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Mechanistic interpretation of base-catalyzed depolymerization of polystyrene

Oh Sang Woo, Nancy Ayala, Linda J. Broadbelt *

Department of Chemical Engineering, Center for Catalysis and Surface Science, Northwestern University, Evanston, IL 60208, USA

Abstract

The effect of a base catalyst, MgO, on the decomposition of polystyrene was studied through degradation of both a monodisperse polymer (number average molecular weight = 50,500 g/mol) and a polystyrene mimic, 1,3,5-triphenylhexane (TPH), to determine the potential of applying base catalysts as an effective means of polymer recycling. The presence of the catalyst increased the decomposition rate of the model compound but decreased the degradation rate of polystyrene as measured by evolution of low molecular weight products. Although the model compound results suggest that the rate of initiation was enhanced in both cases by the addition of the catalyst, this effect is overshadowed for the polymer by a decrease in the 'zip length' during depropagation due to termination reactions facilitated by the catalyst. Due to the small size of the model compound, this effect does not impact its observed conversion since premature termination still affords a quantifiable low molecular weight product. A decrease in the selectivity to styrene monomer in the presence of MgO was observed for both polystyrene and TPH. Reconciliation of our results with those of Zhang et al. [Z. Zhang, T. Hirose, S. Nishio, Y. Morioka, N. Azuma, A. Ueno, H. Ohkita and M. Okada, Industrial and Engineering Chemistry Research, 34 (1995) 4514.] based on differences in the reactor configuration used is discussed. ©2000 Elsevier Science B.V. All rights reserved.

1. Introduction

With the public concern that has developed for the environment in recent years, alternatives for the disposal of spent plastic products are being sought. Disposal through landfilling is becoming a less viable option, as the number of landfills closing each year exceeds the number being opened [2]. Since approximately 80% of the municipal solid waste stream (MSW) is landfilled, this will have a dramatic impact on waste disposal practices for used products [3]. Furthermore, landfilling is an inefficient use of resources since it does not attempt to recover any of the residual value of used products. Therefore, alternative methods of disposal or conversion of spent products into others that retain some or all of the original value must be sought.

A significant portion of the MSW, approximately 18% by volume, is comprised of plastic products [3]. The US alone produces 60 billion pounds of plastics annually, and their production is projected to increase [4]. For example, due to the legislative push to reduce fuel consumption, a greater portion of automobiles will be constructed from plastic components due to their high strength-to-weight ratios as compared to metals [5]. Because of the widespread and growing use of plastics, public pressure to extend the useful lifetime of plastic products through recycling has intensified. The simplest option, incinerating plastics for energy recovery, is viewed adversely by the

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* Corresponding author. Tel.: +1-847-491-5351; fax: +1-847-491-3728
E-mail address: broadbelt@nwu.edu (L.J. Broadbelt)

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public and is, therefore, an unattractive approach. A second method of recycling plastics, mechanical recycling, in which mixed plastics are ground, melted, and then shaped into new products, results in a loss of material strength from degradation during heating [6]. In addition, the possibility of contaminants limits the applicability of the 'plastic lumber' produced by mechanical recycling.

Another method for plastics recycling is feedstock or tertiary recycling. The polymers that make up plastics are broken down into their corresponding monomers or into petrochemicals and fuels. In contrast to the materials produced by mechanical recycling, products made from these low molecular weight chemicals are not limited in their applicability. This method of recycling plastics also does not have the negative connotation associated with incineration.

Tertiary recycling can be performed either thermally or chemically. Chemical recycling has been most widely applied to condensation polymers, such as polyamides or polyesters, since addition of a small molecule may easily cause depolymerization [7,8]. However, addition polymers, such as polyethylene, polypropylene, and polystyrene, require cleavage of carbon-carbon bonds in the backbone through the addition of heat or a chemical agent. Thermal degradation is the simplest form of tertiary recycling of addition polymers; the carbon-carbon bonds that make up the backbone of polymers are broken by the application of heat, typically in the range of 250–500°C. Most studies of chemical recycling of addition polymers have been performed with acid catalysts due to their widespread use by the petroleum industry and their known ability to cleave carbon–carbon bonds. In contrast, relatively few studies have been performed using base catalysts to effect the degradation process [9,10].

The application of base catalysis to degrade polystyrene is a particularly attractive alternative to acid catalysis. In the presence of acid catalysts, polystyrene affords low-valued indane derivatives, other polycyclic compounds, benzene, and only minor yields of styrene monomer [11–15]. In contrast, a single study in which base catalysts were used suggested that the yield of styrene monomer from polystyrene increased compared to thermal and acid-catalyzed degradation [1]. However, it has also been shown that the products can be a strong function of the reactor configuration and the polymer-catalyst contacting pattern [12–15]. To probe the effect of base catalysts on the decomposition of polystyrene further, a comprehensive understanding of the controlling reaction pathways was sought. A logical strategy was to begin with well-defined systems of both polystyrene and a model compound to determine the underlying kinetics and product selectivities. Because decomposition of high molecular weight polymer chains can complicate the interpretation of the degradation process, model compound studies are sometimes employed to understand the reaction chemistry of the parent polymer [16]. In our study, the polystyrene mimic, 1,3,5-triphenylhexane (TPH), was synthesized in our laboratory and investigated to probe the degradation of the polymer. Both pyrolysis and base catalysis experiments were performed for both reactants, allowing the effect of addition of the catalyst to be evaluated and comparison of the results with those reported in the literature. Consequently, the purpose of this study was to determine the fundamental changes in the chemistry of depolymerization of polystyrene in the presence of a base catalyst to assess its potential application to polymer resource recovery.

2. Experimental

2.1. Degradation experiments

For each batch pyrolysis experiment of the polystyrene model compound, ca. 20.0 mg of 1,3,5-triphenylhexane were weighed into a borosilicate glass, 3 ml gold band ampule (Wheaton). In order to ensure good contact between the catalyst and the reactant, a high catalyst to reactant ratio was used; ca. 30.0 mg of finely powdered magnesium oxide (Alfa) were added to the ampule. The catalyst was weighed into the reactor in ambient air shortly after pretreatment at 400°C for 2.5 h in vacuo. Studies in which the MgO was loaded in an argon-filled environment resulted in no noticeable changes from those in which the catalyst was loaded into the reactor in ambient air. The surface area of MgO was determined by nitrogen adsorption using the method of Brunauer, Emmett, and Teller (BET) and determined to be 420 m^2/g. The ampule was purged with argon for 2 min and flame sealed. The 1,3,5-triphenylhexane model compound was reacted by suspending the ampules for a series of reaction times ranging from 1 to 360 min in an isothermal, fluidized sandbath at 350°C. After removal from the high temperature sandbath, the ampules were cooled to room temperature in another fluidized sandbath at room temperature. Experiments were similarly carried out with monodisperse polystyrene synthesized via anionic polymerization and with a number average molecular weight (M_n) of 50,500 g/mol and a weight average molecular weight (M_w) of 57,600 g/mol. These two molecular weight averages are based on the number and weight of chains of different lengths, respectively. The same catalyst to reactant ratio used for TPH degradation was employed for the polymer degradation studies. Reactors were loaded with ca. 20.0 mg of polymer and ca. 30.0 mg of catalyst. Most reactions were at minimum triplicated to provide the error estimates reported below.

2.2. Product analysis

The reaction products of 1,3,5-triphenylhexane decomposition were dissolved in 6.0 ml methylene chloride (Fisher), and ca. 20.0 mg biphenyl (Aldrich) were added as an external standard. The product solution was injected into a gas chromatography (GC) vial using a syringe with a 0.45 mm polypropylene filter (Alltech) attached to remove the catalyst and to prepare the solution for analysis by gas chromatography. For quantification, standard solutions containing some of the major reaction products (toluene, ethylbenzene, styrene, and α-methylstyrene (Aldrich)) and 1,3,5-triphenylhexane and an external standard, biphenyl, were also prepared. The reaction products were identified with a HP 6890 series gas chromatograph with a HP-5MS 5% phenyl methyl siloxane capillary column (30.0 m × 250 μm × 0.25 μm nominal) and equipped with a mass selective detector (GC–MS). Decomposition products were quantified with an HP 6890 series gas chromatograph equipped with a flame ionization detector and the same type of capillary column. The temperature was initially held at 40°C for 5 min, ramped up to 140°C at 10°C/min, ramped to 175°C at 5°C/min, and then ramped at 10°C/min to 300°C where it was held for 5 min. The pressure was initially held at 3.5 psi (24.1 kPa) for 5 min, ramped up to 18.5 psi at 1.50 psi/min, ramped up to 24.0 psi at 0.75 psi/min, and then ramped at 1.50 psi/min to 35.0 psi where it was held constant until the end of the analysis.

For analysis of the degraded polymer, 2.0 ml of HPLC grade methylene chloride (Aldrich) was used to dissolve each sample, and the product solution was injected into a gel permeation chromatography (GPC) vial using a syringe and filter. The molecular weight of the degraded polymer was analyzed with a Waters Gel Permeation Chromatograph equipped with a differential refractometer. For quantification of smaller volatile products produced during polymer decomposition, the low molecular weight fraction (<500 amu) of GPC elutant was collected with a Waters fraction collector. Biphenyl was added to this liquid product fraction, and the solution was analyzed by gas chromatography.

3. Results

3.1. Polymer studies

Styrene monomer was the major product of polystyrene pyrolysis, accounting for ∼60 wt.% of the product distribution. Table 1 indicates the product distribution during polystyrene degradation after 60 min of reaction. The only other major products observed during pyrolysis were 2,4-diphenylbutene and 2,4,6-triphenylhexene, which accounted for 21 and 12 wt.% of the products, respectively. The conversion reported refers to the total weight of liquid products (<500 amu) divided by the initial mass of the polymer. The representative product distribution reported

Table 1
Polystyrene product distribution during pyrolysis[a]

Liquid products	Weight fraction
Toluene	0.016
Styrene	0.581
α-Methylstyrene	0.010
1,3-Diphenylpropane	0.016
2,4-Diphenylbutene	0.207
Other diphenyls	0.027
2,4,6-Triphenylhexene	0.122
Other triphenyls	0.005

[a] Reaction time = 60 min, Conversion = 0.433.

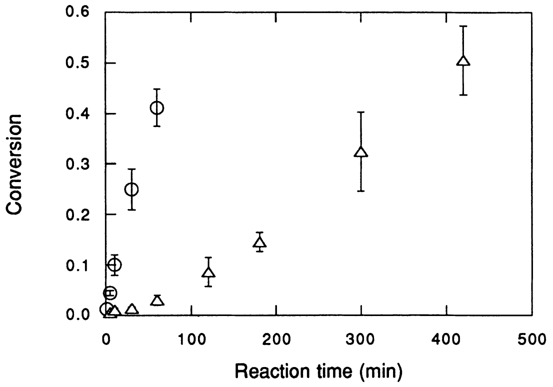
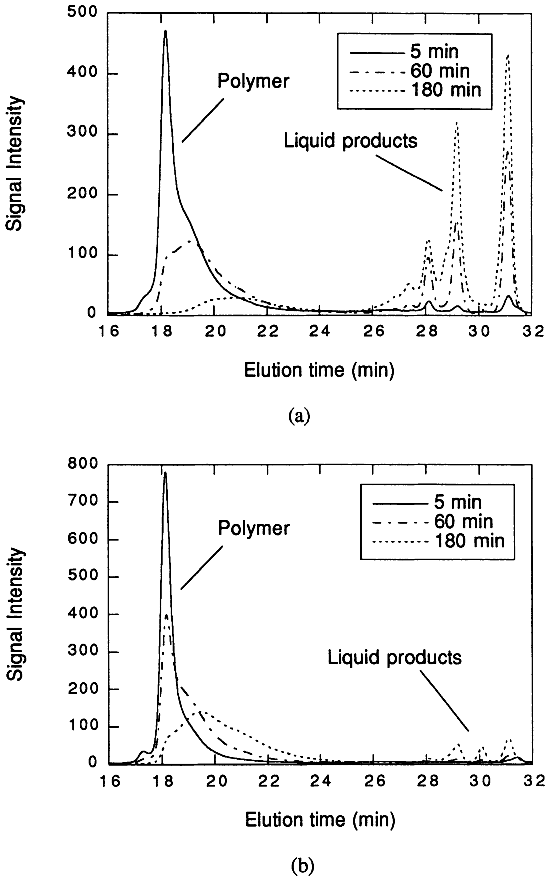


Fig. 1. Conversion achieved during polystyrene (○) pyrolysis and during (△) MgO-catalyzed degradation at 350°C.



(a)

(b)

Fig. 2. Gel permeation chromatograms after decomposition of polystyrene during (a) pyrolysis and during (b) MgO-catalyzed degradation.

in Table 1 is consistent with literature reports of polystyrene pyrolysis, in which styrene was observed to be the product of highest yield [11,14,15,17–21].

The addition of MgO resulted in significant changes to both the product distribution and the rate of decomposition of polystyrene as compared to those observed during pyrolysis. Decomposition in the presence of MgO resulted in a much slower rate of degradation as indicated in Figs. 1 and 2. As in Table 1, the conversions shown in Fig. 1 were determined based on the mass of liquid products divided by the mass of the original polymer. A conversion of approximately 40% was achieved after 1 h of reaction when the polymer was pyrolyzed. However, to achieve the same conversion when MgO was present, a reaction time of 6 h was required. The effect of the catalyst was not only to reduce the rate of evolution of low molecular weight liquid products but to retard the overall rate of degradation as measured by changes in the molecular weight of the polymeric product fraction. The molecular weight distributions as a function of reaction times are shown in Fig. 2 for both pyrolysis and catalysis. As degradation proceeds, the polymer peak both broadens and decreases in height, indicating the disappearance of the polymer as it depolymerizes into smaller polymers and liquid products. Liquid products are indicated by the peaks at higher elution times. By comparing Fig. 2a and b, it is clear that for the same reaction time, a larger fraction of the initial polymer still remains when the MgO catalyst is present.

The selectivities to various products also changed considerably when compared to those observed during pyrolysis (Fig. 3). As shown in Fig. 3 for products of polystyrene decomposition, the selectivities for styrene, 2,4-diphenylbutene, and 2,4,6- triphenylhexene decreased, while the selectivities to toluene, ethylbenzene, α-methylstyrene, 1,3-diphenylpropane, and 1,3-diphenylbutane increased. Most notably, the production of styrene decreased by a factor of 2 compared to that achieved during thermal degradation.

4. Model compound studies

In contrast to polystyrene, the presence of MgO resulted in a significant enhancement in the decomposition rate of the model compound (Fig. 4). Whereas

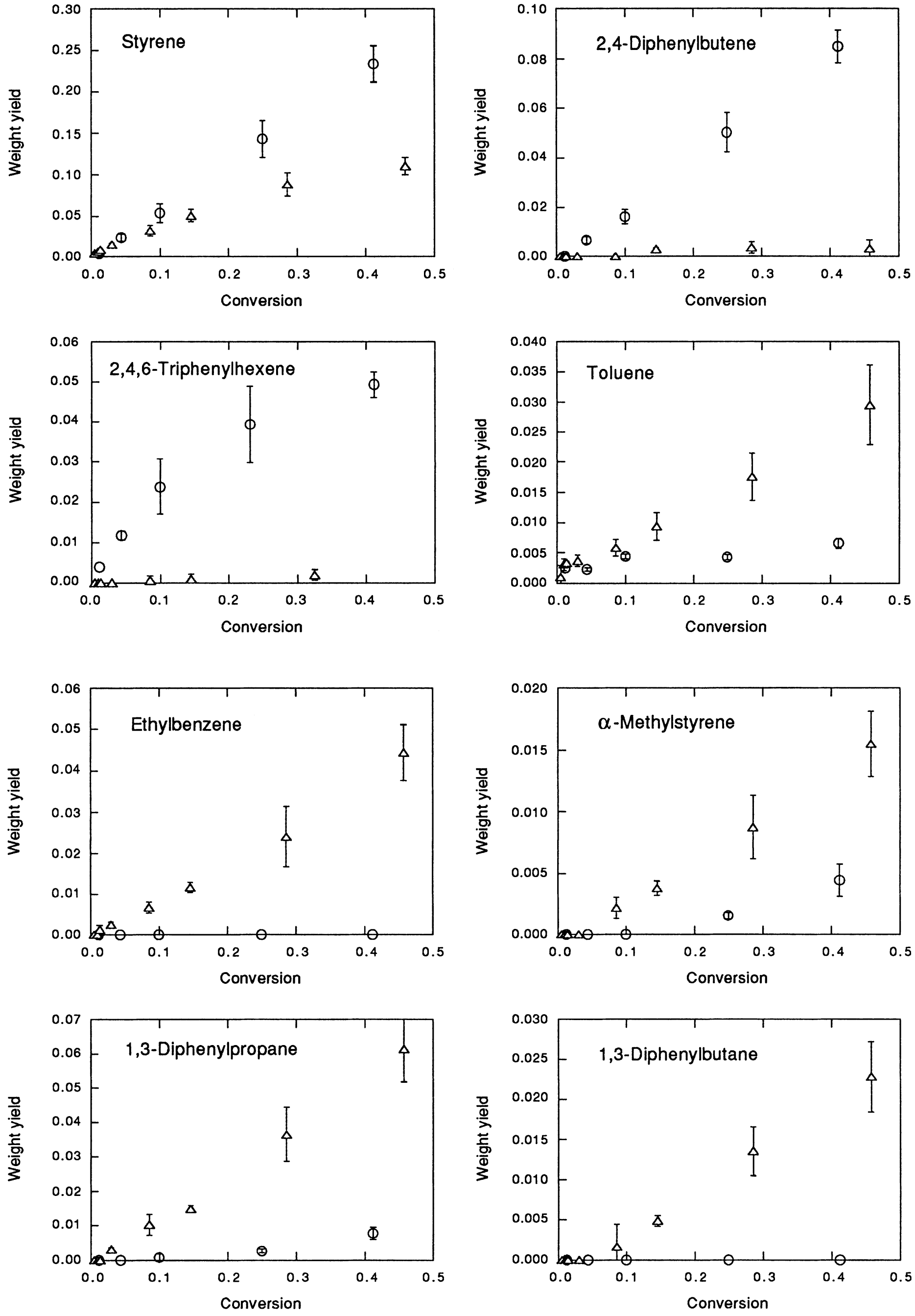


Fig. 3. Comparison of the yields during polystyrene (○) pyrolysis and during (△) MgO-catalyzed degradation for each of the products: styrene, 2,4-diphenylbutene, 2,4,6-triphenylhexene, toluene, ethylbenzene, α-methylstyrene, 1,3-diphenylpropane, and 1,3-diphenylbutane.

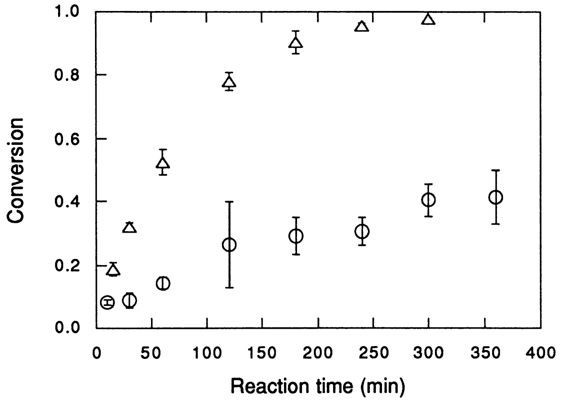


Fig. 4. 1,3,5-Triphenylhexane conversion as a function of reaction time during (○) pyrolysis and during (△) MgO-catalyzed degradation.

Table 2
Model compound product distribution during pyrolysis[a]

Liquid products	Weight fraction
Toluene	0.115
Ethylbenzene	0.124
Styrene	0.349
α-Methylstyrene	0.206
Other monophenyls	0.016
1,3-Diphenylpropane	0.086
1,3-Diphenylbutane	0.022
2,4-Diphenylbutene	0.026
Other diphenyls	0.044
Triphenyls	0.013

[a] Reaction time = 240 min, Conversion = 0.275.

a conversion of only 30% was observed during pyrolysis after a reaction time of 180 min, a conversion of 90% was achieved in the presence of the base catalyst.

The product distribution from pyrolysis of 1,3,5-triphenylhexane was qualitatively similar to that observed during the pyrolysis of polystyrene. Major products in order of decreasing yield consisted of styrene > α-methylstyrene > ethylbenzene ≈ toluene ≈ 1,3-diphenylpropane > 2,4-diphenylbutene ≈ 1,3-diphenylbutane. These seven aromatic compounds accounted for at least 87 wt.% of the product distribution. Identification and quantification of minor products resulted in mass balances greater than 94% for all reaction times studied. Table 2 indicates the product distribution observed during pyrolysis at a reaction time of 240 min at which a conversion of 27.5% was achieved. As indicated by the table, styrene was the product with the highest yield, but significant amounts of toluene, ethylbenzene, α-methylstyrene, and 1,3-diphenylpropane were also formed. All product yields increased with increasing reactant conversion, and the relative ordering of the yields of the products was insensitive to changes in conversion. Consistent with the decomposition of polystyrene, no significant amounts of gaseous products were observed during pyrolysis of the model compound.

The presence of the base catalyst resulted in similar changes to the product distribution as those observed during the polymer studies. For example, a decrease in the production of styrene was observed. In fact, styrene was no longer the dominant product of the model compound decomposition. Instead, the yields of the major products were in the following order: 1,3-diphenylpropane > α-methylstyrene > styrene ≈ 1,3-diphenylbutane ≈ ethylbenzene > toluene > 2,4-diphenylbutene. These differences are captured in the plots of Fig. 5 which report the weight yields of the individual products as a function of reactant conversion. In addition to the decrease in styrene production, the production of toluene and 2,4-diphenylbutene decreased as well. In contrast, the yields of 1,3-diphenylpropane and 1,3-diphenylbutane increased with the addition of MgO. No significant change was observed for the selectivities to ethylbenzene and α-methylstyrene.

5. Discussion

Although the presence of MgO qualitatively altered the product distribution of the polymer and TPH similarly, it is difficult to compare these changes quantitatively due to the large difference in size between the two reactants. Comparison of the measured pore size distribution of MgO and an estimated size of 1,3,5-triphenylhexane suggests that the model compound has access to basic sites on both the external and internal surface of the metal oxide. The large polymer chains, in contrast, will have access to only a small fraction of the catalyst surface area. It is clear, however, that if the polymer chains had negligible access to the basic sites of the catalyst, results similar to that of thermal degradation should be observed. Because we observed a large deviation of the results between

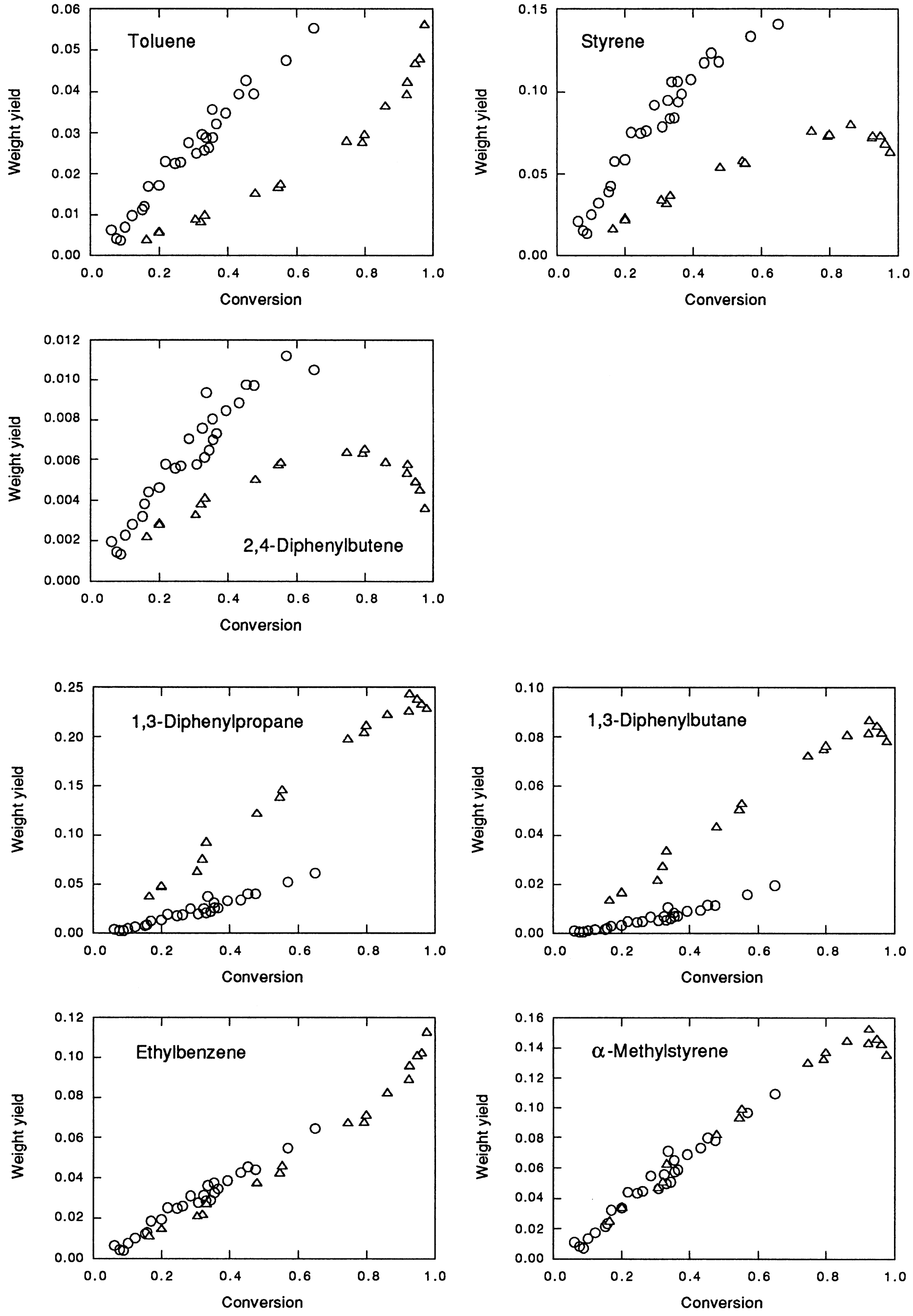


Fig. 5. Comparison of the yields during (○) pyrolysis of 1,3,5-triphenylhexane and during (△) MgO-catalyzed degradation for each of the major products: toluene, styrene, 2,4-diphenylbutene, 1,3-diphenylpropane, 1,3-diphenylbutane, ethylbenzene, and α-methylstyrene.

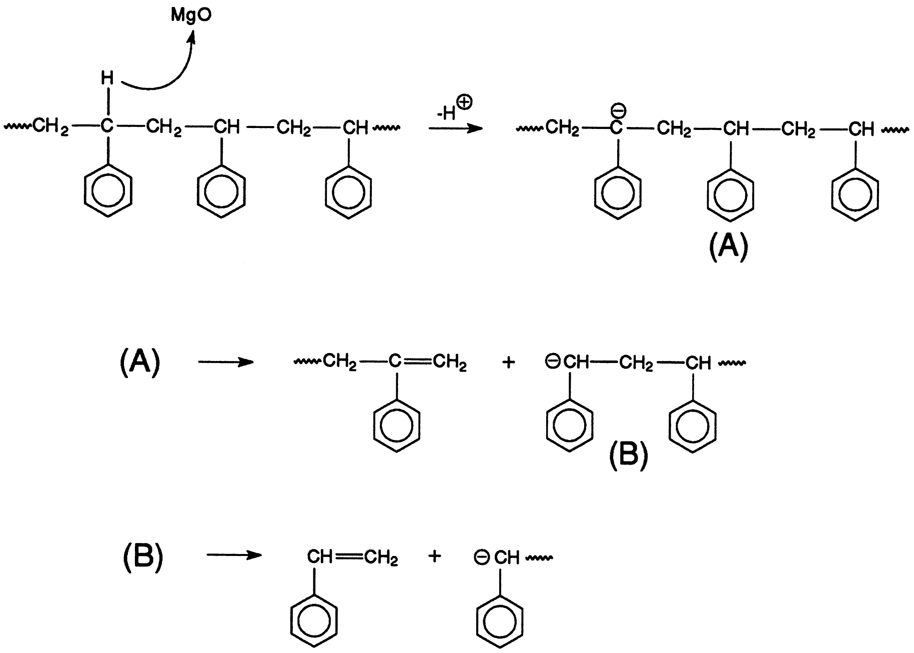


Fig. 6. Mechanism proposed by Zhang and coworkers [1] for the initiation and depolymerization of polystyrene in the presence of base catalysts.

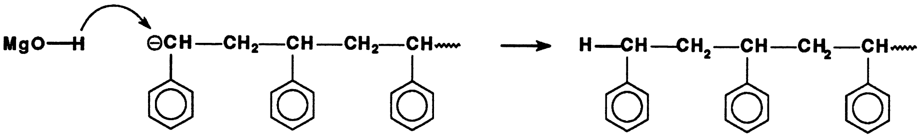


Fig. 7. Termination mechanism for depropagating polystyrene chains due to abstraction of proton from the catalyst.

base-catalyzed depolymerization and pyrolysis, this suggests that basic sites are accessible to both reactants. Furthermore, a relatively large ratio of catalyst to reactant (1.5 : 1) was used in our study to ensure good contact between both reactants and the active catalytic sites.

However, an apparent discrepancy between the changes in the rate of degradation between the model compound and polystyrene in the presence of MgO was observed. This may be explained by examining the effects that the catalyst would have on individual steps of the depolymerization mechanism. The mechanism of depolymerization during pyrolysis is believed to be similar to that of polymerization and includes initiation, depropagation, hydrogen abstraction, and termination steps [22–25]. The proposed mechanism for depropagation in the presence of base catalysts is similar except that degradation proceeds through the formation of anions (Fig. 6) [1]. Zhang and coworkers propose that an increase in the rate of depolymerization occurs in the presence of base catalysts due to an increase in the rate of initiation when a proton attached to a backbone tertiary carbon is removed by the base catalyst. Facile chain scission may occur when a carbon–carbon bond beta to the anionic center is cleaved. The newly formed end-chain anion may then undergo the same type of cleavage, resulting in depolymerization that affords progressively shorter end-chain anions and monomer. However, a depropagating anionic chain may potentially terminate by recovering a proton from the catalyst surface as indicated in Fig. 7. The number of depropagation steps through subsequent β-scission reactions before termination takes place is referred to as the ‘zip length’

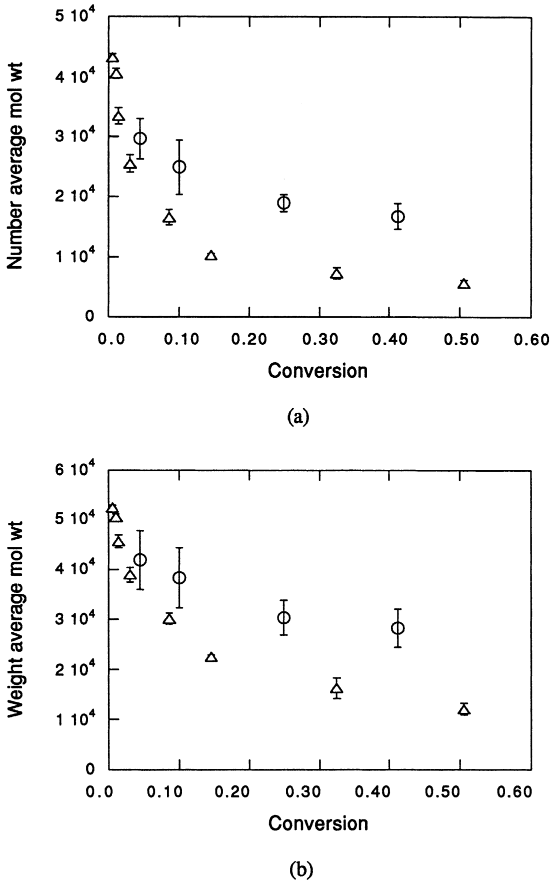


Fig. 8. Changes in the (a) number average and (b) weight average molecular weights of the polymer fraction at various levels of conversion during (○) pyrolysis and during (△) MgO-catalyzed degradation.

[26]. Our results suggest that the presence of the base catalyst results in a polystyrene zip length lower than that observed during pyrolysis. It is possible that a rate enhancement does occur due to the presence of the catalyst by an increase in the rate of initiation, but this enhancement is outweighed by the effect of premature chain termination as the depropagating chains recover protons from the catalyst surface. Fig. 1 shows the conversion (as defined by the production of low molecular weight, GC-quantifiable products) as a function of reaction time during degradation of polystyrene and indicates that the rate of production of liquid products is lower in the presence of MgO. Fig. 8 shows the number average and weight average molecular weights of the polymer fraction as a function of conversion. This figure indicates that for the same conversion, the molecular weight of the polymer fraction is lower in the presence of MgO than during pyrolysis. During pyrolysis there is only a slight shift in the polymer distribution as chains depolymerize into liquid products. In the presence of MgO, the shift in the polymer molecular weight distribution is more pronounced, indicating that the chains are not depropagating to the extent observed during pyrolysis. Polymer chains are undergoing fewer depropagation steps due to facile termination and are forming smaller chains instead of depolymerizing fully to low molecular weight liquid products. In order to degrade these chains of intermediate size, it becomes necessary to reinitiate depolymerization through proton abstraction. Thus, the polymer undergoes a greater number of cycles of initiation, depropagation, and termination before decomposing fully to liquid products, and accordingly, a lower rate of degradation is observed. If an increase in the rate of termination is occurring due to facile release of protons from basic sites, the problem may be overcome by using a stronger basic catalyst to allow depolymerization to compete more effectively with termination. Also, it may be possible that the reduction in the rate of depolymerization is related to the structure of the catalyst. Once a proton is abstracted from a polystyrene chain within a pore, the newly formed anion may be unable to diffuse out of the pore and depolymerize due to its limited mobility within the narrow pores. The continued close proximity of the anionic chain and the abstracted proton eventually leads to termination through re-abstraction. If limited mobility is the cause of the reduction in the rate of decomposition, the use of a catalyst with larger diameter pores may improve the degradation rate.

The rate enhancement observed during our study of the mimic in the presence of MgO is consistent with the results obtained by Zhang and coworkers [1]. In their study, the polymer was first thermally degraded by the free radical mechanism. Volatized styrene oligomers passed through a catalyst bed and underwent further decomposition through the formation of anions; the resulting products were removed from the reactor with a nitrogen stream. Because no in situ measurements were made, it is impossible to quantify the exact composition of the volatile stream contacting the base catalyst. However, at the temperatures they used, the volatile styrene oligomers contacting the catalyst are likely comparable in size to the model compound used in our study. Thus, the catalyst helps to decompose small styrene oligomers into even smaller molecules, such as the monomer and dimer, by reinitiating the degradation process through the formation of anions. Similarly, we observed an increase in the rate of decomposition of the polystyrene mimic into smaller monophenyls and diphenyls.

Although we observed a decrease in the styrene selectivity during base catalysis of both the model compound and the polymer, Zhang et al. reported an increase in the fraction of styrene making up the recovered oil. This indicates that the styrene oligomers contacting the base catalysts employed in their study are decomposing predominantly to monomer. Since they report their yields at a specific reaction time, and not at a constant conversion, it is difficult to determine the magnitude of the changes in their product distributions due to the presence of a catalyst versus changes due to variations in conversion. In contrast, we observed a decrease in the production of styrene from the polymer mimic at a given conversion in the presence of MgO, showing explicitly that the selectivity of TPH to styrene was decreased. Thus, the model compound employed in our study may not be representative of the styrene oligomers undergoing base-catalyzed degradation in the study of Zhang et al. The oligomers undergoing catalytic degradation in their study may be largely composed of styrene dimer and trimer, 2,4-diphenylbutene and 2,4,6-triphenylhexene, respectively. These oligomers are produced in significant quantities during polystyrene thermal degradation [11,15,25,26] and are volatile at the reaction temperature employed. However, because no in situ measurements were carried out in their study, the exact composition of the volatile stream can not be determined.

Another factor which may account for the inconsistency between the product distribution in the study of Zhang et al. and our results is the influence of the reactor configuration on the contributions of secondary reactions. For our studies with both polystyrene and the model compound, we observed a decrease in the production of the monomer compared to that observed during pyrolysis at the same conversion. Since the reactions performed in our study take place in sealed reactors, primary products such as styrene can undergo further decomposition. To probe this further, we carried out similar studies in which styrene was degraded thermally and in the presence of MgO and found that the decrease in the production of styrene may be partly due to enhanced decomposition of the monomer in the presence of the catalyst. However, in the study by Zhang et al., smaller volatile molecules such as styrene are carried out of the reactor by a nitrogen stream and so do not undergo secondary reactions.

6. Conclusions

The effect of a base catalyst, MgO, on the decomposition of polystyrene was studied through degradation of both the polymer and a model compound, 1,3,5-triphenylhexane, to determine the potential of the application of base catalysis as an effective means of feedstock recycling. The catalyst had the effect of increasing the rate of decomposition of the model compound but decreased the degradation rate of polystyrene. This discrepancy is attributed to an increase in the rate of initiation which is being overshadowed by a decrease in the zip length of polystyrene during depolymerization. The model compound already has a very short zip length due to its small size and so is not affected by termination reactions mediated by the base catalyst.

In contrast to the results obtained by Zhang et al. [1], we observed a decrease in the selectivity to styrene in both the polymer and model compound studies. Since the compounds that actually contact the base catalyst in their study are not polymeric but styrene oligomers of which the exact composition is not known, a direct comparison with the results of their study is difficult. However, the discrepancy in the product distributions between our study and the study of Zhang et al. may be partly due to differences in reactor configurations since primary products, such as styrene, produced in our batch experiments may undergo secondary reactions to by-products.

Acknowledgements

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1,3,5-triphenylhexane would not have been possible. The authors would also like to thank Sarah Vos for synthesizing the model compound for our experimental study. This work was supported by the MRSEC program of the National Science Foundation (DMR-9632472) at the Materials Research Center of Northwestern University. The support of the Engineering Research Equipment Grant Program of the National Science Foundation (CTS-9622375) and the office of solid Waste Research is also gratefully acknowledged.

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