, $J=2$ Hz), and 6.76–7.43 ppm (s, 15H, aromatic protons).



Scheme 1.

RESULTS AND DISCUSSION

Effects of Catalysts

The dimerization of α -methylstyrene by binary metal oxides has been reported.⁷ It was shown that linear olefinic dimers were the principal products among the reaction products, and that the terminal olefin dimer could be selectively synthesized through an appropriate choice of binary metal oxides. It was also shown that the inner olefin isomer was isomerized from the terminal olefin dimer. The reaction scheme for the dimerization of α -methylstyrene is shown in Scheme 1.

In contrast to the acid clay which gave indan dimer exclusively, the synthetic binary metal oxides gave olefinic dimers as the major products. Although it is not clear as to what species is responsible for the formation of the indan dimer, Higashimura *et al.* maintain that the freer ionic the propagating species, the greater the amount of indan dimer formed in the oligomerization of substituted styrene derivatives.^{10–12} Generally, oxo acid derivatives are considered to give a greater yield of olefinic dimers and Lewis acids, a greater yield of the indan dimer. This has also been shown by Hamaya *et al.*^{13,14} The distribution of the trimers by several initiators is shown in Table I. Strong acids such as acid clay, trifluoromethanesulfonic acid, or BF_3OEt_2 gave the indan type trimer in a considerable amount. But in contrast to this, titanium deposited alumina⁹ gave the terminal olefin trimer HT-1 as the major component in the trimer fraction.

Effect of Water on Catalytic Activity

In order to investigate the effect of water on catalytic activity, the reactions were carried out under three different anhydrous conditions (see experimental) and the results are shown in Table II.

Table I. Distribution of trimers in the polymerization of α -methylstyrene by various initiators^a

No.	Initiator	Time h	Conversion %	Yield of trimers %	Distribution ^b %		
					HT-1	HT-2	INDT
1	BF ₃ OEt ₂ ^c	1	98	19	0	35	65
2	CF ₃ SO ₃ H ^c	1	96	13	0	48	52
3	Acid clay	12	98	23	25	24	51
4	Al ₂ O ₃ (500, TiOH) ^d	24	91	13	81	19	0
5	Al ₂ O ₃ -TiO ₂ (9:1) ^e	48	23	3	94	6	0
6	Al ₂ O ₃ -TiO ₂ (9:1) ^f	48	78	14	34	66	0

^a 30°C, bulk, with initiator 5 wt% to the monomer.^b Determined by ¹H NMR.^c 0.6 mol% to the monomer.^d Prepared by the reaction of titanium chloride at 180°C with alumina (calcined at 500°C), followed by hydrolysis.⁹^e Prepared from alkoxides.^f Prepared from chlorides.**Table II.** Product distribution in the polymerization of α -methylstyrene by binary metal oxides-effect of water

No.	Initiator	System ^a	Temp °C	Time h	Yield %	wt% of dimers and oligomers			
						PT-1	PT-2	IND	Oligomers
1	Al ₂ O ₃ -TiO ₂ (9:1)	A	30	90	90	40	23	2	25
2		B	30	24	90	57	14	—	19
3		C	30	24	36	24	3	—	9
4	Al ₂ O ₃ -TiO ₂ (9:1) ^b	B	0	96	88	61	4	—	23
5		A	30	90	40	26	1	—	13
6		B	30	90	90	58	8	—	24
7		C	30	90	41	28	3	—	10
8	TiO ₂ -ZrO ₂ (1:1)	A	30	90	10	7	—	—	3
9		B	30	90	60	48	4	1	7
10		C	30	90	2	—	—	—	—

^a See experimental section.^b From alkoxides.

In all catalyst systems, the activity of system B was the highest. Compared to system A, the catalyst in system B was considered more active since the carbon dioxide covering the active site was removed by evacuation. Judging from the fact that catalytic activity of system C was lower than B, water is considered to act as a cocatalyst, and a small amount of water is necessary to make the catalyst active. Although with a shorter reaction time by system B, more terminal olefin dimer PT-1 is formed than by either system A or C, if the reaction time is

long enough, the product distribution becomes quite similar for each catalyst system. These facts suggest that water acts as a cocatalyst and causes the catalyst activity to be high in the initiation, but does not affect very much the isomerization site from PT-1 to PT-2. Similar trends were also observed for systems with Al₂O₃-TiO₂ (1:1) from alkoxides, SiO₂-Al₂O₃ (4:1), and TiO₂-ZrO₂ (1:1) as initiators. Thus, water is considered to act on metal oxides to form the same type of initiating sites.

Table III. Effect of the baking temperature of Al₂O₃-TiO₂ (9:1) on product distribution in the polymerization of α -methylstyrene at 30°C

Baking temp °C	Time h	Yield %	wt% of dimers and oligomers			
			PT-1	PT-2	IND	Oligomers
300	43	21	17	1	—	3
500	43	83	45	17	3	18
700	43	77	39	15	3	21

Table IV. Acidity distribution of binary metal oxides

Binary metal oxide	Acid amount (mmol g ⁻¹) at different pK _a 's			
	+1.5 ≤	≤ -3.0 ≤	≤ -5.6 ≤	≤ -8.2
Al ₂ O ₃ -TiO ₂ (9:1)	0.637	0.521	0.102	0.025
Al ₂ O ₃ -TiO ₂ (9:1) ^a	0.517	0.583	0.059	0.020
Al ₂ O ₃ -TiO ₂ (1:1) ^a	0.848	0.116	0.075	0
SiO ₂ -Al ₂ O ₃ (4:1)	0.690	0.101	0.050	0
TiO ₂ -ZrO ₂ (1:1)	0.360	0.210	0.040	0

^a From alkoxides.**Table V.** Effect of baking temperature on acidity distribution of Al₂O₃-TiO₂ (9:1)

Temp °C	Acid amount (mmol g ⁻¹) at different pK _a 's			
	+1.5 ≤	≤ -3.0 ≤	≤ -5.6 ≤	≤ -8.2
300	0.324	0.210	0.052	0
500	0.637	0.521	0.102	0.025
700	0.449	0.330	0.075	0.016

Effect of Calcination Temperature

In order to study the effect of the calcination temperature on catalytic activity and products distribution, the oligomerization of α -methylstyrene was carried out by the Al₂O₃-TiO₂ (9:1) system prepared from metal chlorides and calcined at different temperatures. The results are shown in Table III. Calcination at 500°C gave the most active catalyst, and it can be seen that a greater amount of inner olefin dimer was formed by this catalyst.

Acid Amount and Strength

Because the initiation reaction is the protonation reaction, two factors affecting the catalytic activity are the amount of the acid and its strength. The results of titration (see experimental) are shown in

Table IV. When we look at the reported activity of binary metal oxides in α -methylstyrene oligomerization⁷ in terms of acid strength, it can be qualitatively said that catalytic activity increases in proportion to the amount and strength of the acid. At present, a quantitative correlation between the catalytic activity and acid strength and amount is difficult to determine; however, it is suspected that acid stronger than pK_a -8.2 is responsible for the isomerization of PT-1 to PT-2 since metal oxides of an acid strength lower than pK_a -8.2 usually did not isomerize PT-1 to PT-2 and gave PT-1 selectively.⁷ The effect of the calcination temperature on catalytic activity can also be interpreted by the change in acid strength. This change in acid strength and amount by calcination temperature is shown in

Table VI. Effect of added pyridine on the product distribution in the oligomerization of α -methylstyrene at 30°C

Catalyst (5 wt% to monomer)	Pyridine	Time	Yield	wt% of dimers and oligomers			
	(mmol g ⁻¹ cat)	h	%	PT-1	PT-2	IND	Oligomers
Al ₂ O ₃ -TiO ₂ (9:1)	0	90	90	40	23	2	25
	0.01	90	88	42	17	2	27
	0.02	90	83	42	13	2	26
Acid clay	0	0.5	94	4	2	65	23
	0.025	0.5	42	8	2	21	10
	0.050	0.5	22	5	1	8	8
	0.100	0.5	10	3.5	0.4	3.1	3.0

Table V. Calcination at 500°C gave the most active catalyst. This can be understood as a result of the greatest amount of acid and strongest acidity (0.025 mmol g⁻¹ at pK_a -8.2). The catalyst calcined at 300°C (no acid site at pK_a -8.2) had a lower activity in the oligomerization, and did not isomerize PT-1 to PT-2. This fact is consistent with the discussion above that an acid stronger than pK_a -8.2 is responsible for the isomerization. Poisoning experiments with pyridine were carried out and the results are shown in Table VI. By the addition of pyridine, the acid site on the metal oxide is considered to be poisoned at the stronger acid sites. In the case of the Al₂O₃-TiO₂ (9:1) system, poisoning of the strong acid site should result in a decrease in the amount of PT-2. Although the total yield also decreased, the relative amount of PT-2 decreased with the addition of pyridine. This fact supports the above speculation. In the case of acid clay, poisoning of the strong, free ionic site should result in relative decrease of IND and oligomers compared to olefinic dimers. This can be seen from the table.

The Nature of the Active Sites

The difference in product distribution in the isomerization of α -methylstyrene dimer by various initiators is shown in Table VII. PT-1 is slowly isomerized to PT-2 by Al₂O₃-TiO₂, and not to IND. PT-1 is slowly isomerized to both PT-2 and IND by acid clay. All olefinic dimers are isomerized to IND and higher oligomers by BF₃OEt₂ or CF₃SO₃H. Since protonation of olefinic the dimers PT-1 and PT-2 should give the same intermediate [I] in Scheme 1, the distribution of these products (PT-1, PT-2, and IND) can strongly be considered to be controlled by the nature of the counter ion X⁻. The

Table VII. Product distribution in the isomerization of the olefinic dimer of α -methylstyrene at 30°C for 2h

Catalyst ^a	PT-1	PT-2	IND	Oligomer
Original	72.4	14.0	3.0	10.6
None	72.4	14.0	3.0	10.6
Al ₂ O ₃ -TiO ₂	72.0	14.2	3.0	10.8
Al ₂ O ₃ -TiO ₂ ^b	51.0	35.2	3.1	10.7
Acid clay	71.1	16.6	3.0	9.9
Acid clay ^b	36.5	21.7	23.6	18.2
BF ₃ OEt ₂ ^c	—	8.0	63.2	28.8
CF ₃ SO ₃ H ^c	—	—	57.0	43.0
PdSO ₄ ^d	20.7	50.3	3.9	25.1

^a 5 wt% to the starting mixture.

^b 72h.

^c 0.6 mol% to the starting mixture.

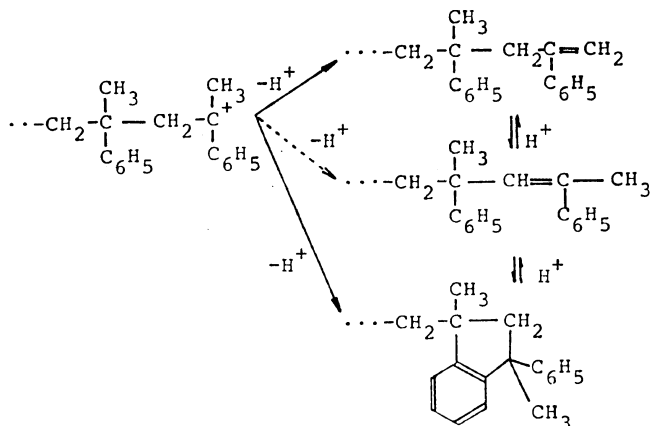
^d 2.0 mol% to the starting mixture at 95°C in acetic acid.

weakly nucleophilic counter ion CF₃SO₃⁻ or BF₄⁻ gave IND.

The main fraction in the oligomers was the trimer in the reaction at 30°C. It was noted that the inner olefin and terminal olefin trimers were formed by Al₂O₃-TiO₂. However, the indan type trimer was also formed by strong acids like CF₃SO₃H or BF₃OEt₂. The indan type trimer was even the major component in the trimer fraction by BF₃OEt₂, acid clay or CF₃SO₃H. Thus, more free ionic species was shown to give the IND dimer and trimers which are rich in the indan type INDT.

Judging from the structures and distribution of the trimers, Scheme 1 may be extended to the general scheme of proton elimination leading to oligomers in the polymerization of α -methylstyrene, as shown in Scheme 2.

Cationic Oligomerization by Solid Acids



Scheme 2.

The loss of a proton from the growing end leads to the formation of a terminal olefin or indan. Although the direct formation of inner olefin oligomers is not confirmed, isomerization from the terminal dimer to an inner olefin dimer is established.⁷ Indan derivatives are formed only by strong acids which are considered superacids. As shown in Table VII, superacids can isomerize PT-1 to IND, and very strong acid sites are considered necessary to isomerize olefinic oligomers to indan oligomers. Binary metal oxides gave only olefinic oligomers. These may be said to be weak acids, and their contact ionic nature makes proton elimination from the growing end easy.

It is interesting to point out here that, contrary to the fact that the indan dimer and trimer are formed mainly in α -methylstyrene polymerization by trifluoromethanesulfonic acid, olefinic dimer, trimer, and oligomers were formed primarily in the polymerization of styrene derivatives (ref. 10–14). The stability of the growing carbocationic species seems to play an important role in determining product distribution. Lowering the reaction temperature in case of $\text{Al}_2\text{O}_3\text{-TiO}_2$ resulted in a relative decrease in PT-2, probably because the isomerization from PT-1 to PT-2 was suppressed (Table II, No. 4). In the case of acid clay, the amount of IND decreased by lowering the temperature. The electrophilic substitution reaction was considered to be suppressed.

Although there was no great change in the reaction conditions, the polymerization of styrene derivatives may be considered to be propagated by two species different in the extent of their dissociation (see also ref 10–14). The stability of each

species, and accordingly the effective concentration of actual chain carrier are determined by the kind of solvents, temperature, structure of the growing end (or monomer) and counter ions. Apparently, a more stabilized (long lived) carbocation (growing end of α -methylstyrene and *p*-methoxystyrene^{1,2}) tends to bring about a greater yield of oligomers and indan structure in the polymerization.

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