

Acid-Catalyzed Cracking of Polystyrene

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Received 27 February 1996; accepted 20 August 1996

ABSTRACT: The effects of catalyst acidity and the restricted reaction volume afforded by HZSM-5 on the volatile cracking products derived from poly(styrene) are investigated. Three catalysts: silica/alumina, HZSM-5, and sulfated zirconia, were employed as cracking catalysts. Styrene, which is the principal radical depolymerization product from poly(styrene), is a minor catalytic cracking product. The most abundant volatile product generated by catalytic cracking is benzene. Alkyl benzenes and indanes are also detected in significant yields. Various thermal analysis techniques are employed to obtain volatilization activation energies for polymer-catalyst samples and to elucidate probable reaction pathways. Detected products are explained by reaction mechanisms that begin with protonation of poly(styrene) aromatic rings. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1287–1298, 1997

Key words: polymer cracking; catalytic cracking; polymer recycling

INTRODUCTION

A variety of plastic waste recycling methods have been established and new recycling approaches are being developed to avoid placing polymers into landfills. One approach to waste plastic recycling, known as tertiary recycling, consists of decomposing plastics into useful chemicals. For a recycling scheme to be economically viable, the costs of collecting and sorting waste and for reclaiming products from waste must be recovered. Recent studies supported by the Packaging Research Foundation have shown that, based on the current price of oil, these costs cannot presently be recovered for tertiary plastic waste recycling methods.¹ However, future increases in landfilling costs coupled with lower collecting and sorting costs may make tertiary plastic waste recycling economically viable in the future.

Large-scale plastic waste tertiary recycling will require efficient and selective catalytic cracking

of waste polymers. The development of waste polymer cracking processes will require detailed knowledge of the relationship between catalyst properties and cracking product distributions. In order to compare the polymer cracking properties of different catalysts, it is preferable to examine the effects of catalysts without complications due to reactions of primary cracking products with polymer residue. Secondary reactions can be minimized by limiting the contact between primary volatile products and the polymer-catalyst mixture. This can be accomplished by maintaining high catalyst-to-polymer ratios and providing efficient and rapid removal of volatile products.²

Because poly(styrene) is used in consumer product packaging and to make disposable containers, it comprises a significant fraction of municipal plastic waste. Although the thermal decomposition of poly(styrene) has been the subject of numerous studies,^{3–12} relatively few studies have focussed on the catalytic cracking of poly(styrene).^{13–19} In those studies, catalysts were employed either to reform volatile thermal degradation products that had been generated by radical thermal degradation processes^{13–16} or to produce volatile products by direct cracking of poly-

Correspondence to: Robert L. White.
Contract grant sponsor: National Science Foundation.
Contract grant number: CTS-9509240.

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Table I LPS Decomposition Products at 400°C

Product	Neat LPS	LPS-Si/Al	LPS-ZrO ₂ /SO ₄	LPS-HZSM-5
Benzene		31	31	52
Toluene	1	1	3	3
Ethyl Benzene		20	10	5
Styrene	41	1		1
Isopropyl benzene		6	6	
Methyl styrene				
Indane		10	10	7
Indene		1		3
Methyl indane		17	25	7
Methyl indene				3
Naphthalene		4	2	7
2-Methyl naphthalene		4	2	6
1-Methyl naphthalene		2	2	
Dimer	11			
Trimer	35			

mer chains.¹⁷⁻¹⁹ In this article, thermal analysis results obtained from samples prepared by coating silica-alumina, HZSM-5, and sulfated zirconia catalysts with thin layers of poly(styrene) are compared. By comparing the thermal properties of poly(styrene) in contact with these three catalysts, the influence of catalyst acidity and HZSM-5 channel structure on volatile catalytic cracking product distributions can be assessed and used to characterize reaction pathways.

EXPERIMENTAL

Two poly(styrene) polymers were used in this study: a high molecular weight poly(styrene)

(HPS) (MW = 850,000), and a low molecular weight poly(styrene) (LPS) (MW = 2,700). Both were purchased from Aldrich Chemical (Milwaukee, WI). Neat polymers and poly(styrene) coated on silica-alumina, HZSM-5, and sulfated zirconia cracking catalysts were employed as samples in this study. Samples contained 10–20% polymer by weight. The silica-alumina catalyst was obtained from Condea Chemie GmbH (Hamburg, Germany). The silica-alumina catalyst contained 11.8% by weight alumina and had a surface area of 282 m²/g. The HZSM-5 zeolite catalyst was obtained from Mobil Oil (Paulsboro, NJ) and was characterized by a 355 m²/g surface area and a 1.5% alumina content. The HZSM-5 crystal structure contains two intersecting channels.²⁰

Table II HPS Decomposition Products at 400°C

Product	Neat HPS	HPS-Si/Al	HPS-ZrO ₂ /SO ₄	HPS-HZSM-5
Benzene		30	33	60
Toluene			3	2
Ethyl benzene		14	12	2
Styrene	68	4		2
Isopropyl benzene		9	8	
Methyl styrene				1
Indane		15	9	3
Indene				3
Methyl indane		17	8	6
Methyl indene				3
Naphthalene		3	7	3
2-Methyl naphthalene		2	5	3
1-Methyl naphthalene		2	5	1
Dimer	6			
Trimer	16			

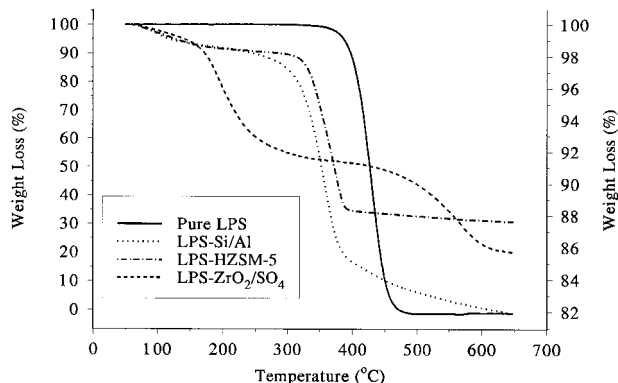


Figure 1 TG-MS weight loss curves for neat LPS poly(styrene) (left axis) and LPS-catalyst samples (right axis) obtained by heating samples at a rate of 10°C/min in He.

One channel is straight and has a nearly circular opening (0.54×0.56 nm), and the other channel is sinusoidal and somewhat more elliptical (0.51×0.55 nm). The sulfated zirconia catalyst was synthesized following procedures described previously.^{21,22} The sulfated zirconia catalyst had a surface area of 157 m²/g and contained 9% by weight sulfate. Poly(styrene)-catalyst samples were prepared by dissolving poly(styrene) in cyclohexane, adding catalyst, and then rotoevaporating the mixture to remove the solvent. The resulting polymer coated catalyst samples were dried for several hours at 90°C. The apparatus used for TGMS and pyrolysis-GC/MS measurements have been described previously.^{2,23} For TG-MS studies, samples were heated from 50 to 600°C in He at rates of 1, 10, 25, and 50°C/min. Pyrolysis-GC/MS separations were achieved by using a 60 m DB-5 column (0.25 μm film thick-

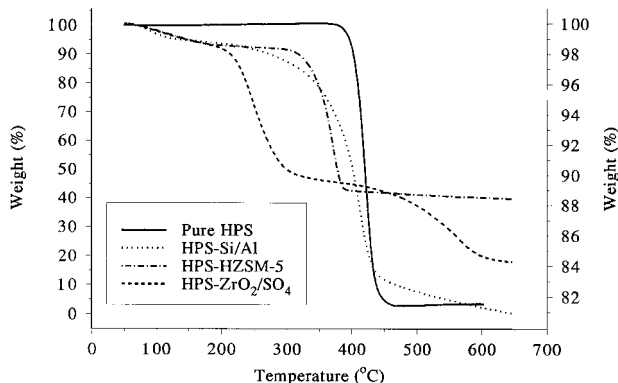


Figure 2 TG-MS weight loss curves for neat HPS poly(styrene) (left axis) and HPS-catalyst samples (right axis) obtained by heating samples at a rate of 10°C/min in He.

Table III Volatilization Activation Energies (kcal/mol)

Catalyst	LPS	HPS
None	46.4 ± 1.2	48.5 ± 0.8
Si-Al	33.8 ± 0.5	38.6 ± 0.5
ZrO ₂ /SO ₄	24.4 ± 2.9	28.9 ± 1.9
HZSM-5	34.6 ± 0.5	36.0 ± 1.3

ness) and a temperature program consisting of a 2-min isothermal period at -50°C followed by a 10°C/min ramp to 280°C, and then another isothermal period at 280°C for 5 min. For TG-GC/MS studies, a Valco Instruments, Inc. (Houston, TX) heated eight port external volume sample injector was employed to divert small volumes (ca. 85 μL) of TG effluent into a 30 m DB-5 capillary column (0.25 μm film thickness) for GC/MS analysis. A 5°C/min heating rate from 50 to 600°C in 20 mL/min He was used to heat samples in the thermogravimetric analyzer. When samples reached 100°C, TG effluent was sampled. Above 100°C, TG effluent sampling was repeated at 3-min intervals during TG-GC/MS analyses. A 5 mL/min He carrier gas flow rate through the TG-GC/MS chromatographic column was employed and the column temperature was maintained at 100°C during separations. TG-GC/MS column effluent was split prior to entering the mass spectrometer to maintain an ion source pressure of 5×10^{-5} Torr.

RESULTS

Pyrolysis-GC/MS

The most abundant volatile thermal decomposition products derived from polymer and polymer-catalyst samples were identified by using pyrolysis-GC/MS. Samples were rapidly heated to 400°C in a microfurnace injector that was connected to a gas chromatograph and separated decomposition products were identified by using mass spectrometry. The primary volatile thermal decomposition products generated from neat polymers and polymer-catalyst samples are listed in Tables I and II. Radical depolymerization of neat poly(styrene) samples produced large quantities of monomer (styrene), and chain end back biting yielded substantial amounts of dimer and trimer. The relative yield of trimer was about three times that of the dimer and the relative yield of styrene was greater for the high molecular weight poly-

mer (HPS) than for the low molecular weight polymer (LPS). Compared to product distributions detected for the neat polymer samples, little styrene was detected from polymer-catalyst samples. The most abundant volatile species detected from the polymer-catalyst samples was benzene. About 30% of the volatile material produced from the polymer-Si/Al and polymer-ZrO₂/SO₄ samples was benzene. For the polymer-HZSM-5 samples, the relative yield of benzene was over 50%.

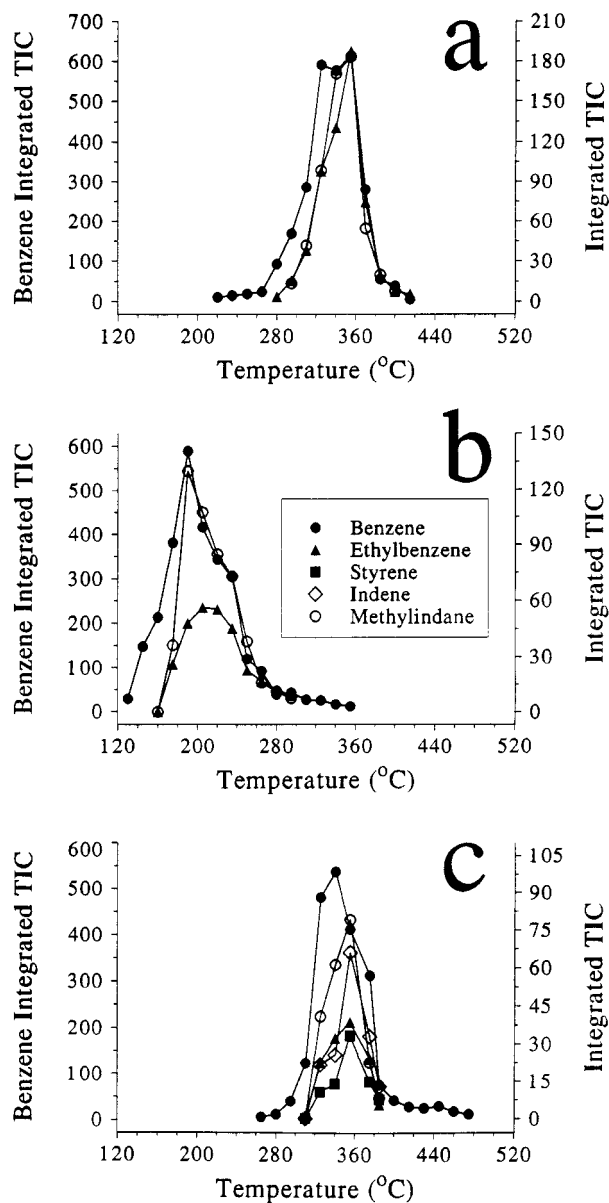


Figure 3 TG-GC/MS chromatographic peak areas derived from LPS-catalyst sample decompositions as a function of the TG sample temperature: (a) LPS-Si/Al, (b) LPS-ZrO₂/SO₄, (c) LPS-HZSM-5. The left axis scale represents benzene peak areas and the right axis scale represents all other peak areas.

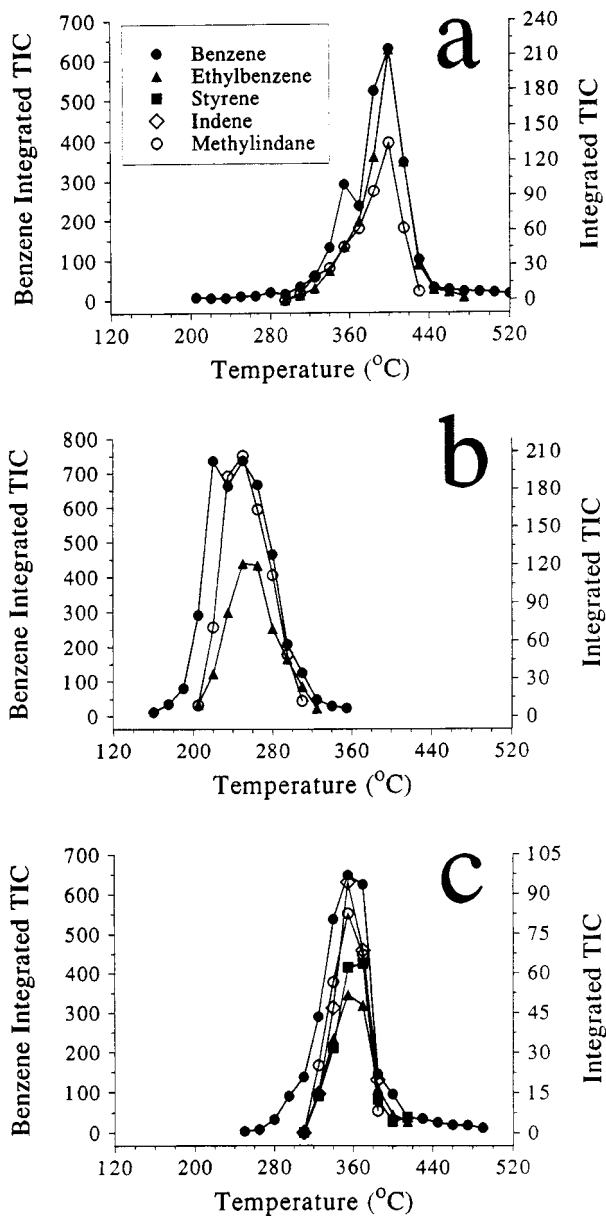


Figure 4 TG-GC/MS chromatographic peak areas derived from HPS-catalyst sample decompositions as a function of the TG sample temperature: (a) HPS-Si/Al, (b) HPS-ZrO₂/SO₄, (c) HPS-HZSM-5. The left axis scale represents benzene peak areas and the right axis scale represents all other peak areas.

Other volatile products detected from the polymer-catalyst samples in substantial yield included: alkyl benzenes, indanes, and naphthalenes. For both LPS and HPS polymers, the relative yields of alkyl benzenes were greatest for the samples containing Si/Al and ZrO₂/SO₄ catalysts. In contrast to these samples, the polymer-HZSM-5 samples produced fewer alkyl benzenes but significantly larger quantities of indenes.

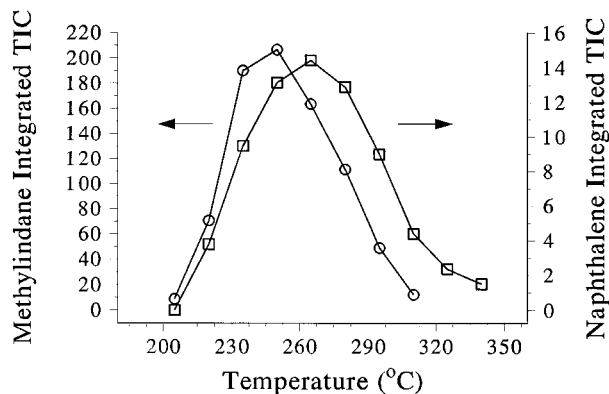


Figure 5 TG-GC/MS chromatographic peak areas as a function of sample temperature representing methylindane (open circles) and naphthalene (open squares) derived from the HPS-ZrO₂/SO₄ sample.

TG-MS

TG-MS was employed to correlate the evolution of volatile thermal decomposition products with sample weight loss and to calculate volatilization activation energies. Weight loss curves obtained by heating samples at 10°C/min in He are shown in Figures 1 and 2. Compared to neat polymer thermal decompositions, all three catalysts lowered the temperature at which significant sample weight loss occurred. The catalytic effect was greatest for the samples containing the ZrO₂/SO₄ catalyst. Comparing the curves in Figures 1 and 2 reveals that, for the same catalysts, the weight loss onset temperature was lower for the LPS polymer than for the HPS polymer. Weight loss curves shown in Figures 1 and 2 exhibit a gradual decrease in sample mass above 400°C for samples containing the Si/Al catalyst. Mass spectrometric analysis of species evolved above 400°C revealed that this weight loss was due to loss of water from the catalyst. Similar weight loss rates were observed when neat Si/Al catalyst was analyzed by TG-MS. The weight loss curves for the polymer-ZrO₂/SO₄ samples exhibit two distinct steps. TG effluent mass spectra confirmed that the low temperature weight loss step was caused by poly(styrene) decomposition. The high temperature step, which occurred above 450°C, resulted from catalyst decomposition and corresponded to SO₂ evolution. Similar two-step weight loss curves were obtained when ZrO₂/SO₄ was employed for poly(ethylene) cracking.²

Multiple TG-MS analyses with different sample heating rates were performed to obtain volatilization activation energies by using the Friedman technique²⁴ (Table III). The highest volatilization activation energies were obtained for the neat

polymer samples, and the activation energy for the neat HPS polymer was slightly higher than that for the neat LPS polymer. The lowest volatilization activation energies were calculated for samples containing ZrO₂/SO₄ catalyst, which was the strongest acid catalyst of those employed in this study. For samples containing the same catalyst, those containing the LPS polymer exhibited a lower volatilization activation energy than those containing the HPS polymer. The neat poly(styrene) activation energies listed in Table III are in agreement with previously published values.^{5,25} Conversely, the polymer-Si/Al volatilization activation energies listed in Table III are very different from those reported by Audisio et al.¹⁷ However, Audisio et al. provided no error estimates for their values, which were obtained from single measurements by using the Freeman and Carroll²⁶ method. The activation energy error estimates reported here were standard deviations derived from four separate TG measurements for each sample.

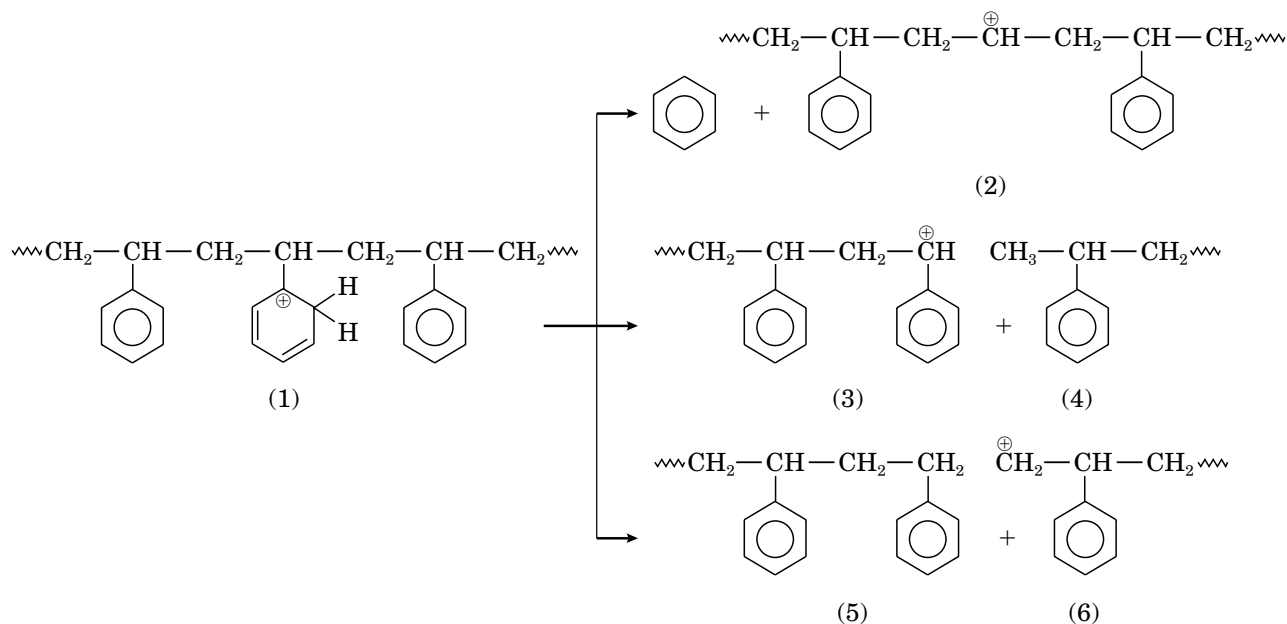
TG-GC/MS

Mass spectra obtained during TG-MS analyses could not be used to profile the temperature dependent evolutions of the primary thermal decomposition products because species specific ions could not be identified. By placing a gas chromatograph between the thermogravimetric analyzer and mass spectrometer, it was possible to separate the primary volatile species produced in the thermogravimetric analyzer prior to mass analysis. In fact, all of the cracking products listed in Tables I and II were detected by TG-GC/MS. However, TG-GC/MS sensitivity was poor compared to the pyrolysis-GC/MS sensitivity because the TG He purge significantly diluted product mixtures prior to injection into the gas chromatograph. As a result, minor thermal decomposition products detected by pyrolysis-GC/MS at 400°C were not detected by TG-GC/MS. In addition, because TG-GC/MS separations were performed isothermally and with a shorter column, the chromatographic resolution obtained by TG-GC/MS was inferior to that obtained by pyrolysis-GC/MS. Despite these limitations, chromatographic peak areas representing the yields of the most abundant thermal decomposition products were obtained after deconvoluting overlapping elutions in TG-GC/MS chromatograms by using curvefitting. Figures 3 and 4 contain plots of TG-GC/MS chromatographic peak areas (integrated total ion current) as a function of sam-

ple temperature for benzene and styrene as well as selected products representing alkyl aromatics (ethyl benzene), indanes (methyl indane), and indenenes (indene) evolved from polymer-catalyst samples. For all samples analyzed, benzene was by far the most abundant volatile product. All of the polymer-catalyst samples produced alkyl benzenes and indanes; however, samples containing the HZSM-5 catalyst generated significantly lower relative yields of these products than the other samples. Styrene and indenenes were only detected from samples containing HZSM-5 catalyst. Figures 3 and 4 show that significant quantities of benzene were detected at temperatures well below those at which the other volatile products were detected. In addition, thermal decomposition product yields obtained by TG-GC/MS were not the same as those derived from pyrolysis-GC/MS analyses at 400°C, suggesting that decomposition mechanisms that dominated when samples were rapidly heated to 400°C were less important when samples were heated at the much lower rates employed for TG analysis.

DISCUSSION

Because catalysts were not calcined prior to use and water was not rigorously excluded during sample preparation, all catalysts employed in this study can be assumed to have been in the Brönsted rather than Lewis form. Consequently, the formation of the primary poly(styrene) catalytic cracking volatile products can be explained by initial electrophilic attack on polymer aromatic rings by protons.^{17,18} Protons would preferentially attack the ortho and para ring positions because the aliphatic polymer backbone would be an electron releasing group for the aromatic rings. Most of the products detected by pyrolysis-GC/MS and TG-GC/MS can be derived from mechanisms beginning with ring protonation. Thermal decomposition of ortho protonated aromatic rings in the polymer chain (1) can lead directly to the liberation of benzene, the primary catalytic cracking product, or may result in chain shortening.



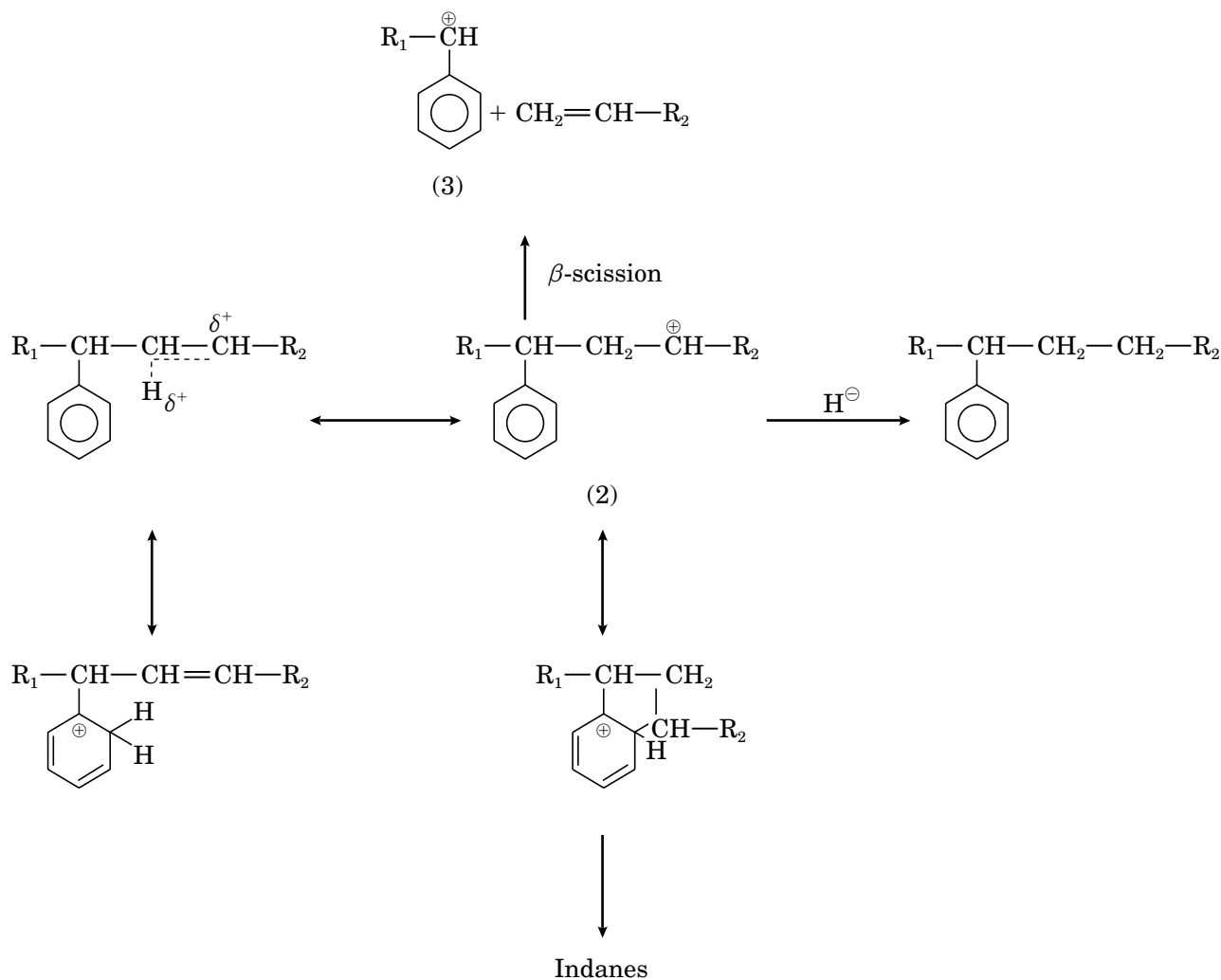
Benzene cannot be obtained directly from para protonated aromatic rings in the polymer. However, para protonated rings can react with neighboring polymer chains to yield the same chain scission products that can be formed by ortho protonation.

The macro cation remaining after benzene evolution (2) may undergo chain shortening β -scission to produce (3) and an unsaturated chain end, rearrange to form an internal double bond and protonate a neighboring aromatic ring (either by

intra- or intermolecular proton transfer), cyclize to form an indane structure, or abstract a hydride to produce a saturated chain segment. The substantial quantities of indanes obtained by poly(styrene) catalytic cracking suggests that cyclization of (2) to form indane structures is a favored process. This is supported by Nanbu et al., who reported that benzene and indane structures were the only products detected when poly(styrene) was cracked by using a strong acid catalyst at

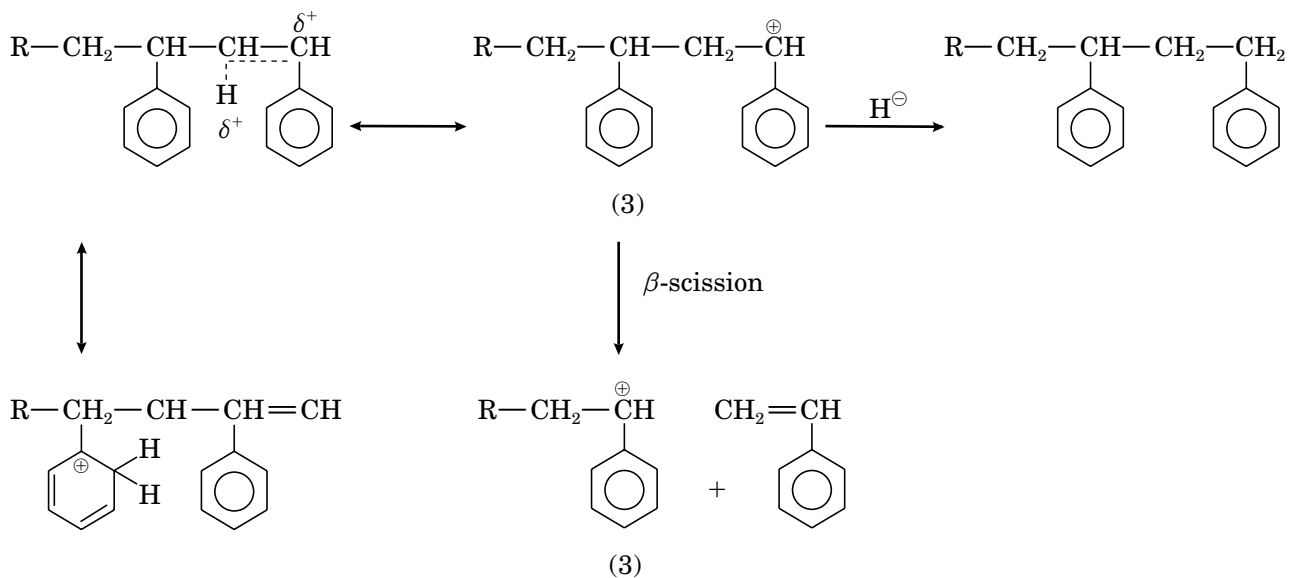
50°C.¹⁸ A consequence of chain unsaturation resulting from (2) might be the formation of conju-

gated polyene segments that may subsequently cyclize to form naphthalenes.



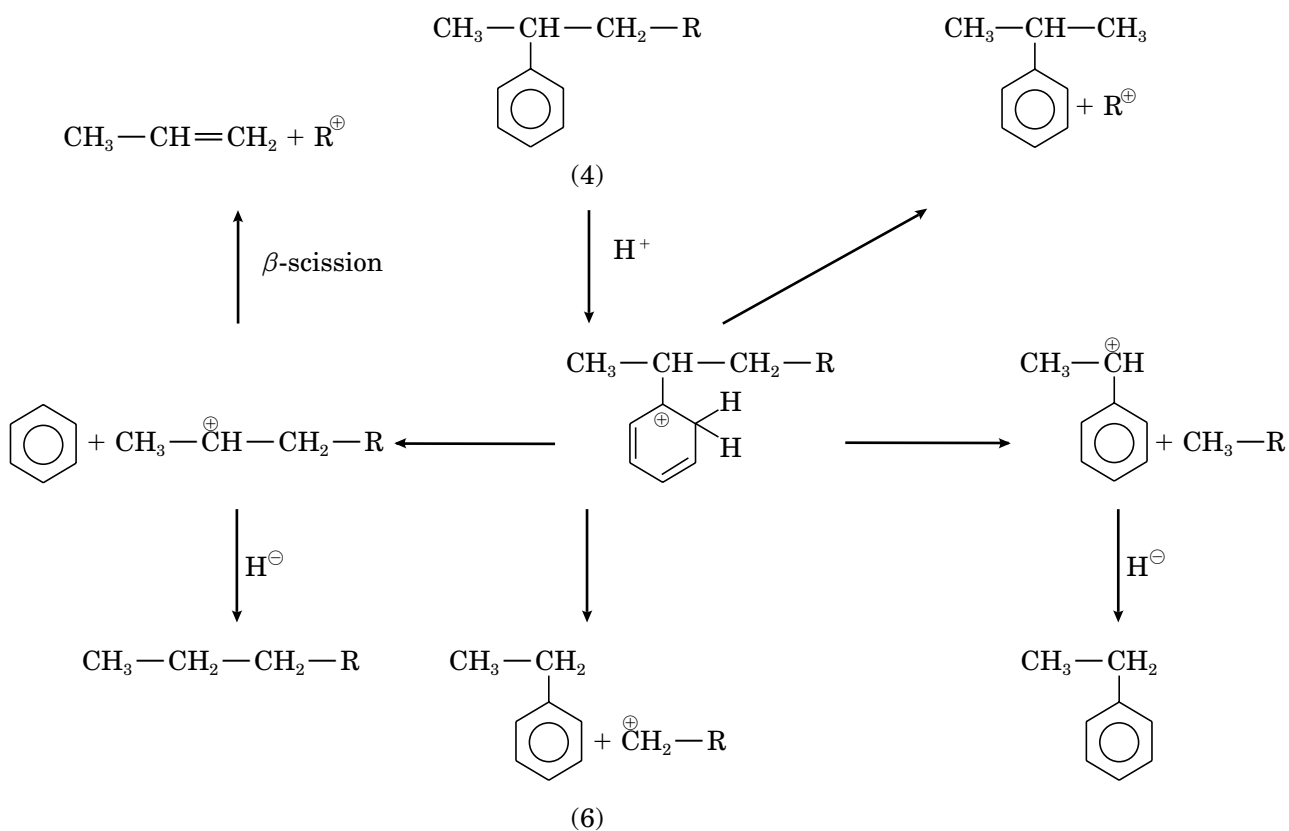
A minimum of three conjugated double bonds must be created in polymer chains before naphthalenes can be formed. As a result, naphthalene evolution during TG sample heating should be delayed relative to the evolution of alkyl benzenes and indanes, which can be formed from polymer segments without conjugated unsaturation. TG-GC/MS results revealed that the maximum rates of evolution of naphthalene and methyl naphthalenes from heated samples occurred at temperatures 15–20°C higher than those at which the maximum evolution rates of alkyl benzenes and indanes occurred, indicating that formation of naphthalenes was indeed delayed. This is illustrated by Figure 5, which shows the temperature dependent yields of methyl indane (open circles) and naphthalene (open squares) derived from TG-GC/MS analysis of the HPS-ZrO₂/SO₄ sample.

Decomposition of (3), which might be formed from (1) or (2), can result in the formation of styrene or may lead to chain end unsaturation and neighboring ring protonation. Hydride abstraction by (3) would result in a saturated chain end. The lack of significant styrene production from any of the polymer-catalyst samples suggests that β -scission of (3) to form styrene is not a dominant decomposition pathway at low temperatures. Chain end unsaturation derived from (3) may result in formation of indenes, which were detected in substantial amounts only when HZSM-5 catalyst was present. The restricted volume of the HZSM-5 channels apparently inhibited hydride abstraction pathways for (3), which resulted in increased production of indenes and styrene for the polymer-HZSM-5 samples compared to the other polymer-catalyst samples.



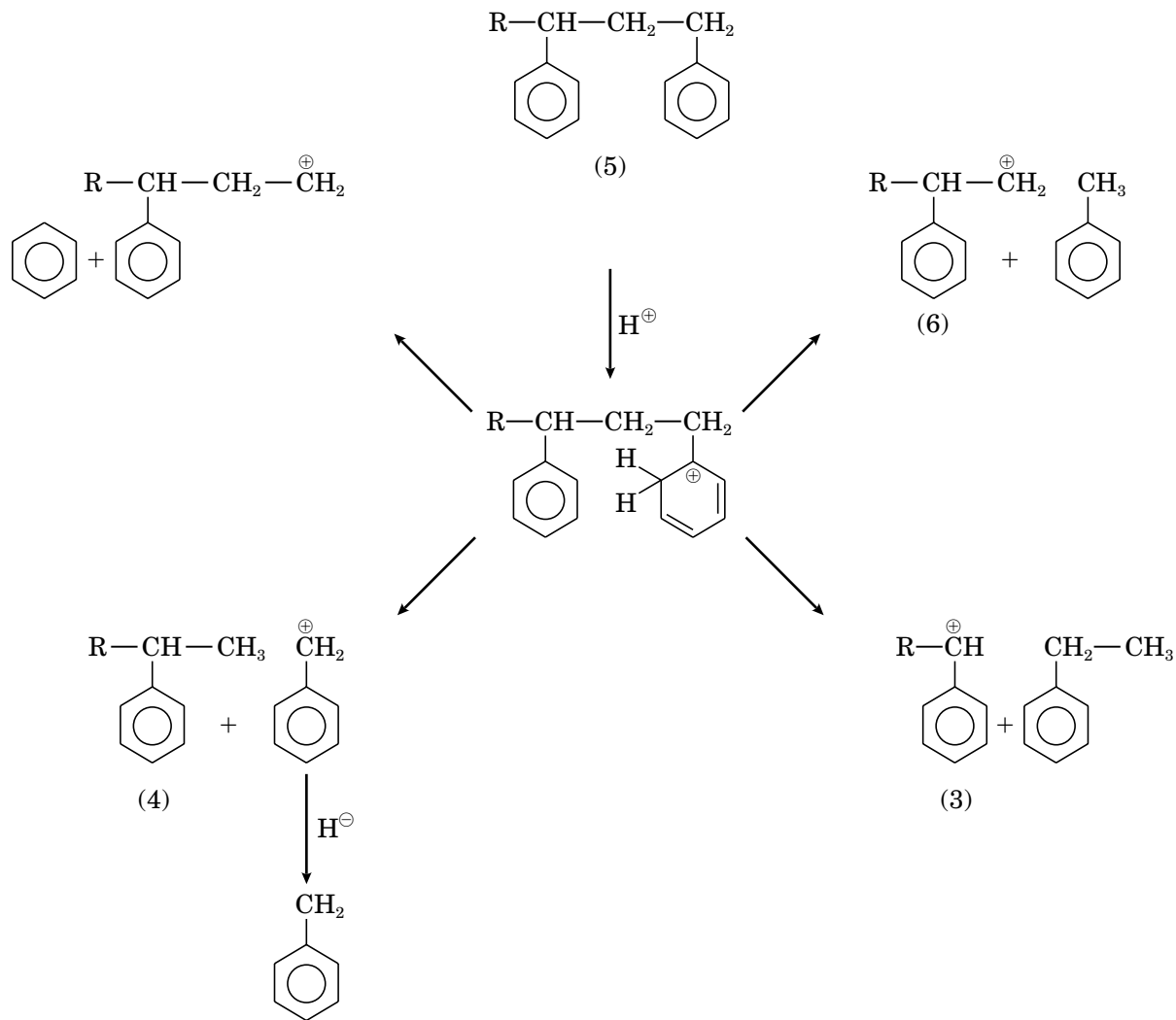
Protonation of aromatic rings adjacent to methyl terminated chain ends (4) can result in the forma-

tion of alkyl benzenes, propene, and benzene, depending on how the macro cation decomposes.

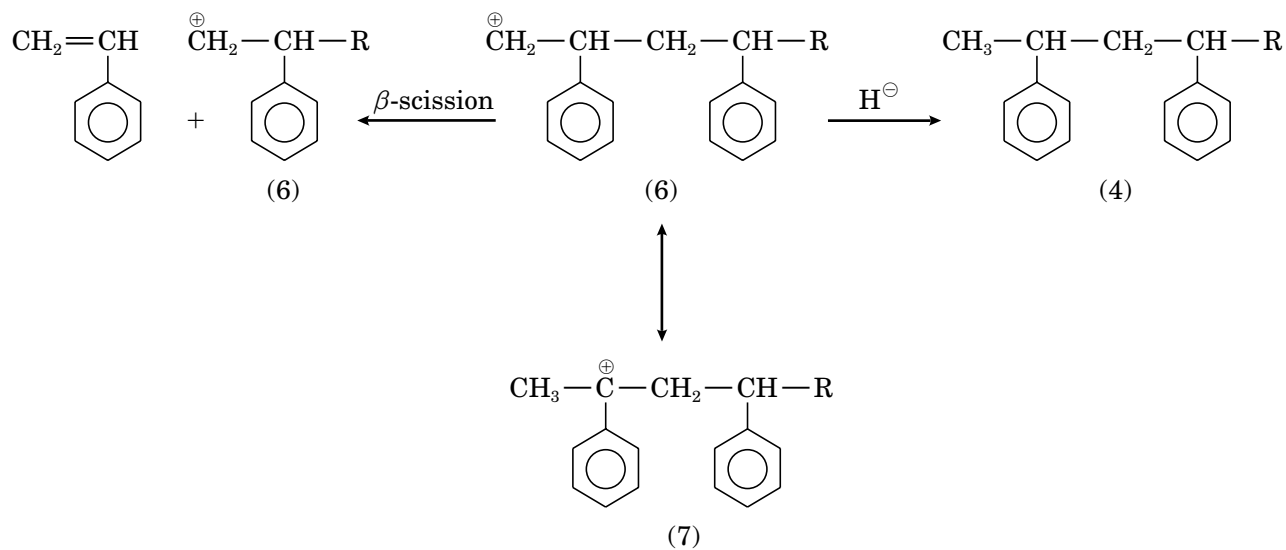


Although not included in Tables I and II, propene was detected as a minor decomposition product by pyrolysis-GC/MS at 400°C for several of the poly-

mer-catalyst samples. Protonation of aromatic rings at styrene terminated chain ends (5) can also result in the formation of benzene and alkyl benzenes.

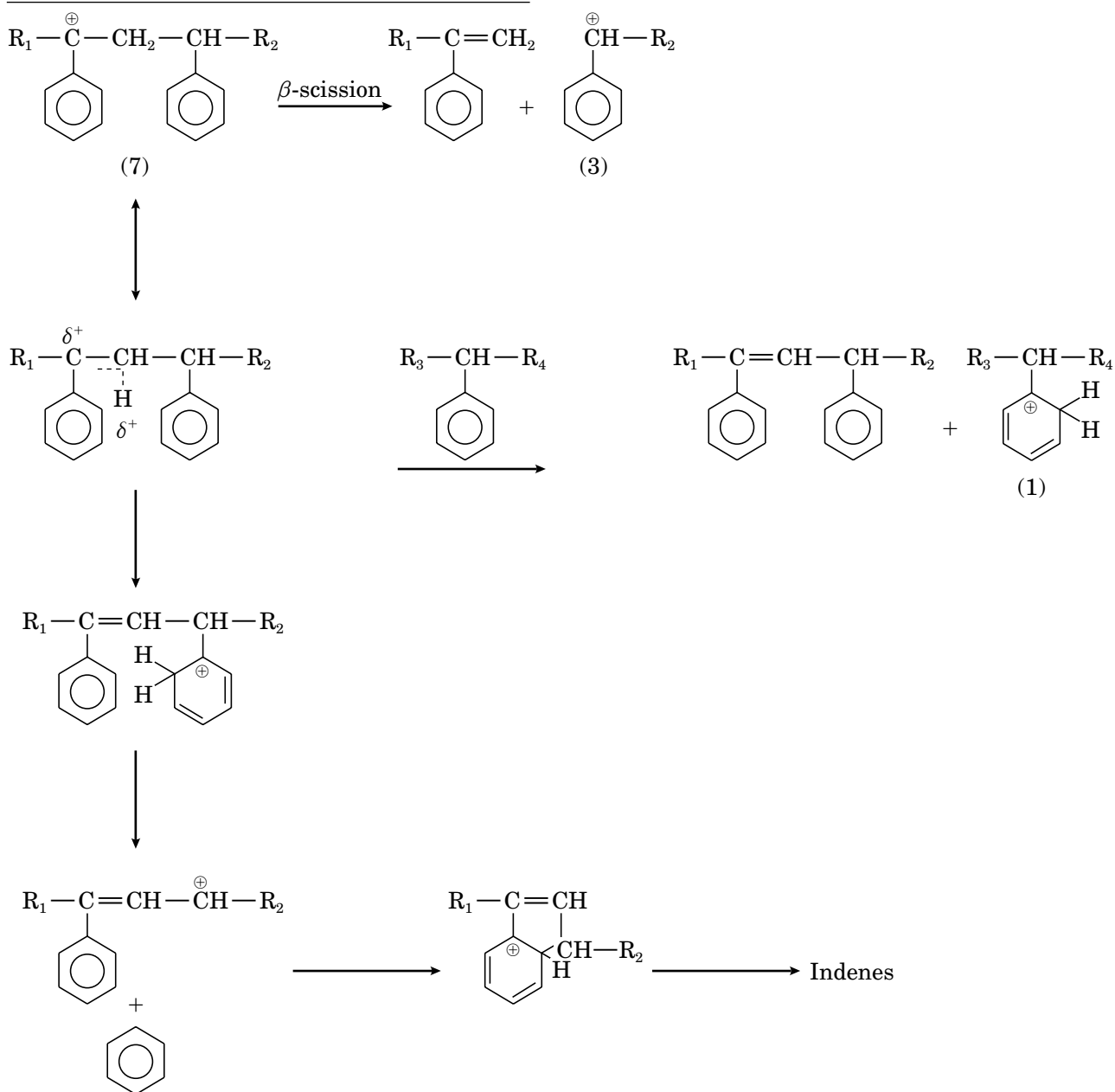


Macro cation (6), which can be formed from (1), (4), or (5), can undergo β -scission to form styrene, rearrange to form a tertiary benzylic cation (7), or may abstract a hydride to form (4).



The tertiary benzyl cation (7), which would be preferentially formed by hydride abstractions in addi-

tion to rearrangement of (6), may be a precursor for chain unsaturation and for the formation of indenenes.



If rearrangement of (7) results in chain unsaturation and intramolecular ring protonation, volatile indenenes may ultimately result. If intermolecular ring protonation occurs, macro cation (1) would likely be formed.

Figure 3(b) shows that benzene can be obtained by poly(styrene) catalytic cracking at temperatures as low as 130°C. The fact that the temperature at which volatile decomposition products were detected from polymer-catalyst samples was dependent on the catalyst acidity suggests

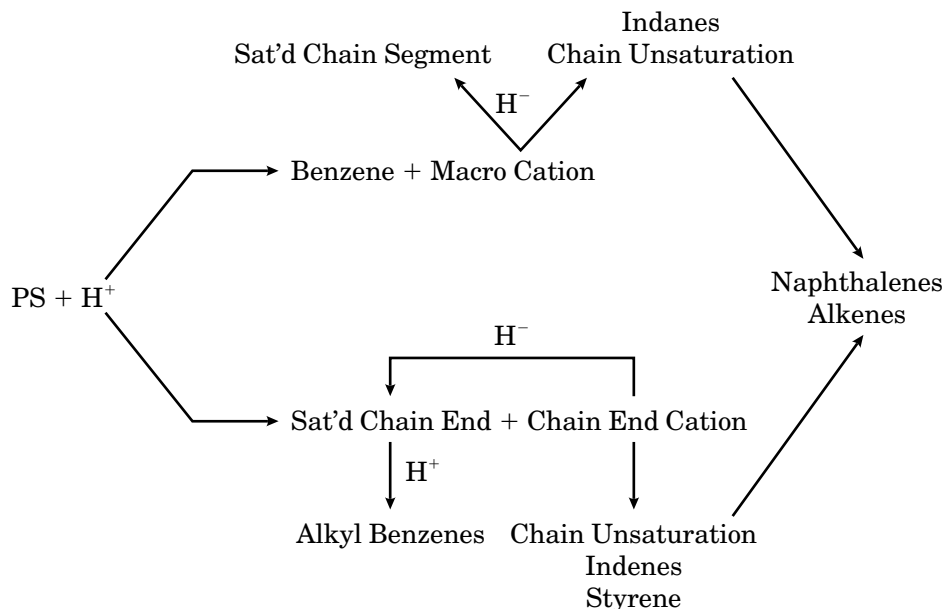
that the rate-limiting step in the acid-catalyzed decomposition of poly(styrene) was aromatic ring protonation. For all polymer-catalyst samples, benzene was the first volatile product detected when samples were heated in the thermogravimetric analyzer, which suggests that processes leading to benzene liberation were favored over those that resulted in the products detected at higher temperatures. This is consistent with the reaction schemes proposed here, which show that benzene can be easily formed from (1), but that formation

of other volatile decomposition products is more difficult and may require macro cation rearrangement, hydride abstraction, or successive protonations.

Volatilization activation energies listed in Table III and species specific evolution profiles shown in Figures 3 and 4 indicate that the catalytic effect of each acid catalyst was greatest when they were in contact with the LPS polymer. The large difference in molecular weights for these polymers (2700 vs. 850,000) suggests that the polymer chain length may be an important factor in catalytic cracking processes. It might be expected that successive cleavage of short polymer chains would more quickly lead to volatile products than cleavage of longer chains. However, low temperature benzene production, which does not require chain cleavage, was always found to occur at a higher rate for the LPS polymer than for the HPS polymer. This suggests that low temperature benzene production may result from chain ends, which would be more abundant for the LPS polymer than for the HPS polymer. Chain end aromatic rings should be somewhat more susceptible to electrophilic attack because electron release from the polymer backbone into these rings should be slightly greater than for the other aromatic rings in the polymer. Because the samples containing the LPS polymer had more chain ends than the HPS polymer, low temperature reaction rates for the LPS polymer would be consistently higher than for the HPS polymer, which would lead to the observed higher benzene evolution rates at low temperatures for samples containing the LPS polymer.

CONCLUSIONS

The predominance of benzene and indanes in the volatile catalytic cracking products derived from the poly(styrene)-catalyst samples employed in this study is consistent with the results of other researchers who also investigated the direct acid catalyzed cracking of poly(styrene).^{17,18} Although acid-catalyzed poly(styrene) cracking appears to involve many different parallel reactions and is quite complicated, the following general reaction scheme can be used to represent the primary reaction pathways. The initial step in poly(styrene) cracking is protonation of polymer aromatic rings, which may result in chain shortening, yielding a chain end cation and a saturated chain end. Ortho protonation can readily lead to benzene evolution and the formation of a secondary macro cation, which may subsequently cyclize to form an indane structure. The fact that Nanbu et al.¹⁸ detected only benzene and indane structures from acid-catalyzed poly(styrene) cracking at 50°C suggests that reactions that form these species are favored and that ortho ring protonation is the rate-limiting step for the evolution of benzene. Hydride abstraction appears to be an important reaction pathway for chain end cations, except when the catalyst restricts the movement of polymer chains (e.g., HZSM-5). Saturated chain ends are the likely source of alkyl benzenes, which can be formed after protonation of chain end aromatic rings. Rearrangements and β -scissions of macro cations can lead to chain unsaturation, or, for chain end cations, the formation of unsaturated volatile products such as styrene and indenenes. Conjugated polyene chain segments resulting from macro cation rearrangements can back bite to form naphthalenes.



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