Para-Methylstyrene - A New Monomer and Polymer for Industry

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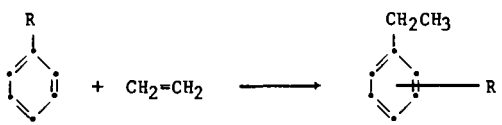
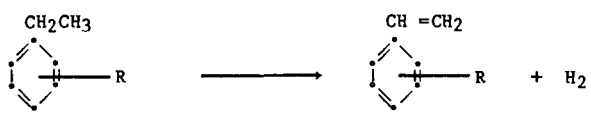
INTRODUCTION. The present large volume styrene industry began during World War II as part of the effort to produce synthetic rubber to replace supplies of natural rubber which were suddenly cut off from sources in Asia (1,2). A rapid growth in polymer technology eventually followed. A considerable number and variety of new monomers were synthesized, purified and polymerized to establish the principles and products of the large volume styrenics plastics industry as we know it today.

VINYLTOLUENE. When toluene was substituted for benzene in the alkylation step, ethyltoluene was produced, Equation 1 ($R=CH_3$). The corresponding vinyltoluene was obtained by a subsequent catalytic dehydrogenation, Equation 2, in a manner analogous to the process for producing styrene (3). By contrast with styrene, however, a mixture of three isomers was formed. Different polymer



(1)



(2)

properties of these individual isomers and various mixtures were observed giving rise to more complex separation and purification steps. The vinyltoluene of commerce which eventually emerged from this work is composed of approximately 35% para and 65% meta isomers determined primarily by the ratio produced during alkylation with an $HCl-AlCl_3$ catalyst and practical isomer separation limitations (4).

Styrene is the simplest vinyl aromatic with the fewest production and purification problems. Polymer properties of styrene were also favored by comparison with the vinyltoluene mixtures which could be efficiently produced with the catalysts and processes available. As a result, styrene has become the dominant vinyl aromatic monomer and polymer in the marketplace.

ZEOLITE CATALYTS. During the past three decades, interest and knowledge of the structure and catalytic properties of the naturally occurring zeolites has grown (5,6). More recently, this effort has expanded dramatically with the development of techniques for manufacture of many of these materials and especially with the discovery of unique, new synthetic zeolites not found in nature which have demonstrated desirable catalytic properties (7).

Zeolite catalysts are crystals composed of silicon and aluminum oxides which contain pores and channels of precise and uniform dimensions. Chemical reactions occur primarily within the pores at catalytic sites, often acidic protons, present on the internal framework structure. The dimensions of Mobil ZSM-5 class zeolite pores are sufficient to admit certain substituted benzene derivatives.

However, analogues with bulky side-chains or polycyclic rings can not diffuse in or out of the pores to undergo a chemical reaction or be produced within the pores. Zeolite catalysts have shape selective properties by virtue of the limited space within the pores (7).

Toluene can be alkylated with ethylene to produce ethyltoluene over (unmodified) HZSM-5 catalyst containing acidic sites, Equation 1 (8). The starting materials and products can diffuse in and out of the pores. The composition of products observed, however, differs significantly from that found with an $HCl-AlCl_3$ catalyst. The amount of ortho isomer was reduced by an order of magnitude, Table 1. An examination of the relative minimum dimensions of the ethyltoluene isomers, Table 2, indicates that the para isomer is smallest (9). The small difference between the ortho and meta isomers is also significant. We believe that the product mix observed was a result of the precise dimensions of the zeolite catalyst pores. A subtle distinction was made between the meta and ortho isomers based on size, favoring the smaller isomer, either by rate of formation and/or rate of diffusion out of the pore (10).

PARA-SELECTIVITY. To magnify this effect, methods have been developed for reducing the effective pore and channel dimensions as originally synthesized by modification of the catalyst with physical treatments and chemical reagents. Para-selective alkylation catalysts were produced. A dramatic difference was observed for the alkylation reaction. Ninety-seven percent of the ethyltoluene product produced was the smallest para isomer. The largest ortho isomer was virtually eliminated. The rates of diffusion between the para and ortho/meta isomers were increased by three orders of magnitude with modified para-selective catalysts (10).

The use of a modified zeolite catalyst offers several advantages for production of ethyltoluene by comparison with the $HCl-AlCl_3$ catalyst. The undesired ortho isomer, which is produced, and must be separated and recycled is virtually eliminated. Production of di- and polyethylated toluene is inhibited because of the confined space within the pores. In addition, all of the problems of corrosion, disposal and separation encountered with the use of $AlCl_3$ are eliminated.

POLY-PARA-METHYLSTYRENE. Samples of 99+% p-methylstyrene were prepared in the laboratory. However, we have selected a 97% para-, 3% meta-methylstyrene mixture, designated PMS, for initial polymerization studies. A comparison of typical monomer properties of PMS with styrene and commercial vinyltoluene is shown in Table 3. In broad terms, PMS is similar to styrene in its polymerization behavior. PMS polymers, with a variety of molecular weights and melt flow properties, have been prepared. Analogous copolymers were also made by substituting PMS for styrene. A study of polymer properties reveals some differences as well as similarities with polystyrene, Table 4.

A potentially important advantage of poly-PMS is its lower density relative to styrene which translates to a 4% reduction in weight required to fabricate a desired product. Poly-PMS has a glass transition temperature of 113°C, 11°C higher than polystyrene, Table 4. In addition to providing an extra margin of safety for higher temperature use and storage, decreases in molding cycle times, better mold fill properties and higher melt strengths have been observed.

A potential application where poly-PMS can give a significant improvement compared with polystyrene is in the area of flame retardancy (FR) or ignition resistance. PMS-based impact resins require lower loadings of FR reagents to meet the desired ratings.

Polystyrene is very difficult to crosslink by radiation without destroying its properties. As a result, applications using this property have not been developed. The methyl group of poly-PMS, however, provides susceptible positions for crosslinking at commercially viable levels of electron beam radiation. This

converts a thermoplastic to a thermoset resin, significantly improving its grease resistance and flammability behavior.

SUMMARY. Styrene has enjoyed a special position among vinylaromatic monomers because of its lack of isomers and consequent ease and simplicity of production. Our discovery of novel technology to produce p-ethyltoluene has enabled us to manufacture a substituted vinyl aromatic monomer selectively. Since much benzene is produced from toluene, the direct use of toluene for PMS eliminates the first process step for styrene. Quantities of PMS from a semi-commercial plant are now available for the critical cost/performance test in the marketplace to eventually determine its place in the polymer industry.

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Table 1. Alkylation of Toluene with Ethylene
Composition of Typical Product Streams

Compound, wt%	Catalysts		
	$HCl-AlCl_3$ [a]	ZSM-5 Class Zeolite	
		Unmodified	Modified
Light gas and Benzene	0.2	1.0	0.9
Toluene [b]	48.3	74.4	86.2
Ethylbenzene and Xylenes	1.2	1.2	0.5
p-Ethyltoluene	11.9	7.0	11.9
m-Ethyltoluene	19.3	14.7	0.4
o-Ethyltoluene	3.8	.3	0
Aromatic C_{10}+	14.4	1.4	0.1
Tar	0.9	0	0
Total	100.0	100.0	100.0
Ethyltoluene Isomers, %			
Para	34.0	31.8	96.7
Meta	55.1	66.8	3.3
Ortho	10.9	1.4	0

(a) Ref. 4
(b) Excess toluene is used to prevent polyalkylation and resultant build-up of C_{10}+ and tars.

Table 2. Minimum Dimensions of Alkyl Aromatics [a]

Hydrocarbon	Minimum Cross Section Å
Benzene	7.0
Toluene	7.0
Ethylbenzene	7.0
o-Xylene	7.6
m-Xylene	7.6
p-Xylene	7.0
o-Ethyltoluene	7.7
m-Ethyltoluene	7.6
p-Ethyltoluene	7.0

(a) From Fischer-Hirschfelder-Taylor hard sphere molecular models.

Table 3. Typical Monomer Properties

	PMS	Styrene	Vinyltoluene
Purity (wt% vinyl)	99.7	99.7	99.2
Isomer Distribution			
Para	97	--	33
Meta	3	--	66.7
Ortho	--	--	0.3
Refractive Index (np25)	1.5408	1.5440	1.5395
Density, $g \cdot cm^{-3}$ (25°C)	0.892	0.902	0.893
Viscosity, cps (25°C)	0.79	0.72	0.78
Surface Tension, $dynes\text{-}cm^{-1}$ (25°C)	34	32	31
Boiling Point (°C @ 760 mmHg)	170	145	168
Freezing Point (°C)	-34	-31	-77
Volume Contraction on Polymerization (% Calculated @ 25°C)	12	14	12
Heat of Polymerization ($Kcal\ mole^{-1}$)	15-17	17	15-17

Table 4. Properties of Typical Polymers

Properties	Poly PMS [a]	Polystyrene
Specific gravity, gm/ml	1.01	1.05
Melt flow rate (condition G)	2.5	2.5
Thermal		
Glass transition temp. (°C)	113	102
Vicat Softening (°C)	116	109
Heat distortion temp. (°C)	95	89
Mechanical		
Tensile strength at break (psi x 10^{-3})	7.0	7.6
Elongation (%)	3.0	3.0
Tensile modulus (psi x 10^{-5})	3.2	3.6
Flexural strength (psi x 10^{-5})	12	13
Hardness (Rockwell M)	82	74
Izod impact (ft.lbs./in.)	0.3	0.3

(a) 97% para, 3% meta isomers