Hydrous Pyrolysis of Silica-Supported Polystyrene

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ABSTRACT: Thermal degradation of polystyrene has been studied in the presence of water under subcritical conditions (hydrous pyrolysis). The experiments were performed in closed systems under inert atmosphere, in the temperature range of 300–320°C, for 1–24 h. The results showed that the presence of water increases the yields of the volatile products, mainly in the first steps of the pyrolitic process, with a higher selectivity of monomer. In order to improve the effective phase contact between water and the polymer during the degradation, hydrous pyrolysis runs have been carried out on silica-supported polystyrene. Some of these experiments were performed using a stirred reactor. Under these conditions, the above effects appeared to be greatly emphasized. Qualitative and quantitative analyses of the degradation products have been reported for the series of runs investigated. The best recovery of styrene has been achieved at 320°C and 8 h, being close to 71%. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2291–2298, 1998

Key words: polystyrene; hydrous pyrolysis; water; degradation; silica

INTRODUCTION

In the last few decades, waste plastics disposal has been recognized as a serious environmental problem because of their poor biodegradability. In this light, various alternative methods for recycling plastic waste have been proposed,[1–2] among which pyrolysis seems to be particularly promising and economically viable in the near future.

Pyrolysis of plastics, namely, the thermal treatment in the absence of air, can simultaneously generate oil and gases, which are suited for chemical utilization or generation of energy. Thus, the aim of reducing pollution can be associated to that of reutilizing the potential energy content of these wastes.

Polyolefins, such as polyethylene, polypropylene, and polystyrene (PS), dominate the production and use of plastics. Consequently, they constitute a considerable part in the plastics portion of municipal solid waste (approximately 80% w/w in Western Europe).[3] The thermal degradation of these polymers, carried out under various conditions, has been extensively studied; also, the use of catalysts has been investigated. Employing catalysts leads to an enhancement of the reaction rate, which allows one to operate at lower temperatures, making the process less expensive. Furthermore, by using appropriate catalysts, the degradation can be more easily directed to useful products.

The most frequently employed catalysts in this process are zeolites and silica–aluminas,[4–6] but, also, other degradative agents have been considered in the literature. In particular, water has been employed in the degradation of low-density polyethylene at the temperature of 450°C and a pressure higher than 160 atm.[7] A marked catalytic effect of water has been also observed in the thermal decomposition of a natural polymeric ma-

terial, such as cellulose.[8] Furthermore, steam has been used as a fluidizing agent in the pyrolysis of polyolefins in the range of 600–800°C.[9]

When water is maintained in the liquid state under subcritical conditions, the hydrothermal treatment is named hydrous pyrolysis.[10] Such a treatment has been successfully employed for simulating kerogen degradation in laboratory experiments directed to assess the potential of sedimentary basins in oil formation.[11–14]

In a previous work,[15] we have studied the hydrous pyrolysis of PS, chosen as an example of polyolefins. Several articles in the literature are concerned with the thermal degradation of PS; on the contrary, the catalytic degradation of this polymer has been studied much less.[16–22] The aim of our work was to elucidate the role of liquid water in the degradation carried out under inert atmosphere in the temperature range of 300–350°C. In particular, our intention was to obtain a high percentage of the monomer in the light products fraction and to minimize the crosslinking reactions. It was found that liquid water near to its critical point significantly affects the course of PS degradation, leading to much higher yields in monomer than those observed operating without water.

The purpose of this work was to further develop the hydrous pyrolysis procedure for the degradation of PS ameliorating the phase contact between water and the polymer. Such an improvement has been attempted by adsorbing the polymer on silica, a support with negligible activity in the degradation of PS, and by carrying out the reaction in a vigorously stirred reactor. The use of appropriate interfacial agents has been also considered.

The hydrous pyrolysis of silica supported PS in a stirred reactor has given more than positive results in terms of styrene production, even if operating at relatively low temperatures.

EXPERIMENTAL

EDISTIR 1380, a commercially available PS produced by radical polymerization, was supplied by Montepolimeri (Mantova, Italy). Its average molecular weight (M_w) was 215,900; the polydispersity index (M_w/M_n), 2.8; and density, 1.05 g/cm^3.

Various types of silica gel (Si), generally used in preparative chromatography, were employed as a support of PS. The characteristics of silica, purchased from Merck (Germany), are reported in Table I. Supported PS samples were prepared by dissolving the polymer (approximately 4 g) in 80 mL of tetrahydrofuran (THF). After the addition of Si, approximately 20 g, the solvent was removed by rotoevaporation, and the resulting supported polymer (PS/Si = 1/5 w/w) was dried at 60°C under vacuum.

The first reactions were carried out under an argon atmosphere in a high-pressure stainless steel bomb (71 mL). In a typical run (named RPSHSi), a sample of PS supported on silica (6 g) was reacted in the presence of deionized water (11 mL) and of a sufficient quantity of argon to ensure operating pressure values around 18 MPa, regardless of the temperature and relevant water pressure employed. The isothermal conditions (within ±1°C) were obtained by immersing the autoclave in a Techne (UK) Model FB-08 fluidized alumina thermostatted bath. The temperatures explored were in the range of 300–350°C and the reactions times were in the range of 1–72 h. The heating system provided a very rapid heat-up of the reactor so that preheating periods could be neglected. At a given time, the reaction was stopped by drawing the bomb out of the bath and cooling it to room temperature by tap water. After venting, the autoclave was opened, and the products mixture was worked up (Fig. 1). The degradation products were recovered with THF. The residue in the bomb was dissolved in acetone, separated from silica by filtration, and quantified. The separation of the THF phase and water was ameliorated by adding 10 mL of n-pentane (nC5). An aliquot of the resulting organic phase (3 mL) was added to a known amount of biphenyl (5 mg, Aldrich Chemical Co. (USA), purity grade > 99%) used as an internal standard, treated with further nC5 (80 mL) to precipitate heavy products, filtered through a paper filter, and analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) for the qualitative and quantitative determination of light products (LP). The solvent of the remaining organic solution was removed by evaporation under controlled vacuum, and the residue, washed with nC5 to dissolve the residual LP, was quantified (heavy products, HP) and analyzed by size exclusion chromatography (SEC).

When the degradation of the polymer supported on silica was carried out in the absence of water (runs named RPSSi), an analogous procedure was followed.

Hydrous pyrolysis experiments were repeated in a Parr (USA) Model 4564 stainless steel stirred

Figure 1 Work-up of the reaction products in hydrous pyrolysis of silica-supported polystyrene.

GC, GC–MS, AND SEC ANALYSES

GC runs were performed on a Varian (USA) Model 3700 chromatography equipped with a programmed temperature vaporizer (PTV) Dani (Italy) 332 injector and a flame ionization detector. The PTV operated under splitless conditions. As a separation column, a fused silica capillary column Supelco (USA) SPB-5, 30 m × 0.32 mm i.d., with a film thickness of 0.25 μm, was used. The carrier gas was helium at a linear flow rate of 30 cm/s. The GC oven temperature was initially set at 30°C for 5 min, then programmed to 270°C at a

(600 rpm) reactor (160 mL). Some reactions were carried out on silica-supported PS (runs named sRPSHSi) operating with a (PS + Si)-to-water weight ratio of 15/40. Eventually, some runs, named sRPSH, were performed on pure polymer with a PS-to-water weight ratio of 5/50. Runs sRPSHSi and sRPSH were performed at two different temperatures, 300 and 320°C, for 1–8 h. The procedure employed for the separation of the reaction products was similar to that above described.

rate of 7°C/min, holding the final temperature for 10 min. Data acquisition was accomplished with a Hewlett-Packard (USA) 3365 Series II ChemStation.

The gas chromatography flame ionization detector response factors were determinated for the main degradation products using a series of known concentration solutions. Each mixture was analyzed three or more times: the response factors were calculated as the average values obtained from these runs.

The identification of the light products was performed on a Hewlett–Packard 5985 B/5980 Series II GC–MS apparatus operating in electron impact (EI) mode. The system was equipped with a capillary column identical to that used for GC analysis. Mass spectral data were obtained under the following conditions: ionizing energy, 70 eV; emission current, 0.3 mA; ion source temperature, 200°C; scanning rate, 1.5 scans over the mass range $m/z = 33$–350.

The heavy products were characterized by means of SEC analysis. The SEC system consisted of a Waters (USA) Model 600 E pump equipped with four Ultrastyragel columns (10^5, 10^4, 10^3, and 500 Å pore size), a Waters 490 E ultraviolet detector and a Waters 410 differential refractive index detector. THF was used as mobile phase at a flow rate of 1 mL/min. The calibration curve of the SEC system was generated using a set of narrow PS standards with the molar mass ranging from 162 to 3.2×10^6 g/mol.

RESULTS AND DISCUSSION

The pyrolysis of PS carried out under the conditions employed in this work, that is, in a closed system in the presence of liquid water, has given at its completion, as ultimate products, toluene (T), ethylbenzene (EB), and cumene (C). The formation of saturated compounds at the end of PS degradation requires the presence of hydrogen in the reacting system; this derives mainly from the crosslinking processes occurring at long times. The contribution of liquid water as a hydrogen donor has been previously found to be less important.[15] The overall amount of T, EB, and C has accounted for more than 95% of the final light products.

When the hydrous pyrolysis of PS has been stopped at times of the order of hours or tens of hours, the following main intermediate products have been obtained, together with T, EB, and C:

Table I   Abbreviations Used for the Different Pyrolysis Experiments

Abbreviation	Definition
RPS[a]	Runs carried out on pure polystyrene
RPSH[a]	Runs carried out on pure polystyrene in the presence of water
RPSSi	Runs carried out on silica-supported polystyrene
RPSHSi	Runs carried out on silica-supported polystyrene in the presence of water
sRPSH	Runs carried out in a stirred reactor on pure polystyrene in the presence of water
sRPSHSi	Runs carried out in a stirred reactor on silica-supported polystyrene in the presence of water

[a] The results relative to these pyrolysis runs are reported in a previous article.[15]

styrene (S); α-methylstyrene (αMS); 1,3-diphenyl-propane (DPP); 1,3-diphenylbutane (DPB); styrene dimer, that is, 2,4-diphenyl-1-butene (SS); triphenylpentane (TPP); styrene trimer, that is, 2,4,6-triphenyl-1-hexene (SSS). The internal distributions of these compounds as functions of time and temperature during the course of the hydrous pyrolysis have been already reported in the case of reactions carried out on unsupported PS.[15]

All the above products constitute the light fraction formed in the degradation of PS (light products, LP), while the solid residue constitutes the heavy fraction (heavy products, HP).

In the previous work,[15] a significant increase in the formation of LP fraction, and in the percentage of S inside it, was obtained on going from reactions carried out on PS alone (runs named RPS) to reactions carried out in the presence of liquid water in the vicinity of its critical point (runs RPSH).

In the present work, the role of water has been emphasized, making the phase contact between it and the polymer more intimate. This has been achieved by adsorbing PS on an appropriate support, which results in a more extended polymer area accessible to liquid water, and using a vig-orously stirred reactor, in order to facilitate the transfer phenomena. However, to evaluate the single effects of using support and/or stirring, runs with support without stirring and with stirring without support have been also performed. A summary of the various pyrolysis experiments carried out on polystyrene is reported in Table I.

Silica has been chosen as an appropriate support due to its quite negligible catalytic activity in PS degradation, as it was previously demonstrated with runs carried out in the absence of water.[20,22] In this work, the absence of effects due to the presence of silica has been confirmed also in the case of hydrous pyrolysis; degradations of unsupported PS carried out at 320°C and 8 h, under stirring with excess silica suspended in water, substantially gave the same results obtained without silica (in terms of LP formation, 32.8 versus 31.7%).

For obtaining an effective phase contact between water and polymer, it seemed important to look for an adequate typology of the silica support. As shown in Table II, seven types of silica have been considered with pore dimensions in the range of 40–100 Å; a specific surface area in the range of 300–800 m^2/g; grain sizes of 35–70, 70–

Table II   Characteristics[a] of Silica Used as a Polystyrene Support in Hydrous Pyrolysis Experiments

Sample Code	Pore Dimension (Å)	Grain Size (mesh)	Acidity (pH)	Surface Area (m^2/g)
Si 11	40	35–70	5.5 ± 0.5	800
Si 12	40	70–230	5.5 ± 0.5	800
Si 21	60	35–70	7.0 ± 0.5	500
Si 22	60	70–230	7.0 ± 0.5	500
Si 23	60	230–400	7.0 ± 0.5	500
Si 31	100	35–70	6.5 ± 0.5	300
Si 32	100	70–230	6.5 ± 0.5	300

[a] Specified by producer.

Table III   Comparison Between the Light Products Yields (Wt %)^a in Runs sRPSHSi Carried Out at 320°C and 8 h Obtained Using Various Silica Supports

Surface Area (m^2/g)	Grain Size (Mesh)		
	35–70	70–230	230–400
800	81.3	90.5	nd
500	65.5	88.3	73.1
300	36.0	75.0	nd

^{a} Average values.

230, and 230–400 mesh; and pH in the range of 5.5–7. The behavior of these silica support has been determined carrying out hydrous pyrolysis runs at 320°C and 8 h under stirring, conditions that have been revealed, in the context of this work, as the most interesting to be explored. The results, collected in Table III in terms of LP formation, show that there is a progressive increase in reactivity with increasing surface area of the support, given a constant grain size. Thus, it seems that the surface area of the support is the determining factor for optimizing the phase contact between water and molten polymer and, thus, maximizing the reactivity. As regards the influence of grain size, the best results have been achieved using silica with a mesh size of 70–230, indipendently from the specific area of the support. It can be hypothesized that this range of grain size is the more suitable to prepare a silica-supported polystyrene and, consequently, to exploit a more extended polymer area.

Interestingly, considering the internal composition of LP fraction, the higher percentages of S, varying from 76 to 81%, have been obtained in the runs carried out in the presence of the supports marked with Si 12 and Si 22 (Table II).

Consequently, the more significant result is the individuation of an optimum in the silica support characteristic, leading to maximize LP yields and, inside it, the monomer concentration.

After choosing the more convenient type of silica, a further improvement of the phase contact between water and supported PS has been attempted by using, separately, appropriate interfacial agents. Two of them, ricinoleic acid and oleic acid, should have facilitated the contact acting as surfactants, that is, enhancing the wettability of the reactant. The other agent, styrene–maleic anhydride copolymer, considered at three

levels of composition (50/50, 65/35, 75/25), being characterized by the presence of a moiety like to PS and a moiety polar as water, should have acted as a bridge between the two phases. However, several hydrous pyrolyses carried out at 320°C and 8 h under stirring on pure PS with increasing amounts of these agents have been evidenced that the effect due to their presence, if any, was substantially negligible.

Thus, for a complete comparison of the best results obtained under the various conditions explored, the spectrum of runs to be considered has been limited to five series: runs RPS and RPSH, carried out in previous work,[15] and runs sRPSH, RPSHSi, and sRPSHSi (where s and Si indicate the presence of stirring and silica, respectively), carried out in the present work.

As regards the HP fraction, the SEC analyses performed on the solid residue show that the values of M_w and M_n are regularly decreasing with time and temperature, that is, with the severity of the pyrolysis conditions, for the five series of runs investigated. Moreover, considering the results obtained for the pyrolyses carried out at 320°C and 8 h, chosen as an example, similar M_w values, in the range between 31,000 and 40,000 Da, have been found for the various runs examined.

The more interesting results of the above series of runs are reported in Figure 2, in terms of LP formation as a function of time. The data in Figure 2(a), at 300°C, and, more clearly, those in

Figure 2   Time courses of the light products formation (wt %) at (a) 300 and (b) 320°C.

Figure 3 Comparison between the internal distributions (χ, wt %) of the main light products formed in runs RPS and sRPSHSi carried out at 320°C and 8 h.

Figure 2(b), at 320°C, show that the production of LP regularly increases in the following sequence: RPS < RPSH < sRPSH < RPSHSi < sRPSHSi. The most significant gap is observed on going from unsupported to silica-supported PS; in fact, the marked increase in LP formation obtained by using supported PS is significantly higher than the further enhancement obtained using the stirred reactor. As an example, at 320°C and 8 h, the highest amount of LP fraction has been reached in runs sRPSHSi (89.2%), closely followed by the amount obtained in runs RPSHSi (78.2%), while the other runs have given much lower values (<32%).

As regards the internal products distribution, a comparison between the results obtained at 320°C and 8 h in runs sRPSHSi and RPS is reported in Figure 3. It can be seen how the presence of liquid water near to its critical point in a close contact with PS induces a very marked change in S percentage in LP fraction, enhancing it to a value as high as 79% from a values as low as 29%. This results reveals that the presence of water lowers the rate of secondary reactions with respect to that observed in the case of PS alone. It can be suggested that some of the free macroradi-

cal sites, formed by scission of the polymeric chain, are terminated by water-derived hydrogen.[12] Therefore, the presence of liquid water, as a hydrogen donor, prevents the intra- and intermolecular hydrogen transfers and the consequent shifts of the radicals sites along the polymer chain, thus decreasing the importance of secondary reactions. At the same time, the crosslinking reactions become less important in favor of LP formation.

Interestingly, the inspection of Figure 3 reveals the presence, among the degradation products, of some isomers of SS and SSS, indicated, respectively, with 208 and 312. In particular, 208 refers to three compounds of M_r equal to 208, corresponding to the formula $C_{16}H_{16}$, and 312 makes reference to two compounds of M_r equal to 312, corresponding to $C_{24}H_{24}$. The comparison between the EI mass spectra of these compounds points out interesting differences. The isomers of SS show similar MS fragmentation pattern with the base peak at m/z 115 due to $(C_9H_7)^+$; characteristic ions of nearly equal abundance (40–50%) are observed at m/z 208 (M^+, the molecular ion), m/z 193 $(M—CH_3)^+$, and m/z 91 $(C_7H_7)^+$. The spectra referring to the isomers of SSS exhibit a base peak at m/z 129 corresponding to $(C_{10}H_9)^+$; other important fragments (abundance 60–80%) appear at m/z 91 and 207. On the contrary, the EI mass spectra of styrene oligomers, SS and SSS, are characterized by the large fragment at m/z 91 due to the tropilium ion $(C_7H_7)^+$. As shown in Figure 3, the formation of these isomers becomes considerable, operating in conditions of effective phase contact between water and polymer (runs sRPSHSi). It can be hypothesized that the presence of water, employed in the vicinity of its critical point, promotes the isomerization reactions, as observed by Sawaguchi et al.[23]

The amounts of S (wt %) in the LP fraction obtained under four different experimental conditions of temperature and time are reported in Table IV for the five types of runs considered. The inspection of this table indicates that the percentage of S regularly increases in the same sequence

Table IV Styrene Amounts (Wt %) in Light Products Fraction

T (°C)/t (h)	RPS	RPSH	sRPSH	RPSHSi	sRPSHSi
300/4	56	67	74	nd	81
300/8	54	55	72	nd	80
320/4	48	54	58	71	82
320/8	29	30	52	70	79

Table V   Styrene Yields (Wt %) in Polystyrene Pyrolysis

T (°C)/t (h)	RPS	RPSH	sRPSH	RPSHSi	sRPSHSi
300/4	1.9	4.6	6.4	nd	48.4
300/8	4.0	6.3	7.2	nd	59.1
320/4	3.8	6.2	10.7	43.2	55.6
320/8	4.3	6.2	16.5	54.7	70.6

above seen for the formation of LP fraction, with the two phenomena being both associated to the lowering of the rate of the secondary reactions. As a result, increasing yields in the same order are expected for S production, as will be seen in the following.

At a fixed type of run, the amount of S (wt %) in LP fraction decreases with the increase of the severity of the treatment. This effect is clearly due to the higher extent of the secondary reactions when time and temperature are raised. Only in the case of runs sRPSHSi, the selectivity to monomer is substantially the same in the range of experimental conditions reported in Table IV.

The most interesting results, namely, the yields in monomer, are reported in Table V. As already stated, the styrene yield progressively increases in the runs employing liquid water, silica-supported PS, and stirring. The best recovery of S has been achieved at 320°C and 8 h, being close to 71%. This value is significantly high and surely promising in view of a practical application of the proposed degradation approach. The main advantage of hydrous pyrolysis is that it is possible to obtain monomer yields comparable or superior to those reported in previous work,[24–27] operating at lower temperatures.

An interesting application for the recovered LP is to close the following cycle: production → use → recovery → recycle → production through polymerization to give new polystyrene. Besides utilizing the styrene monomer, from this point of view, the light oligomers, that is, the dimer and trimer, might be used in the feedstock. The maximum yield in useful products has been obtained in runs sRPSHSi performed at 320°C and 8 h, being higher than 81%.

CONCLUSIONS

The results presented in this work evidence the catalytic role of liquid water in the thermal degradation of polystyrene.

The presence of water, employed in the vicinity of its critical point, modifies the reaction course, increasing the yields of the volatile products, mainly in the first stage of the pyrolytic processs, with higher selectivity of the monomer. It can be suggested that the presence of water, as a hydrogen donor, depresses the inter- and intramolecular hydrogen transfers between or along the macromolecules, thus decreasing the occurrence of the secondary reactions. At the same time, the crosslinking reactions are unfavored.

The phase contact between water and polymer has been improved by adsorbing the polystyrene on silica. A further enhancement has been obtained performing the degradation runs in a stirred reactor.

Under these conditions, high conversion to monomer, close to 71%, has been achieved at rather mild conditions (320°C and 8 h). This result suggests that hydrous pyrolysis may be a promising way for the chemical recycling of polystyrene waste.

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