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Catalytic routes towards polystyrene recycling

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Abstract: Polystyrene (PS) is one of the most popular plastics due to its versatility, which renders it useful for a large variety of applications, including laboratory equipment, insulation and food packaging. However, its recycling is still a challenge, as both mechanical and chemical (thermal) recycling strategies are often cost-prohibitive in comparison to current disposal methods. Therefore, catalytic depolymerization of PS represents the best alternative to overcome these economical drawbacks, since the presence of a catalyst can improve product selectivity for chemical recycling and upcycling of PS. This minireview focuses on the catalytic processes for the production of styrene and other valuable aromatics from PS waste, and it aims to lay the ground for PS recyclability and long-term sustainable PS production.

Introduction

Today, plastic is ubiquitous because it is an affordable, versatile and durable material. By 2020, roughly 367 million tonnes of plastic materials were being produced annually,^{1,2} and since the majority of them takes centuries to be degraded, plastic recycling is more than ever a powerful tool to fight pollution. Particularly concerning is the case of marine pollution, as up to 13 million tonnes of plastics end up in the oceans every year. Furthermore, by recycling plastics, the overall oil consumption, use of natural resources and greenhouse gas emissions can be substantially decreased. It has been estimated that by recycling all global plastic waste generated it would be possible to save the energy equivalent of up to 3.5 billion barrels of oil per year.^{1,2} Circular economy and reduction of plastic waste are becoming high priorities for society. In fact, in several of the world's leading economies, including the European Union, stricter legislations regarding plastic recycling are being proposed.^{1,2} However, at present, the plastic recycling policies have been deeply flawed and dangerously inefficient. By 2015 only 9% of plastic waste (of the 31 million tonnes of post-consumer plastic) was being recycled in the US,¹⁻⁴ with the vast majority ending up in incinerators or landfills. In contrast, two-thirds of paper, a third of metals, and a quarter of glass waste were recycled that year.¹⁻⁴ In Europe, less than 30% of the 25.8 million tonnes of plastic waste generated each year is collected for recycling in a process that typically also includes separation and sorting, baling, washing, grinding and compounding and pelletizing. Gravelly, a significant fraction of this amount is sent to be treated in other countries, where different environmental standards may apply.¹⁻⁴

Polystyrene (PS) is one of the more widely used polymers as its advantageous properties like being a colorless, non-flexible, hard plastic, make it an ideal candidate to be used for food containers, cutlery and

disposable razors.^{3,5-14} It is for this reason that PS is responsible for a substantial fraction of the total plastic waste generated (Fig. 1).³ Furthermore, while 10% of the polyethylene waste is recycled, only 1% of PS waste is recycled.³

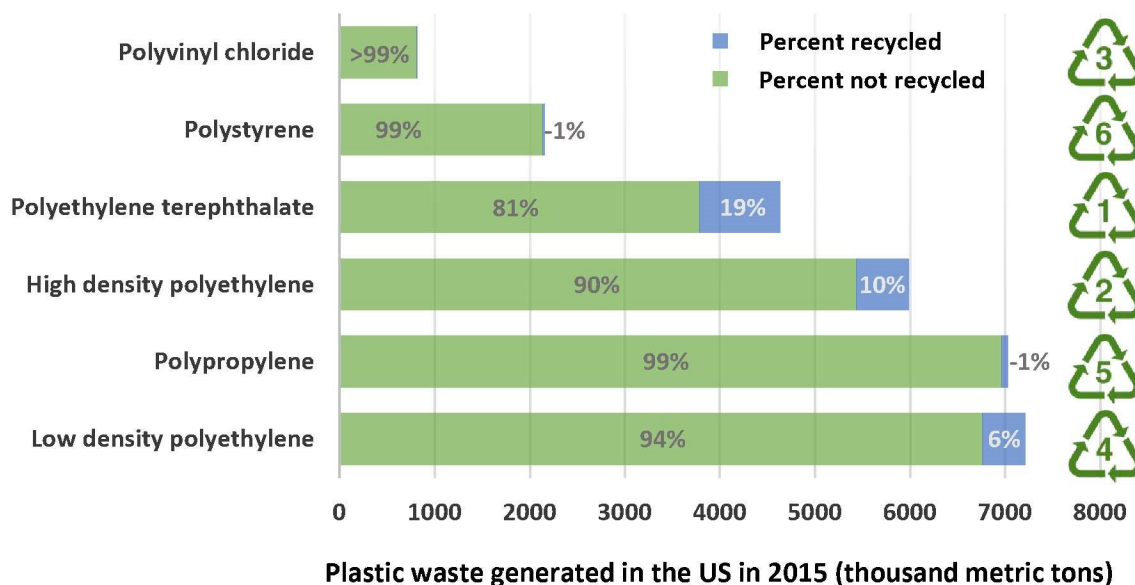


Fig. 1. Comparison of waste produced (and recycled) by type of polymer.³

While in principle PS can be readily recycled, it is very difficult to do it in a profitable manner. Nowadays, the most common method for recycling plastic waste is mechanical, where plastics are turned into other products without significant changes in their chemical structures. Mechanical recycling is, however, generally hindered by contamination and by the large variety of plastics found in the waste streams. Furthermore, the plastics that end up being recycled usually get turned into less valuable products and gradually degrade by being exposed to heat, light, mechanical shear, etc.¹⁵ These factors cause polymer chain scission leading to a reduction of the average polymer molecular weight.¹⁶ Such processes not only affect the final properties of the material, since the presence of oxygenated groups on the polymer chain (mostly produced by degradation during its lifetime) also impacts the reprocessing itself. The presence of some low molecular weight compounds formed (volatile, oxygenated fragments of the original polymer) has been found to cause corrosion in reprocessing equipment. For example, in the case of polypropylene, these volatile compounds include low molecular weight aldehydes, ketones, alcohols and mostly aliphatic carboxylic acids. Degassing of the recycling equipment is necessary to circumvent this issue.^{4,17,18}

A way around some of the shortcomings of mechanical recycling is chemical recycling, which consists of technologies like pyrolysis and gasification (routes leading to syngas), and catalytic cracking, catalytic depolymerization, etc., where the final products can be the starting raw materials. These processes will possibly eliminate downcycling and the problems associated to degradation. Additionally, the transportation of waste to third countries would be reduced, thereby making this choice a more environmentally friendly alternative.³ Among all these processes, pyrolysis has gained the greatest interest recently, with many studies dedicated to the potential thermal degradation of various types of plastics. In pyrolysis processes, long chain polymers are degraded into smaller molecules through heat and pressure and in the absence of oxygen. The most desired products obtained during pyrolysis are oil,

gas and char, which are valuable for diverse industries, like refineries.¹⁹ However, although pyrolysis presents its advantages over mechanical recycling, it has some drawbacks that need to be solved, such as being a highly energy consuming process (elevated temperatures, around 500 °C are needed). Besides this, it has been observed that this process happens by a complex mechanism (free radicals) and many side reactions occur. This makes it difficult to control the product yield as it depends on too many variables.¹⁹ On this basis, catalytic chemical paths offer a more controlled way than pyrolysis, allowing to tune product distribution under less energy consuming conditions. Even though catalysis treats only 0.1% of all plastic waste,²⁰ more systematic studies on these processes would uncover their full potential.

While a few reviews^{4,9,20} have dealt with the recycling of polystyrene waste, most of them focus on the traditional methods, mechanical and thermal recycling. Moreover, the potential applicability of catalysis as an attractive alternative to the plastic recycling problem has been mostly directed on polyethylene and polypropylene and the catalytic treatment of PS has been much less described.^{4,9,20} In light of this, the following minireview aims to show how this less explored alternative can be used as an effective process, both as a way to recycle PS in a closed-loop system (from PS waste back to the original monomer) and as an upcycling strategy (from PS waste to more valuable products), depending on the catalytic approach. In more detail, two types of catalytic processes will be discussed: 1) Acid catalyzed degradation of PS, where alkylaromatics are obtained in the highest yields; and 2) Base catalyzed degradation of PS, where styrene is usually the major product. The differences in their respective products are illustrated in Fig. 2. Finally, the achievements and challenges in the catalytic processes of PS degradation will be highlighted.

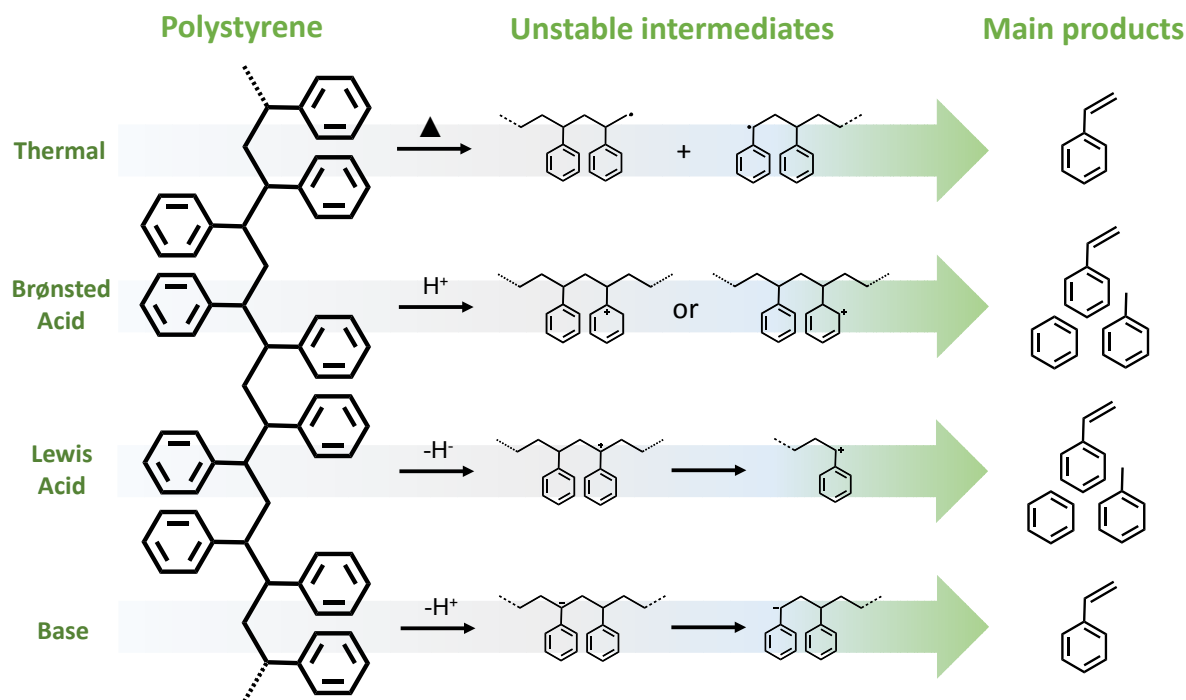
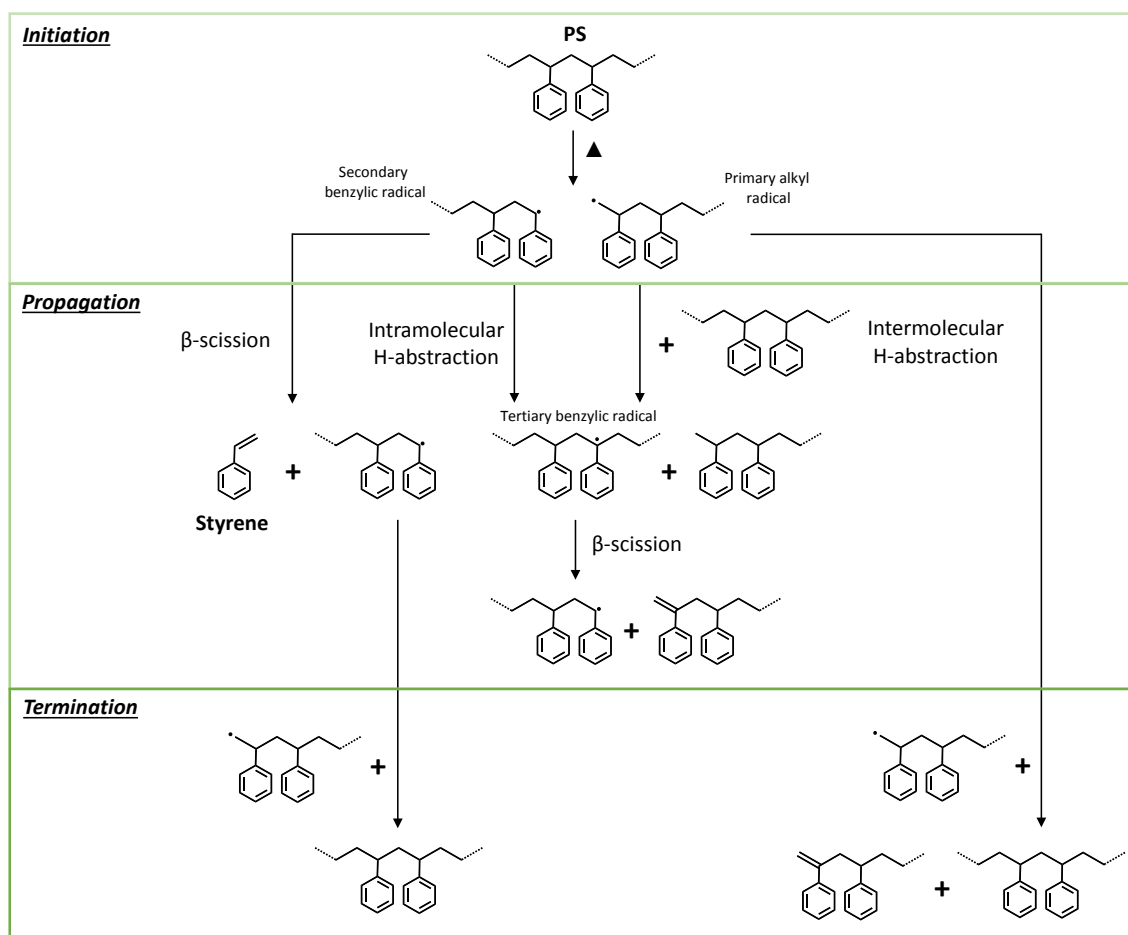


Fig. 2. Comparison of the different products obtained in each type of chemical degradation of PS.

Thermal degradation of polystyrene

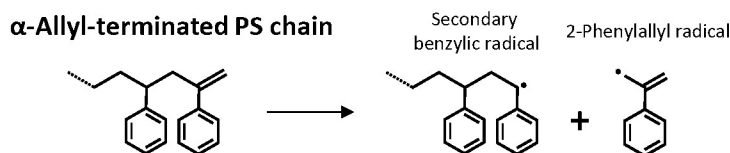
Although it falls out of the scope of this minireview, it is essential to understand the basics of the thermal degradation of polystyrene before giving mechanistic insights and detailed discussions on the acid and base catalyzed degradation of PS. Pyrolysis is still the most common chemical recycling method for PS; it can be carried out in the presence of hydrogen or water, but always in the absence of oxygen.²⁰ Like for most polymers, the thermal degradation of PS is a typical radical chain mechanism, where initiation, propagation and termination reactions are the relevant reaction steps (Scheme 1).²¹



Scheme 1. Radical chain mechanism for the thermal degradation of PS.

In the initiation step, a C-C bond of a polymer chain breaks to form radicals. If a random scission occurs, one primary radical and one secondary benzyl radical (with strong resonance stabilization) are formed. Alternatively, if the scission takes place near the end of an α -allyl-terminated PS chain, one secondary benzylic radical and one 2-phenylallyl radical are formed (Scheme 2). In the propagation step, H-abstraction and β -scission or unzipping reactions occur. There are two types of H-abstraction reactions: (i) intermolecular abstractions, where the radicals abstract the hydrogen from a different molecule, and (ii) intramolecular abstractions (also called back biting reactions), where the primary and secondary (benzyl) radicals form five-, six- or seven-membered ring intermediates, with the final result of a 1-4, 1-5 or 1-6 isomerization of the radical intermediate. In the liquid phase, the back biting 1-5 reaction is the most likely to occur. β -scission of the tertiary benzylic radical formed in the previous step forms a

secondary benzylic radical and a polymer species with an unsaturated end. Finally, in the unzipping reactions, a styrene unit is formed due to the secondary benzylic radical undergoing β -scission. In the termination step, two different second-order reactions occur, namely recombination and disproportionation reactions. One primary radical and one secondary benzyl radical can combine to form a saturated product, or two primary radicals combine rendering two products, one with an unsaturated and another with a saturated end.²¹



Scheme 2. Alternative initiation step of the thermal degradation of PS: Near chain-end scission.²¹

In general, pyrolysis of PS allows the direct recovery of monomers from waste, with a maximum monomer recovery yield between 55-85 wt.%, depending on the type of PS, degradation temperature and operating temperature. Furthermore, during the thermal degradation of PS, the yields of recovered monomer highly depend on the reactor design, which influences temperature profiles and residence time. For example, a fluidized bed reactor offers shorter reaction residence times than other reactor types.^{20,22-24}

Moreover, in order to increase the efficiency of the chemical degradation of PS, it is important to consider the thermodynamics of the polymerization process itself. All polymerizations have a critical temperature (T_c), in most cases referred to as ceiling temperature, at which the equilibrium lies neither to the polymer nor to the monomer (i.e. the change in Gibbs free energy (ΔG_p) is zero).²⁵ In the case of PS, the T_c has been reported to be 310 °C (277 °C in gaseous conditions, 397 °C when melted).²⁶ While in principle, to achieve complete chemical recycling to monomer (CRM) a temperature above the T_c is necessary (Fig. 3), the reaction equilibrium can be driven by specific setup configurations, addition of solvents or product (monomer) removal.²⁵ However, it is worth noting that thermodynamic favorability is not always sufficient to ensure an efficient CRM process, as kinetics should also be taken into account. Thus, catalysts can be used to overcome the associated reaction barrier for depolymerization. Furthermore, catalysis could also aid in the development of successful CRM procedures, since by depending solely on thermal processes, the system becomes too highly reliant on the type of stream. In contrast, catalytic degradation of PS would potentially allow to control the temperature and selectivity of the reaction.²⁵

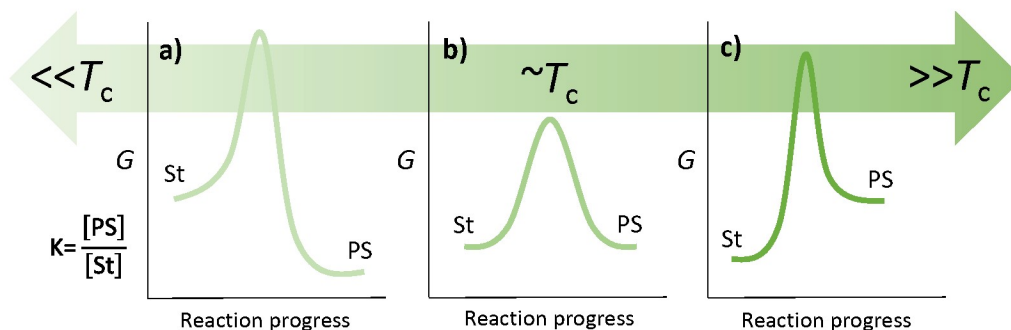


Fig. 3. Gibbs free energy (G) versus reaction progress for polymerization ($\text{St} \rightarrow \text{PS}$) at different reaction temperatures. a) At $T \ll T_c$, the polymerization is favored ($K \gg 1$). b) At $T \approx T_c$, neither reaction is favored ($K \approx 1$). c) At $T \gg T_c$, the depolymerization is favored ($K \ll 1$).^{25a}

Brønsted acid catalyzed degradation of polystyrene

The use of a catalyst in the degradation of PS permits to control the reaction path, which consequently allows to tune the selectivity to different valuable products. When the degradation of PS is initiated by Brønsted acids, the aromatic rings along the chain are protonated to form arenium intermediates, which are either secondary or tertiary carbocations (Scheme 3).²⁷ These undergo fragmentation to yield new cations and neutral fragments; both can be either monoaromatic compounds or shorter polymer fragments.²⁷ From chain fragments with cationic termini, olefins like styrene or α -methylstyrene can be formed, but these are very prone to consecutive acid-catalyzed reactions over Brønsted acid catalysts, therefore give only limited yields of aromatic olefins. Alternatively, benzene or aromatics with saturated side chains are formed, like toluene, ethylbenzene and cumene, which are much more stable products.²⁷⁻²⁹

Benzene, often the most abundant product in the Brønsted acid catalyzed degradation of polystyrene, is directly produced by the attack of an acid proton on a mid-chain phenyl group, forming a secondary arenium ion, followed by β -scission, as presented in Scheme 3. In this reaction, a secondary alkylcarbenium ion is also produced, which can subsequently undergo cyclization via electrophilic aromatic substitution to form an intermediate polymeric ion with an indane structure (Wheland arenium); the latter can further undergo a first β -scission to form a monoalkylated indane. After a second protonation, and a second β -scission, a free indane is formed.^{30,31} If the secondary alkylcarbenium ion undergoes 1,2-hydride shift, cyclization and β -scission instead, then naphthalene derivatives are formed.

As previously mentioned, the protonation of the PS chain can also lead to the formation of a tertiary arenium cation, which could undergo β -scission to give a primary alkylcarbenium ion and a cyclohexadiene terminated polymer, which easily isomerizes to an aromatic ring, forming a benzyl terminated neutral fragment (Scheme 3). The polymeric primary alkylcarbenium ion can then undergo β -scission to give styrene, and/or undergo an internal rearrangement by a hydride ion shift to form a more stable tertiary benzylic cation. This cation can undergo β -scission to give α -methylstyrene and a secondary benzylic cation.^{30,31} The polymeric secondary benzylic cation can undergo β -scission as an alternative route to form styrene. It is important to note that on the basis of the stability of the formed polymeric ions (Fig. 4), the primary alkylcarbenium ion most likely rapidly undergoes internal rearrangement to give the tertiary benzylic cation. Therefore, the formation of styrene probably mainly occurs through the β -scission of the secondary benzylic cation.

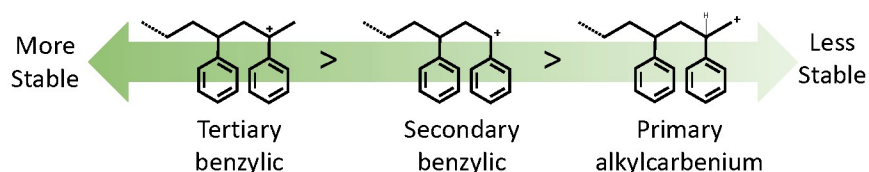
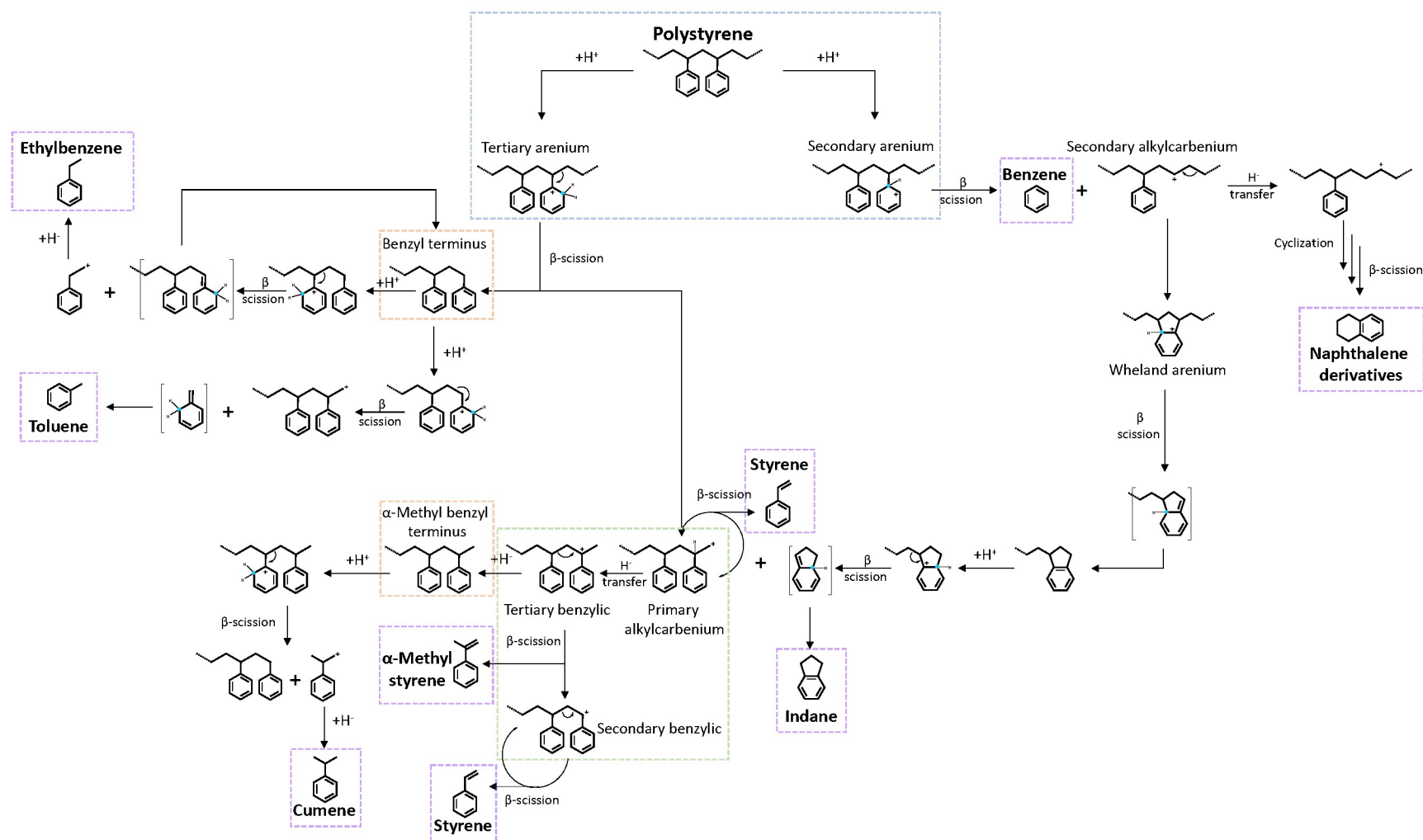


Fig. 4. Stability of carbocationically terminated polymeric ions.

The toluene formation, as seen in Scheme 3, implies the protonation of a terminal phenyl group in the PS chain or in a benzyl terminated neutral fragment, which then, by β -scission, renders the toluene molecule. The ethylbenzene formation implies the protonation of a phenyl group in the penultimate position in the PS chain (or in a benzyl terminus neutral fragment), with the ethylbenzene molecule formed by β -scission followed by intermolecular hydride transfer with another polymer or oligomer chain.³⁰



Scheme 3. Transformation of the PS chain in the presence of Brønsted acid catalysts. Framed in blue, the arenium intermediates resulting from the protonation of the aromatic rings of the PS chain (secondary and tertiary carbocations). Framed in orange, the neutral fragments formed during the degradation process (benzyl and α -methylbenzyl terminus). Framed in green, the carbocationically terminated polymeric ions. Framed in purple, the different products obtained by Brønsted acid catalyzed degradation of polystyrene.

Several examples of Brønsted acid catalyzed degradation of PS can be found in literature,³² mostly focusing on the performance of as-synthesized or modified zeolites and Al₂O₃ supports. Zeolites are the most commonly reported Brønsted acid catalysts in the degradation of PS because of their high activity in the conversion of other plastic wastes, such as polypropylene and polyethylene.³² The amount and strength of the acid sites of the zeolite usually determine the composition of the product mixture. Besides the intrinsic acidity of zeolites, other parameters such as the textural properties and/or the doping with different elements can be modified to enhance the desired properties.³² Furthermore, it should be pointed out that due to the high temperature at which this mechanism is usually studied, thermal decomposition of the PS chains cannot be excluded when analyzing the product mixture.³³

One of the first studies focusing on the mechanism of Brønsted catalyzed degradation of PS using zeolites was reported by Audisio et al.³⁰ Solids with different acid strength including: (i) non-acidic materials or mild acids: SiO₂, Al₂O₃; (ii) medium strength acids: SiO₂-Al₂O₃ and (iii) strong acids: Y-type zeolites were screened as catalysts for the degradation of PS at 350 and 550 °C. In contrast to thermal degradation, where the main products are styrene and its dimers and oligomers,³⁰ the addition of acid catalysts to the process resulted in the recovery of benzene as the most abundant product. Analyses of product mixtures obtained at different temperatures uncovered that even in the presence of the solid catalysts, the production of indane and benzene decreased with temperature, which indicates a relative decrease in importance of the formation of the secondary arenium ion. In contrast, production of styrene and other products derived from the tertiary arenium ion, increased with temperature.³⁰ This may indicate that at high temperatures and in the presence of a catalyst, the latter ion is preferably formed over the former. However, it cannot be ruled out that the thermal, radical mediated degradation dominates at the highest temperature (550 °C), since styrene is the main product recovered from thermal PS degradation processes. Additional studies showed that both at low (350 °C) and high (550 °C) temperatures, the production of benzene and indane is higher using SiO₂-Al₂O₃ and zeolite Y than with rare-earth exchanged zeolite Y.²⁸ However, the lack of any systematic analysis relating the physicochemical properties of the solid catalysts to the obtained catalytic results would not allow to draw any definite conclusions.

A first correlation between the acid features, the textural properties and the activity of solid catalysts was made by Serrano et al.³⁴ The authors studied HMCM-41, HZSM-5 and amorphous SiO₂-Al₂O₃ in the degradation of PS at 375 °C. While these three materials possess a similar Al content (Si/Al ~30-40), they have very distinct acid and textural properties, with HZSM-5 having the strongest acid sites but more micropores, while SiO₂-Al₂O₃ has the most accessible, albeit weakest acid sites. The properties of HMCM-41 fall in between them. A comparison of the catalyzed reactions with the thermal cracking of PS (36% conversion) showed that only HMCM-41 has similar activity (35% conversion), while with the other catalysts conversion halves. This is probably the result of secondary cross-linking reactions promoted by the acid catalysts, forming a solid residue, a cross-linked polymer, that remains in the reactor after 30 min of reaction time. Thermal degradation leads to a higher styrene production. On the contrary, benzene was the main product resulting from the catalytic cracking over HMCM-41 and SiO₂-Al₂O₃.³⁴ This could suggest that due to the non-microporous nature of these catalysts, the acidity has access to the middle of the PS chain. Furthermore, the drastic changes in selectivity observed are once again an indication of different reaction mechanisms in thermal cracking (of radical nature) and in acid catalyzed degradation (of carbenium nature). The lower conversion over the zeolite was attributed to two main factors: a) its microporous nature, which prevents the contact between PS molecules and the acid sites inside the micropores, forcing the reaction to take place only over the external surface acid sites; and b) its strong

Brønsted acidity, which promotes cross-linking reactions of styrene over PS cracking. Therefore, when a more open structure is used, namely HMC-41, the acid sites are accessible to the PS chains and a superior activity is observed.³⁴ Similarly, Lee et al.³⁵ studied the degradation of PS at 400 °C over HZSM-5, SiO₂-Al₂O₃, and a natural clinoptilolite zeolite (HNZ). Styrene was the main product for both thermal and zeolite-catalyzed PS degradation. No differences between both zeolites were observed, neither in the activity nor in the zeolite deactivation. However, SiO₂-Al₂O₃ showed the highest yield of ethylbenzene and the lowest of styrene. This was attributed to possible consecutive acid-catalyzed reactions of styrene (which produces more stable products, such as benzene and ethylbenzene) in the mesopores of the SiO₂-Al₂O₃. This process would be limited in the micropores of HNZ and HZSM-5.³⁵

A more comprehensive screening of zeolites was done by Ojha and Vinu,³¹ who studied eight different zeolites belonging to ZSM-5, zeolite-β, and zeolite-Y families, varying in Si/Al ratio, specific surface area, pore size distribution, surface acidity, and framework structure, as catalysts for the selective production of benzene from PS waste. Fig. 5 illustrates benzene yields for the catalytic (and non-catalytic) fast pyrolysis of PS at 400 °C (polymer to catalyst ratio of 1:2.5). The formation of side products was very dependent on the textural properties of the zeolites. The yield of naphthalene derivatives, for example, increased with the BET surface area and the micropore volume of the zeolites, while the yield of indane derivatives followed a completely opposite trend. High specific surface area ensures that more active sites participate in the cyclization reactions, which enhances the naphthalene derivatives production.

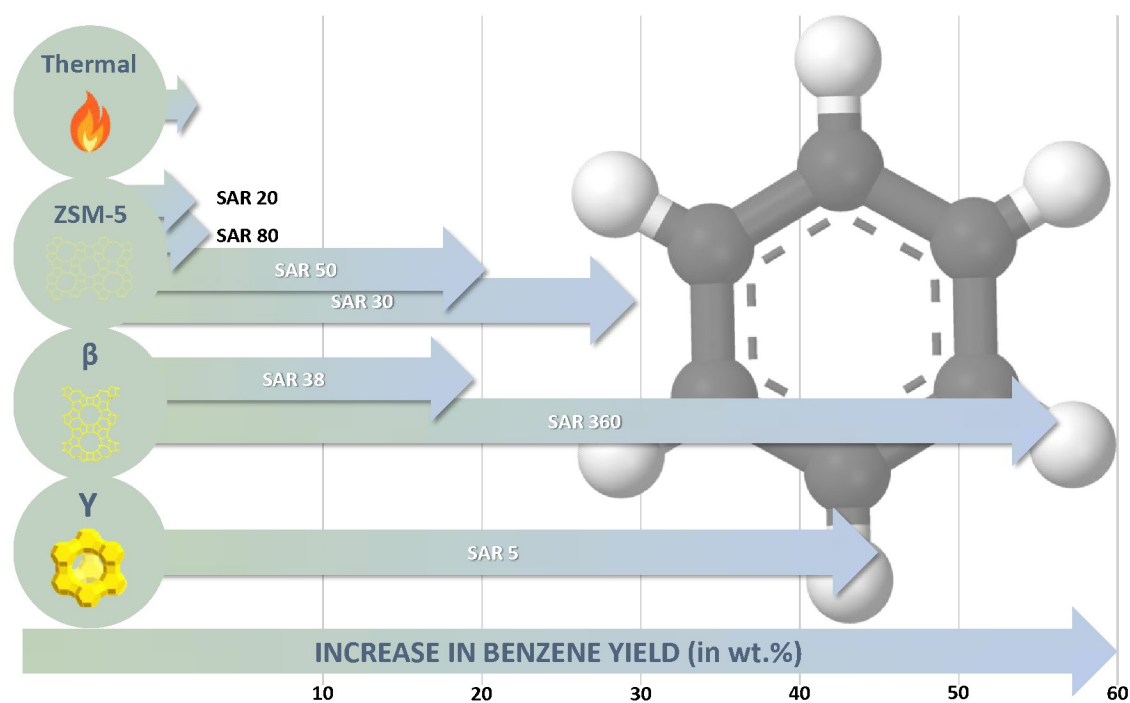


Fig. 5. Benzene yields obtained with each catalytic process studied in the work of Ojha and Vinu.³¹

In an attempt to correlate the acid features of the zeolites with their activity in the selective production of valuable products during PS degradation, the yields of styrene, α-methylstyrene, benzene, and dimers were plotted against an acidity factor, as shown in Fig. 6. This acidity factor was obtained from the area of the 3640 cm⁻¹ band in the IR spectrum, assigned to framework bridged hydroxyl groups and therefore

related to the number of strong Brønsted acid sites.³⁶ The yields of styrene, α -methylstyrene, and dimers decreased with the acidity factor of the catalysts, likely due to the occurrence of secondary reactions (of the styrene) on the acid sites; in contrast, benzene production was increased. This result may suggest that a higher acidity factor leads to preferential formation of the secondary arenium ion, which results in benzene formation (Scheme 2). However, the yield of ethylbenzene, produced via the formation of the tertiary arenium ion, is also higher for highly acidic catalysts, which contradicts the previous hypothesis, even if we consider the higher stability of ethylbenzene, which makes it less prone to degradation. In consequence, no direct correlation can be drawn between the number of (strong) acid sites and the promotion of one protonation pathway over the other (resonance-stabilized tertiary and secondary arenium ions).

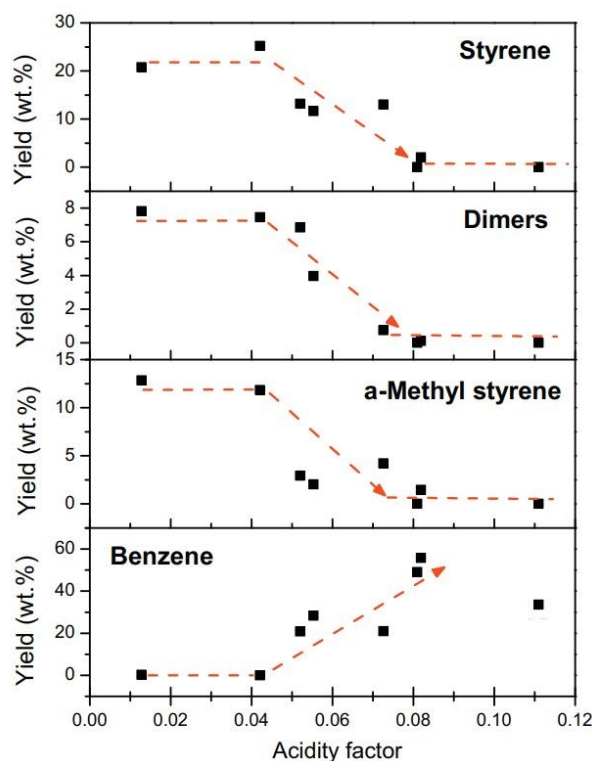


Fig. 6. Variation of the yield of styrene, dimers, α -methylstyrene and benzene with the acidity factor. The acidity factor was obtained from the area of the 3640 cm^{-1} band in the IR spectrum (framework bridged hydroxyl groups) and is linked to the number of strong Brønsted acid sites.²⁹ This analysis covers a series of different zeolites/topologies, namely ZMS-5, β and Y zeolites. Reproduced with permission from ref 31. Copyright 2015 Elsevier.

Other reports in this field focused on post-synthetic modification of solid catalysts, mostly zeolites and Al_2O_3 , in order to tune their acidity and try to increase the selectivity to valuable products, like styrene. In this sense, Chumbhale et al.³⁷ studied the performance of mordenites, modified by dealumination or by P-incorporation in the degradation of expandable polystyrene waste (EPSW) at 360 and 400 °C. Even though the best results were obtained at 400 °C (on the basis of PS conversion and styrene selectivity), at this temperature, the catalytic degradation behaved almost like a thermal degradation, since nearly the same conversion was obtained, regardless of the catalysts used, or even in their absence. The number of acid sites was then reduced by dealumination, with the Si/Al ratio ranging from 13, for the parent

mordenite, to 147, for the most dealuminated sample. A Si/Al ratio of 86 proved to be optimal, exhibiting the highest PS conversion and selectivity to styrene, even outperforming thermal degradation (60% styrene yield vs. 53%). This was ascribed to the moderate acidity of the sample: zeolites with a large number of acid sites favor secondary styrene reactions, decreasing its production, while zeolites with too few acid sites do not convert PS efficiently. Alternatively, the acidity of the zeolite was moderated by P incorporation. The incorporated phosphorous species bind to the zeolite framework, blocking the acid sites.³⁸ P incorporation led to similar results as obtained with dealuminated mordenite: higher styrene yield and selectivity than with thermal degradation (59% styrene yield vs. 53%) and with the parent mordenite as catalyst (54% styrene yield). This was attributed to the decrease in the number of available acid sites due to P doping, which in turn, lowered the occurrence of further styrene reactions.³⁵ When the P loading surpassed 1 wt.%, the styrene yield decreased again. This was due to a diminution of pore volume caused by the high P loading, which hampers the occurrence of necessary cracking reaction inside the zeolite pores.

Zeolites frequently are too acidic for efficient depolymerization of PS into valuable products, necessitating post-synthetic modifications focused on decreasing the number and strength of their acid sites. On the other hand, Al_2O_3 is often too inert to serve as an effective PS degradation catalyst; as a consequence, the post-synthetic modifications center on increasing its intrinsic acid features. In this regard, the acidity of $\gamma\text{-Al}_2\text{O}_3$ was increased by impregnation with sulfuric acid and its effect in the transformation of 1,3-diphenyl-1-butene, a styrene dimer, was studied.³⁹ Test reactions with α -methylstyrene, styrene, *tert*-butylbenzene, cumene and the styrene dimer at 25 °C were used to evaluate the acid strength of the system. While 25 °C is not directly relevant for the PS degradation, this temperature is low enough to analyze the effects of the acid sites on the transformations of the reactants in an isolated manner, i.e., without contribution of a thermal degradation. Upon protonation, styrene and α -methylstyrene are converted to secondary and tertiary benzylic carbenium ions, respectively, which alkylate neutral styrene and α -methylstyrene to form dimers. The reaction of *tert*-butylbenzene is initiated by proton addition on the aromatic ring, resulting in a secondary arenium ion that further reacts and gives products like benzene and di-*tert*-butylbenzene. A similar transformation is observed for cumene, with a secondary propylation as an intermediate in the reaction. Based on the acid strength necessary to catalyze each reaction, an estimation of the Hammett acidity function (H_0) of the catalysts was proposed.⁴⁰ When correlating these results with the decomposition of 1,3-diphenyl-1-butene at 25 °C (Fig. 7), it was found that if the catalyst is not acidic enough ($\gamma\text{-Al}_2\text{O}_3$, $H_0 > -2.2$) the styrene dimer does not decompose and only the isomerization of the double bond present in the dimer takes place. When the sulfate loading was increased and the acidity reached H_0 values between -3.2 and -2.2, the styrene dimers were protonated in the aliphatic unsaturated chains and in the aromatic ring, producing mostly ethylbenzene, cumene and styrene, but still at conversion rates below 10%. A further rise in acidity allows the intramolecular alkylation to occur, with formation of indane and indene derivatives in a higher proportion. The higher acidity also led to a higher conversion to decomposition products overall (>10%) but with the loss of selectivity towards benzene and alkylbenzenes. Similar to previous reports, the production of these valuable compounds in higher proportions is linked to medium strength Brønsted acidity.³⁹

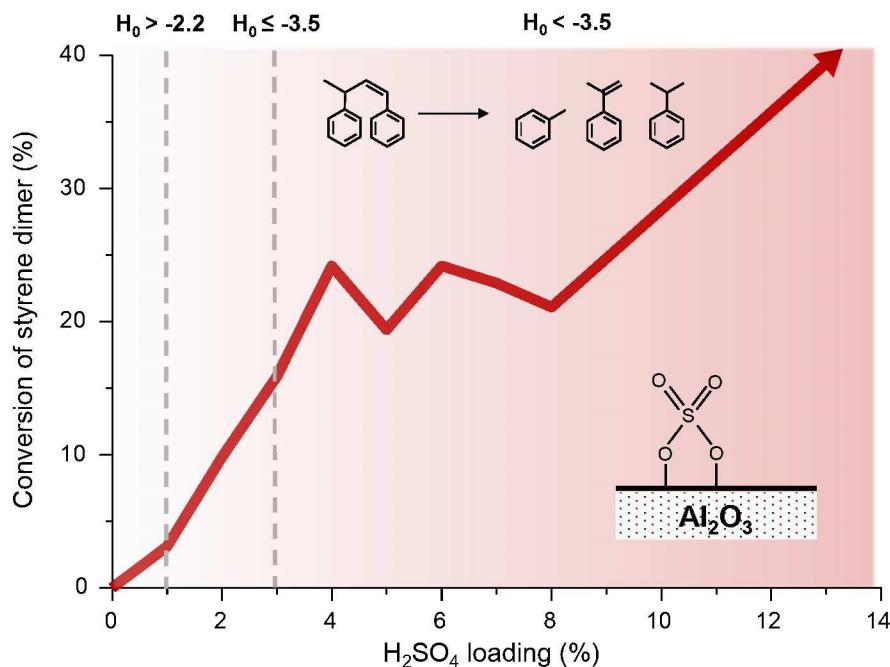
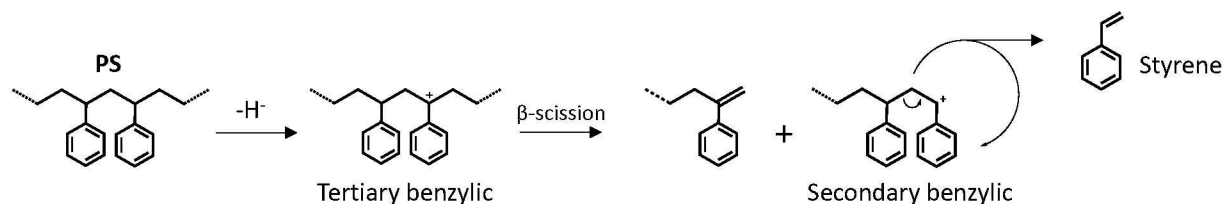


Fig. 7. Catalytic activity of the $\gamma\text{-Al}_2\text{O}_3/\text{SO}_4^{2-}$ system in the transformation of 1,3-diphenyl-1-butene at 25 °C.³⁹

Lewis acid catalyzed degradation of polystyrene

The Lewis acid catalyzed degradation of PS is less documented. It is believed that the mechanism proceeds by the loss of a hydride anion from the benzylic position in the PS chain, which forms a tertiary benzylic carbocation, starting the formation of lower molecular weight products (following Scheme 4).⁴¹ In this regard, early studies focused on the effect of AlCl_3 on a PS melt. The addition of AlCl_3 drastically decreases the molecular weight of the polymer due to a rapid degradation caused by extensive chain cleavage. Initially, it was believed that this degradation followed only a Lewis acid catalyzed mechanism; however, it was later proposed that AlCl_3 does not only behave as a Lewis acid, abstracting a hydride ion, but acts also as a Brønsted acid, donating a proton.⁴² This is due to the fact that AlCl_3 undergoes hydrolysis in the presence of trace moisture. The formation of benzene as the main product supported the assumption that under the reaction conditions (50 °C, presence of water), the effect of AlCl_3 is similar to that of a Brønsted acid.⁴²



Scheme 4. Transformation of the PS chain in the presence of Lewis acid catalysts.⁴¹

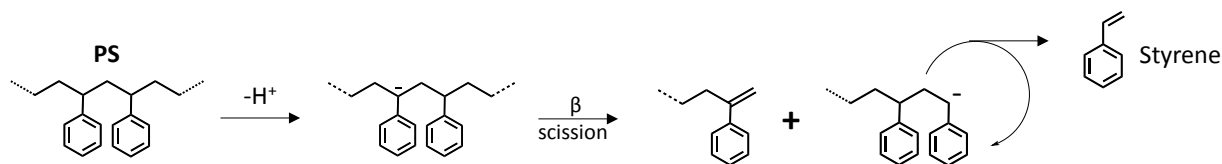
In the early 2000s, Karmore and Madras²⁹ published the first comprehensive study on the degradation of PS in chlorobenzene in the presence of Lewis acids at temperatures between 75 and 125 °C. The degradation rate was enhanced by several orders of magnitude in the presence of the studied acids, with

AlCl_3 promoting the maximum degradation rate for polystyrene among them. Further analysis of the products led to the hypothesis that the Lewis acid-catalyzed degradation of PS starts with a hydride loss to form a benzylic tertiary carbocation, which can occur at different rates, depending on the Lewis acid.²⁹ In relation to the paper previously discussed, traces of water in this system could also be inducing proton formation, providing Brønsted acid sites where the reaction can take place. However, without an analysis of the products formed it is difficult to identify the mechanism underlying the degradation of PS.

In recent years, the study of Lewis acid catalyzed degradation of PS has focused on supported metal oxide catalysts. In this sense, Shah et al.⁴³ prepared a series of Al_2O_3 supported metal oxides catalysts and found that the yield of styrene monomer (and liquid products in general) could be increased with metal impregnation as compared to thermal degradation and pure Al_2O_3 . $\text{ZnO}/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$ were the best performing catalysts, with those containing 20 wt.% of Zn being able to produce styrene with a 63% yield (at 450 °C for 120 min), compared to 30% yield obtained by thermal degradation (500 °C for 150 min). Later on, the same group investigated the catalytic activity of CuO supported on Al_2O_3 , montmorillonite clay and activated charcoal.⁴⁴ The catalysts were found to increase the selectivity to low molecular weight aromatic hydrocarbons as compared to the supports. Among the catalysts, 20 wt.% CuO over Al_2O_3 was found to have the highest activity and selectivity to styrene (~61%).⁴⁴ While these results outperformed the thermal degradation of PS, 450 °C were still necessary to obtain a significant formation of styrene. Additionally, a large number of other aromatic products, such as toluene, ethylbenzene and α -methylstyrene are also produced due to extensive side reactions,^{43,44} which is ultimately, one of the main downsides of the acid catalyzed PS degradation when the aim is a completely circular process. It is also important to note, that while ZnO and CuO are soft Lewis acids with medium to weak acidity strength, they are also oxides with a strong basicity.⁴⁵ Therefore, they could initiate the reaction in different ways, with the degradation of PS proceeding following a different mechanism. The performance of ZnO and CuO as basic catalysts, and also of other oxides with medium weak basicity,⁴⁵ such as Cr_2O_3 and Fe_2O_3 , will also be reviewed in the next section.

Base catalyzed degradation of polystyrene

One of the major drawbacks in the acid catalyzed procedures previously described is the reaction's high selectivity to benzene, toluene, ethylbenzene, α -methylstyrene and cumene as side products in the recovery of styrene. In this sense, other catalytic procedures are needed to increase the formation of the styrene monomer over the other aromatic compounds. Among the possible options, basic catalysts seem to be the most favorable choice because their mode of action involves PS deprotonation (H^+ abstraction from a backbone tertiary carbon), followed by β -scission of a C-C bond in the aliphatic chain, which forms in this way a different type of carbanion, resulting in styrene monomers, dimers and oligomers (Scheme 5).²⁷ The H^+ abstraction from a backbone tertiary carbon is favored over the abstraction from a secondary carbon, because even though the latter is more acidic, in the formed tertiary anion, the charge is delocalized over the phenyl ring, which increases its stability.



Scheme 5. Transformation of the PS chain in the presence of basic catalysts.²⁷

While the use of acid catalysts in plastic cracking is well reported, probably due to their ability of breaking C-C bonds,^{32,46} the base catalyzed PS degradation is less explored. One of the pioneering studies shows how the styrene yield is much lower on solid acids (50% for HZSM-5) than on solid bases (up to 73% for BaO), as observed in Fig 8.⁴⁷ This is related to the involved mechanisms: while on acid catalysts further cracking converts the styrene monomer into e.g. benzene and indanes, this reaction does not occur with basic catalysts. Remarkably, in case of transition metal oxides, like ZnO, Co₃O₄ and Cr₂O₃, the presence of basic sites on their surfaces,^{45,48} allows to have styrene yields similar to those obtained with Group I or II solid base catalysts. A noteworthy case is observed for TiO₂, with the yield of styrene decreasing significantly, once again in favor of the production of benzene and other aromatics. This result is caused by the presence of stronger acid sites on the surface of the TiO₂, as has been observed for some of its phases.⁴⁹ Among the solid bases, BaO, K₂O and MgO exhibited excellent styrene yields. The absence of benzene or indane derivatives in the product mixture confirms the PS degradation mechanism described in Scheme 5.

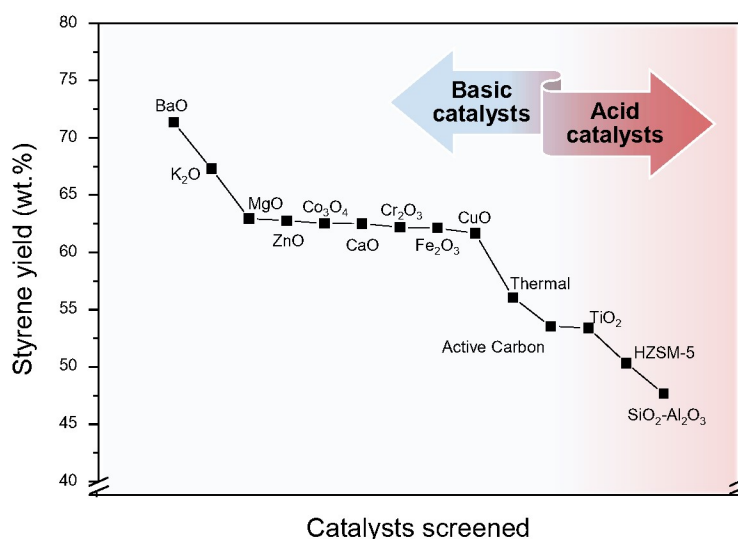


Fig. 8. Recovery of styrene monomer from polystyrene on various catalysts. The styrene yield was determined at full conversion, 350 °C and using 10 wt.% of catalyst.⁴⁷

Furthermore, the degradation rates obtained in presence of basic catalysts were higher than those obtained by simple thermal degradation, which supports that the process is accelerated by depolymerization through carbanions generated by deprotonation.⁴⁷ Unfortunately, the relation between the obtained styrene yield and the strength and number of basic sites on the surface of the solids was not explored. It is worth to note that in these studies, the catalysts were never in direct contact with the actual polymer chains, but with the vapor products of the thermal degradation of PS at 350 °C. This was done to circumvent the poor access of the polymer to the basic sites; however, upon upscaling, this generates the need for at least two reactor chambers for the total conversion of PS to styrene: one for the thermal degradation, for the generation of styrene dimers and oligomers, and another for the catalytic degradation by H⁺ abstraction, which forces to find different alternatives to further optimize this process.

Therefore, materials with large pores (~ 4 nm diameter) and large surface area have been explored as supports for basic oxides, as an alternative to the small surface area offered by oxides like BaO. In a first

attempt,^{50a} a siliceous MCM-41⁵¹ was impregnated with aqueous solutions of KNO_3 to obtain a series of $\text{K}_2\text{O}/\text{MCM-41}$ samples (K_2O wt.% = 5, 9 and 12). Two different trends were observed: while the increase of the K_2O wt.% from 0 to 9% results in higher styrene yields (69% at 400 °C and 0.5 h), further loading of the K_2O in MCM-41 (to 12 wt.%) leads to a decrease in activity. The most plausible reason behind the enhanced activity should be the increase of the basicity of all samples with the K_2O wt.%. However, when the K_2O loading reaches 12 wt.% the mesoporous structure is destroyed, as evidenced by XRD. More recently,^{50b} BaO-SBA-15, as a support, was also loaded with K_2O . BaO-SBA-15 was synthesized by direct synthesis using $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ as precursor, a triblock copolymer (P123) as structure directing agent, tetraethyl orthosilicate (TEOS) as silica source, and HCl to make the aqueous medium acidic.⁵² The $\text{K}_2\text{O}/\text{BaO-SBA-15}$ catalysts were then prepared by the impregnation method using aqueous solutions of KNO_3 . When the loading of K_2O increased from 0% to 9%, the styrene recovery was enhanced, which was attributed to the superior basic strength of the catalyst with the K_2O introduction, as evidenced by CO_2 -TPD. After 0.5 h reaction time, a high styrene yield of 86% was obtained with the sample 9% $\text{K}_2\text{O}/\text{BaO-SBA-15}$. In comparison, 70% of styrene yield was obtained under thermal conditions. Nevertheless, it is unclear whether the chains of molten PS (with high molecular weight) actually intruded into the monodimensional, cylindrical channels with a diameter of a few nm (< 8 nm) and the reaction still required high temperatures (370 °C) to proceed. Similar results were obtained by Jin et al.,⁵³ synthesizing a sepiolite-derived MCM-41 exhibiting both a good catalytic activity and selectivity to styrene ($T = 410$ °C). Sepiolite, a fibrous hydrated magnesium silicate was converted into MCM-41 by treatment with HCl (for Mg extraction) followed by dispersion in water and hexadecyltrimethylammonium bromide (CTAB). Various synthesis conditions, including crystallization time, pH, ratio of surfactant to SiO_2 and Mg content in the sepiolite were studied. Even though the synthesis procedure included the extraction of Mg (as presented in Fig. 9), during reaction at 410 °C, some basic MgO species remaining from the sepiolite, suppressed the reactions and crosslinking that lead to less desired side products, like ethylbenzene and benzene, and increased the selectivity to styrene. The highest selectivity to styrene and the highest catalytic activity for the cracking were obtained with the sample MCM-41 containing 0.36% of Mg.

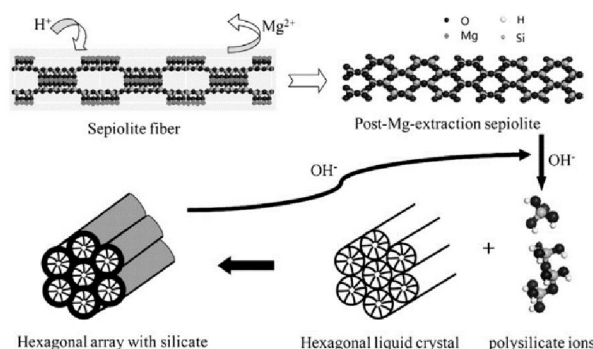
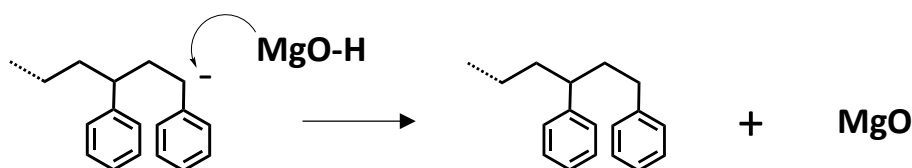


Fig. 9. Schematic representation of formation of MCM-41 from natural sepiolite.⁵³ Reproduced with permission from ref 53. Copyright 2012 Elsevier.

To have a deeper understanding of the reaction chemistry, the influence of steric hindrance on the overall activity of basic catalysts was documented by Woo et al.⁵⁴ A PS mimic, 1,3,5-triphenylhexane (TPH), was synthesized and its degradation was compared with the results obtained with actual PS chains. In both cases, the experiments were carried out in a batch reactor at 350 °C using MgO as catalyst. The presence of MgO increased the decomposition rate of TPH but decreased the reaction rate when PS was used as

reagent. This discrepancy was explained by examining the effects that the catalysts would have on each individual step of the depolymerization. As shown in Scheme 5, the PS degradation in the presence of a base proceeds through the formation of carbanions. The depolymerization rate is enhanced in presence of a base, due to a more rapid initiation caused by the removal of a tertiary proton attached to the PS backbone by the catalyst.⁴⁷ However, if the abstracted proton and the newly formed anion remain in close proximity, premature termination of the depolymerizing propagation steps could occur, as presented in Scheme 6. The obtained results suggest that under these catalytic conditions, the termination occurs more often than under thermal conditions, resulting in lower conversion. While it is possible that indeed a rate enhancement does ensue from the H⁺ abstraction caused by a solid base (initiation step), this may be outweighed by the effect of the premature chain termination.



Scheme 6. Termination of anionic, depolymerizing polystyrene fragment due to recombination with a proton on the catalyst surface.⁵⁴

If termination is related to release of the protons from the basic sites, this problem may be overcome by using a stronger basic catalyst that would allow the depolymerization to compete more successfully with the termination step.⁵⁴ Nevertheless, up until now, the number and strength of the basic sites on the PS depolymerization catalysts have been scarcely studied. Few examples can be found in the literature, with the Fe-based catalysts developed by Kim et al.⁵⁵ one of them. There, it was found that the styrene monomer yield was enhanced by the promoter, following the trend $K > Ba > Zn > Mg$. These data were related to CO₂ chemisorption data, with K enhancing the CO₂ chemisorption on Fe/Al₂O₃.⁵⁶ Since CO₂ has acidic character, this molecule tends to preferably adsorb on alkali promoted catalysts.

In order to link the selectivity in PS degradation with the physicochemical properties of the catalysts, the performances of SiO₂-Al₂O₃ (45% Al₂O₃) doped with NaOH (from 1 to 20 wt.%) and of γ -Al₂O₃ containing NaOH (from 1 to 8 wt.%) were analyzed.²⁷ First of all, the basicity of the materials was tested by the transformation of diacetone alcohol at 40 °C. From the results it could be deduced that basic centers, formed by Na⁺-modified SiO₂-Al₂O₃ when the surface concentration of NaOH exceeded 12%, decompose the diacetone alcohol into acetone.⁵⁷ On the other hand, when γ -Al₂O₃ was used, a 3% conversion into acetone was obtained, which increased to 95% when the catalysts were loaded with at least 1% NaOH. A detailed analysis of the characterized catalysts allowed to conclude that the selectivity to the styrene monomer increased with the NaOH concentration, and the transformations leading to ethylbenzene and benzene were suppressed. Conversely, the overall PS conversion was only slightly affected with NaOH concentration (Fig. 10). It is worth to note that the introduction of alkali ions on solid surfaces not only forms basic sites, but also poisons the acid centers,⁵⁸ reducing in this way the decomposition of the primary desired products into other non-desired aromatic compounds, as previously described in the section on acid catalysis.

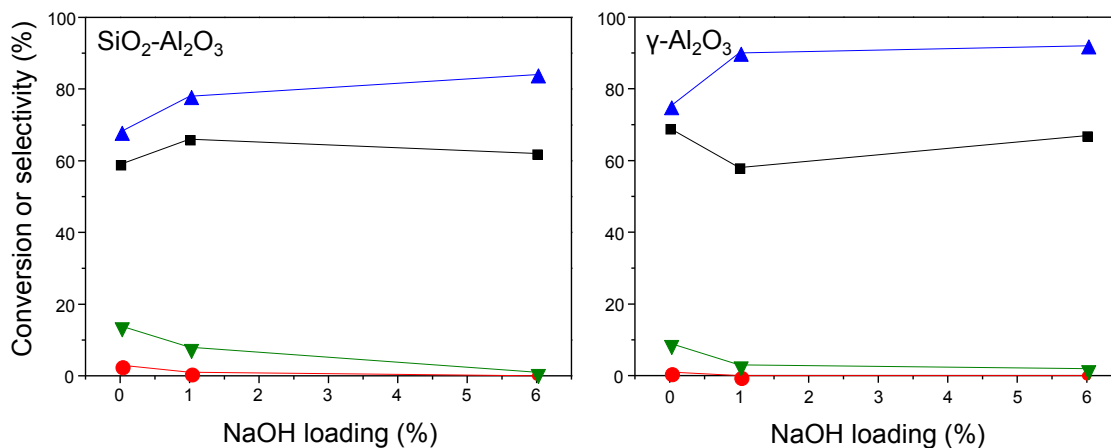


Fig. 10. PS transformation over Na⁺ loaded SiO₂-Al₂O₃ and Na⁺ loaded γ-Al₂O₃: Conversion (■) and selectivity to styrene + dimers (▲), ethylbenzene (▼) and benzene (●). Reaction stopped when liquid products stopped to distill from the reactor (after 60–90 min). Reaction temperature 480 °C.²⁷

Conclusions and outlook

Nowadays, it is hard to imagine a world where plastics do not exist as they play a vital role in our daily lives. Therefore, in an era where plastic has so many applications, its waste is clearly a global issue. In the particular case of PS waste, its effective recycling appears to be challenging mostly due to its high volume, which increases the price of transportation of waste product, making closing the loop very costly. As a result, in most of the cases, it is both easier and cheaper to produce new PS than to collect it and reuse it.⁵⁹

Building on this, in this minireview we have focused on methods that would make PS recycling more cost efficient, in particular catalytic recycling processes. We assessed the reported catalytic routes towards the recycling of PS, concluding that it is imperative to improve the currently achievable styrene yields, especially considering the high energy demand of the non-catalytic process (high operating temperatures needed), its complex radical reaction kinetics and the occurrence of many side reactions.^{19,60} Ideally, all those problems could be solved by the use of a catalyst: 1) The reaction conditions required to degrade the PS chains would be more moderate; and 2) The product mixture could be increasingly controlled.

When acid type catalysts are used, the main products obtained are aromatics belonging to gasoline range, such as benzene, toluene, ethylbenzene, styrene, α-methylstyrene and cumene, but also small amounts of indane and naphthalene derivatives. These are formed from several reactions that the cationic species go through, namely, hydride shifts, C-C bond scissions, isomerizations and cyclizations (Scheme 2). While the formation of fuel range molecules can be seen as an economical solution to the problems of plastic recycling, it may not be the best technology in terms of environmental benefits and its environmental footprint may be already higher than that of current benchmark waste treatments. According to some recent theoretical models,⁶¹ in order to effectively reduce global warming impact, PS should not be recycled to be used as refinery feedstock or fuel. A more efficient alternative would be to treat the PS by energy recovery in cement kilns, where plastic packaging waste can be used as a substitute for lignite. In fact, even when compared to mechanical processes, recycling of PS to liquid fuels, like gasoline, leads to a negative environmental potential in terms of global warming impact.⁶¹

In contrast, base catalyzed degradation of PS results in the preferential formation of the styrene monomer over other aromatic compounds. The role of the base is to generate carbanions which can depolymerize further (Scheme 5). The chemical recycling achieved *via* base catalyzed degradation of PS results in a positive environmental potential when compared to other available technologies, such as energy recovery (incineration and use in cement kilns) and mechanical recycling. Table 1 shows the environmental potentials calculated as the difference between the net environmental impacts of the benchmark waste treatment evaluated and the ideal chemical recycling process. These values represent the maximal environmental benefits based on a comparative Life Cycle Assessment (LCA) of chemical recycling of PS to styrene and the other technologies. The positive benefit of chemical recycling is based on the fact that the global warming impact avoided from conventional styrene production outweighs the positive impact of cement kiln due to increased lignite utilization and the positive impact of the reutilization of plastics.⁶¹ This becomes even more important if we consider the carbon footprint of the fossil feedstocks used in the styrene monomer production (typical well-to-gate carbon footprint of 0.8 ton of CO₂ per ton of product).⁶² Focusing on global warming and fossil resource depletion (major targets of a circular economy for plastic waste),⁶³ when the recovery of the styrene monomer is guaranteed, closed-loop recycling has a superior environmental benefit over open-loop recycling systems. This should incite new scientific and technological developments in the industry to tackle PS recycling in a circular manner, avoiding exportation to third countries, landfilling and incineration, all with the help and the pressure from the pertinent governmental bodies.

Table 1. Environmental potential for global warming impacts and fossil resource depletion of chemical recycling of PS to styrene, compared to other benchmark waste treatments.⁶¹

Benchmark waste treatment ^a	Global warming impact (kg CO ₂ -eq.) ^b	Fossil resource depletion (kg oil eq.) ^c
Energy recovery in incinerators	3.66	1.34
Energy recovery in cement kilns	1.43	1.39
Mechanical recycling	0.21	0.32

^a The direct environmental impact of the benchmark includes all environmental impacts required to treat 1 kg of plastic packaging waste.⁶¹ ^b Global warming impact (kg CO₂-eq) compares the emissions from various greenhouse gases based on their global-warming potential, by converting amounts of other gases to the equivalent amount of carbon dioxide with the same global warming potential. ^c Fossil fuel depletion (kg oil eq.) represents the non-renewable depletion of coal, gas and oil.

Nonetheless, it is important to note that the theoretical results presented in Table 1 are obtained from a comparison between the benchmark waste treatment and the ideal chemical recycling process (monomer recovery), which may significantly underestimate the environmental impact of the latter. For example, in idealized thermodynamic calculations the energy demands are minimal, while the analysis of real chemical recycling processes would increase these demands and the environmental impacts. However, since the majority of the chemical recycling technologies are still in early development, sufficient data and industry-based inventories are not available for a full LCA, which thus deviates from ideality. Therefore, the positive environmental potential values do not imply that the chemical recycling process is necessarily better for the environment than the benchmark, but that it has the potential of becoming more beneficial.⁶¹

Even though there is potential for the discovery of improved catalytic processes for chemical recycling of PS and much progress can be expected soon, the PS recycling field still has some challenges to overcome and to be considered:

- Very few effective methods are able to depolymerize PS at moderate temperatures. Only one report describes the PS degradation at 250 °C using a FeCu/Al₂O₃ catalyst, but as expected with solid acid catalysts, a complex product mixture was obtained, with a very low styrene yield of 30 wt.% in the oil fraction.⁶⁴
- There is a lack of data on the application of highly dispersed basic catalysts. Until now, the low-temperature degradation of PS has been unsuccessful, and this is clearly related to the poor contact between the aforementioned catalysts and the polymer. In this scenario, the action of a catalyst is limited to the few contact points between the two materials, which is why the most successful examples of catalytic PS recycling focus on the degradation of vaporized PS fragments, as presented in Fig. 11.

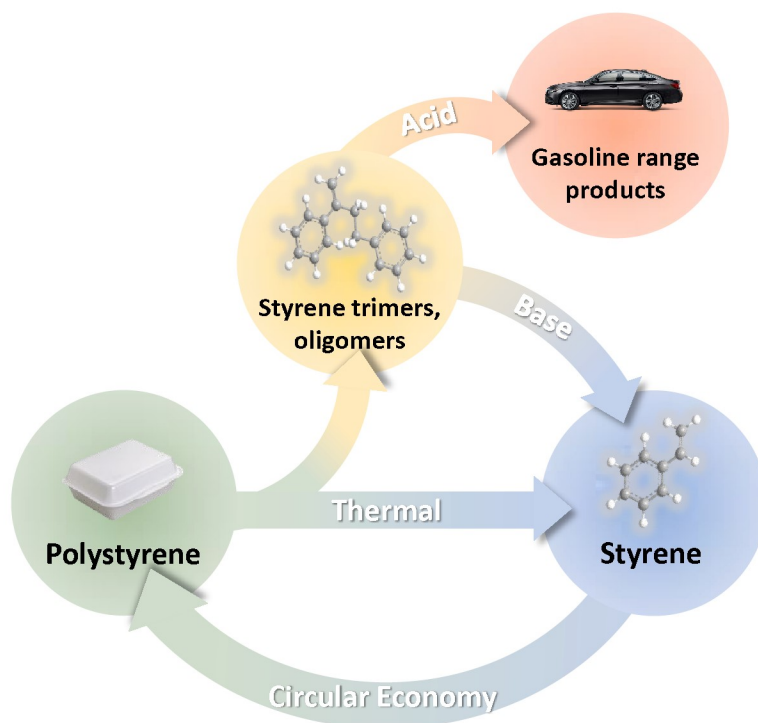


Fig. 11. Summary of the main products obtained from the currently known chemical PS recycling processes.

- Mechanistic understanding of the PS degradation reactions is still insufficient. Such pathways are intrinsically hard to distinguish under the extreme conditions of the reaction, where both thermal and catalytic degradation take place simultaneously.
- The energy required for operating the discussed catalytic routes may be a critical issue in developing a suitable catalytic process for the recycling of PS. In this regard, some optimization studies are available in literature dealing with pyrolysis of plastic waste;⁶⁵ specifically, the work by Song and Hyun^{65a} investigates the pyrolysis of PS aiming at minimizing the energy consumed by the process, which is the lowest when the reaction temperature is kept at the minimum value

possible, even if this represents a maximization of the reaction time.^{65a} Since the use of catalysts in pyrolysis of plastic wastes has a significant influence on the product yields and on the characteristics of the products, and creates the opportunity to potentially operate at lower reaction temperatures, catalytic routes towards PS recycling would further decrease the overall process energy input.²⁰ⁱ

- Finally, only a few studies have commented on the challenges in catalyst development or on the performance of regenerated catalysts, which would be essential to implement catalytic processes at an industrial scale. While most of the catalysts mentioned in this minireview are produced in big batches and used already in the industry sector, the synthesis of more successful and more catalytically efficient materials will likely require new extensive and expensive synthesis techniques. Thus, the rise in the cost of materials will have to be met with a shift in focus towards the reduction of the cost of the degradation process itself.²⁰ⁿ Relevant analyses on the subject proved that the chemical recycling of plastic waste can be profitable for large scale plants,⁶⁶ with the capital costs and operating time having a critical influence on the results. Furthermore, the economic feasibility can be heavily affected by a variety of other factors, such as the volatility in crude oil prices, the feedstock availability, the uncertain investment costs and the price value of the recovered monomer in the market at a specific time.^{65a} If the market value of the recovered monomer is high, the process should focus on producing maximal amounts of monomer at high reaction temperature. Nevertheless, if the market value of the recovered monomer is low, the process should be run at a low temperature. Consequently, if the monomer price falls in the middle of these two extremes, there should be an optimal reaction temperature at which the economic cost attains a minimum value, as shown in Table 2.^{65a}

Certainly, to overcome these obstacles, scientists should work closely with the industry, motivated also by better policy frameworks from the governmental entities aiming at selecting better and more suitable polymer recycling strategies, which should be developed following thorough process optimization techniques.

Table 2. Optimization of on the pyrolysis of polystyrene in a batch reactor. The objective function is the cost of the pyrolysis process.^{65a}

Reaction temperature (°C)	Reaction time (h)	Energy consumption of the reaction (kJ) ^a	Cost objective function ^b
440	2.13	154.4	30.46
450	1.45	156.0	29.88
460	0.99	157.8	29.64
465.3	0.81	159.0	29.62
470	0.68	160.0	29.64
480	0.47	162.3	29.79
490	0.32	164.7	30.05
500	0.23	167.2	30.39

^a The energy consumption during the pyrolysis encompasses three parts: E_1 , the energy necessary to increase the temperature from room temperature to the operating temperature; E_2 , the energy for heat loss compensation; and E_3 , the energy provided to the endothermic pyrolysis reaction.^{65a} ^b The cost objective function depends on the energy consumed for producing 1 kg of styrene monomer, the reaction time, the electricity cost per 1 kJ of energy and the monomer production profit.^{65a}

Conflicts of interest

There are no conflicts to declare.

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