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New Chemical Recycling Methodologies: Hydrous Pyrolysis to Recover Monomers from Polyolefins

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Abstract: Thermal degradation of polystyrene has been investigated in the presence of water under subcritical conditions (hydrous pyrolysis). The experiments were carried out in closed systems under inert atmosphere, in the temperature range 300-350 °C, at pressures up to 180 atm, for 1-120 h. The results showed that the presence of water increases the yields of volatile products, mainly in the first steps of the pyrolytic process, with a high selectivity in the monomer. In order to improve the phase contact between water and polymer during the pyrolysis, some runs have been carried out on silica-supported polystyrene and using a stirred reactor. Under these conditions, the above effects appeared to be greatly enhanced. The best recovery of styrene, close to 71 %, has been achieved at 320 °C and 8 h.

INTRODUCTION

Much interest has been directed in the last few decades to the waste plastic disposal. Even if the idea of pollution from the plastic material has been now neglected, the landfilled post-use polymeric material has been recognized as a serious environmental problem because of its poor biodegradability and its large volume due to its low density. In that light, many alternative methods for reclaiming and recycling plastics waste have been proposed and realized.

All these methods have been classified into four principal categories (Ref. 1):

(a) primary recycling: a mechanical treatment applied to scrap plastic, free of impurities, to obtain products with good properties;

(b) secondary recycling: a mechanical treatment applied to homopolymers containing significant impurities to obtain products with lower performance than that of the original polymers;

(c) tertiary recycling: a thermal or chemical treatment to convert the materials into low-molecular-weight chemicals, which can be used as raw materials for the chemical industry;

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(d) quaternary recycling: burning of plastics to allow an energy recovery.

We are much interested in the tertiary kind of plastic recycling. The research in this field is only at its first stages but we strongly believe that it must be increased and enlarged; from a thermodynamical point of view, in fact, the post-use polymeric material has a very high chemical energy content due to its ordered chemical structure and it could be used as a new starting raw material for all that chemical treatment which, with or without a catalyst, could give rise to useful chemical products.

Today the burning of post-use polymeric materials to obtain energy is surely the most convenient recovery from the economical point of view because other alternative chemical treatments are not yet deeply explored. On the other hand, it seems unreasonable to waste all the chemical energy content of this particular raw material. Hence it might be reasonable to search for chemical reactions useful for this material in order to avoid the waste of this energy in the burning; the quaternary recycling must be kept as the last resort.

By the way, chemical treatments of specific polymer materials have already found industrial use: hydrolysis of poly(ethylene terephthalate), the monomer recovery from pyrolysis of poly(methyl methacrylate) and the recovery of caprolactam from Nylon.

In this framework, we have undertaken a research on the possible chemical reactions that could be carried out on polyolefin materials; in particular, various pyrolyses have been conducted on polyethylene (Ref. 2), polypropylene (Ref. 3) and polystyrene (Refs. 4-5). The most attractive results were obtained in the presence of catalysts such as zeolites and silica-aluminas (Ref. 6).

However, we have noticed that the yield of the pyrolysis products was always lowered by crosslinking, which leads to insoluble and unvolatile residues, often char, and by a simultaneous production of gases. Moreover, high temperatures seem to promote these unfavorable secondary reactions because in the presence of catalysts, hence at lower temperatures, the char and gas formation decreases. In this light, we thought interesting to attempt the thermal degradation in the presence of some hydrogen donors.

We tried to make the degradation in the presence of water (Ref. 7). Liquid water under subcritical conditions has been proposed for simulating kerogene degradation in laboratory experiments, directed to assess the potential of sedimentary basins in oil formation. This hydrothermal treatment is named hydrous pyrolysis (Ref. 8). First of all, we have tried to elucidate a possible role of liquid water in the pyrolysis of polystyrene carried out under inert atmosphere in the temperature range 300-350 °C. In particular, our aim was to minimize the crosslinking reactions and to obtain a corresponding increase in the monomer production.

EXPERIMENTAL

Polystyrene (PS) produced by Montepolimeri (EDISTIR 1380, $\overline{M}$=216 000) was employed. First reactions were carried out under argon atmosphere in a stainless-steel microvessel (15 ml), immersed in a thermostatted fluidized-alumina bath. In a typical hydrous run (PSH), a sample of PS (2 g) was reacted in the presence of deionized water (3 ml) and of a sufficient quantity of argon to ensure operating pressures around 18 MPa, regardless of the temperature and relevant water pressure employed. The temperatures explored were in the range 300-350 °C and the reaction times in the range 1-120 h. At the end of the pyrolysis, the vessel was cooled, vented and the product mixture worked up. Most of the products of the reaction were recovered with tetrahydrofuran (THF). The residue in the vessel was dissolved in acetone and quantified. An aliquot of the THF phase was added to a known amount of biphenyl, used as internal standard, treated with n-pentane to precipitate heavy products, filtered and analyzed by gas chromatography (GC) and gas chromatography - mass spectrometry (GC/MS). The solvent of the remaining organic solution was removed by evaporation and the residue was quantified and analyzed by size exclusion chromatography (SEC). When the degradation of PS was carried out in the absence of water (the runs denoted PS), an analogous procedure was followed.

Other reactions were carried out on silica-supported PS (PS/Si=1/5 w/w) operating with a (PS+silica)/water weight ratio of 6/11. These experiments (denoted PSHSi) were conducted in a 71-ml stainless steel high-pressure bomb. In addition, some pyrolyses of the supported polymers were performed in absence of water (denoted PSSi). In runs PSHSi and PSSi, the temperatures and times investigated were the same as in runs PSH and PS. Also, the work-up of the reacted mixture was similar, apart from minor variations due to the presence of the support.

GC runs were performed on a Varian Model 3700 equipped with a programmed temperature vaporizer injector and flame ionization detector. A fused silica capillary column Supelco SPB-5, 30 m x 0.32 mm i.d., with a film thickness of 0.25 μm was used. The oven was programmed from 30 to 270 °C at 7 °C/min. The identification of the light products was performed on a Hewlett Packard 5985 B GC/MS apparatus operating in the electron impact mode. Heavy products were characterized by SEC analysis performed on a Waters Model 600 pump equipped with four Ultrastyragel columns and a Waters 410 RI detector. THF (1ml/min) was used as mobile phase. The system was calibrated using a set of narrow PS standards.

RESULTS AND DISCUSSION

We have studied the time courses of thermal degradation of PS in argon atmosphere, in the presence of liquid water under subcritical conditions. We have calculated the amounts of volatile light products and the amounts of residue.

Table 1. Comparison of light product yields (%) in runs PSH and PS conducted under various conditions

T (°C)	t (h)	PSH	PS
300	1	1.7	1.1
	4	6.8	3.4
	8	11.4	7.4
	24	21.6	15.9
	72	29.5	23.3
	120	31.8	23.9
320	1	2.8	2.7
	4	11.4	8.0
	8	20.5	14.8
	24	39.2	34.7
	72	59.1	67.6
	120	71.6	77.8
335	1	6.8	4.5
	4	26.1	18.8
	8	47.2	36.9
	24	84.1	70.5
	72	78.4	79.0
	120	68.2	76.1
350	1	42.4	40.9
	4	68.2	71.6
	8	81.8	81.3
	24	84.7	83.0
	72	65.9	69.3
	120	63.1	66.8

Table 1 shows the results of light product formation in runs at various temperatures and times. The runs PSH were carried out in the presence of water, the runs PS without water. The yields of volatile products are higher in the presence of water unless under very severe experimental conditions. We can say that the presence of water influences the degradation producing higher amounts of volatile products, particularly in the first stage of the reaction. The residue was completely soluble and was examined by SEC; the results are shown in Table 2.

As can be seen, the increase in the temperature causes an increase in depolymerization (calculated as $\overline{M}_i/\overline{M}_0$) at the same reaction time as in the presence or in the absence of water.

As regards the production of gas, some test runs of PS pyrolysis under the same experimental conditions have confirmed no relevant gas formation.

In contrast, in the presence of catalysts at 350 °C, the percentage of an insoluble residue was around 28-34 % and the gas production was about 4 % (Ref. 4). The reactions were carried out under dynamic vacuum for 60 min.

Table 2. Variations in the molecular weight ($\overline{M}$) of the polymer residue in the course of the degradation of PS

T (°C)	t (h)	PSH		PS	
		$\overline{M}$	depolym. (%)	$\overline{M}$	depolym. (%)
300	1	165 800	23	181 100	16
	24	56 700	74	55 300	75
	72	20 000	91	16 700	93
320	1	145 900	32	147 200	32
	24	14 600	93	12 200	94
	72	<500	100	<500	100
335	1	88 000	60	79 100	64
	24	7 400	97	6 900	98
	72	<500	100	<500	100
350	1	42 000	80	35 800	84
	24	<500	100	<500	100
	72	<500	100	<500	100

The GC and GC/MS analyses of the volatile degradation products in the PSH runs, in comparison with those obtained without water, clearly show significant qualitative differences. If we consider the percentage distribution data of the volatile products in the first steps of the reaction, we find a greater amount of styrene in the degradation in the presence of water. For example, after 1-h reaction at 350 °C, the styrene percentage in the presence of water is 40.8 % instead of 28.4 % obtained in the run without water. As styrene is the primary product of the depolymerization reaction in the thermal degradation of PS, the greater production probably means that the presence of water negatively influences the occurrence of other kinds of reactions mainly due to intra- and intermolecular hydrogen transfer. The other products obtained are shown in Table 3.

This result induced us to try to improve the contact between the two immiscible phases, water and molten polymer. To reach this improvement, we adsorbed polystyrene on silicagel before the reaction and we used this silica-supported polymer in the reaction.

Table 3. Distribution (wt.%) of the main products in degradation of PS at 350 °C and 1 h in the presence (PSH) or in the absence of water (PS)

Product	PSH	PS
Toluene	7.4	9.0
Ethylbenzene	1.2	1.6
Styrene	40.8	28.4
Cumene	0.1	0.1
α-Methylstyrene	11.9	8.7
1,3-Diphenylpropane	5.3	5.6
1,3-Diphenylbutane	1.7	0.6
Styrene dimer	8.7	15.8
Triphenylpentane	1.4	1.7
Styrene trimer	5.7	8.5
Quaterphenyl	0.3	0.3

A set of hydrous pyrolysis runs with this substrate has been carried out. To control any catalytic action of the silica, the same set of runs have been carried out in the absence of water. The results are reported in Table 4.

Table 4. Light product formation (%) in the degradation of supported and unsupported PS in the presence or in the absence of water

Conditions	300 °C, 4 h	300 °C, 24 h	320 °C, 24 h	335 °C, 24 h	350 °C, 72 h
PSHSi	36.5	72.8	87.6	82.6	80.8
PSSi	<1	14.5	38.3	66.9	79.6
PSH	6.8	21.6	39.2	84.1	65.9
PS	3.4	15.9	34.7	70.5	69.3

PSHSi - PS adsorbed on silica in the presence of water; PSSi - PS adsorbed on silica in the absence of water; PSH - neat PS in the presence of water; PS - neat PS

This table shows that the use of silica-adsorbed PS allows increasing the production of light products and that silica exerts no catalytic action.

This increase in light product formation is particularly pronounced in first steps of the reaction under mildest experimental conditions, in which the hydrogenation could be restricted. In fact, at very long reaction times, the final products are toluene, ethylbenzene and isopropylbenzene. We can conclude that a deep water-polymer contact greatly modifies the degradation process of PS. Qualitatively, the previous results have been confirmed by the data in Table 5: the formation of styrene is significantly increased by the presence of water.

Table 5. Pyrolysis of silica-supported polystyrene: distribution (wt.%) of the main volatile products

	Toluene			Ethylbenzene			Styrene			Cumene			α-Methylstyrene		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
PSHSi	17	19	28	8	21	42	23	13	0	3	7	21	14	12	0
PSSi	13	15	20	35	51	51	13	2	0	13	21	19	10	4	0

a 320 °C/24 h; b 335 °C/24 h; c 350 °C/72 h

If the reaction was carried out with silica-supported PS in a vigorously stirred reactor, the best results were obtained at 320 °C and 8 h. Under these conditions, a light product yield of 90 % was achieved with a fraction of styrene of 79 %, which means the monomer recovery as high as 71 %. This result is surely of practical interest, considering that, actually, the industrial recovery of styrene from PS does not reach values higher than 60-65 %.

Some runs have also been conducted with unsupported polypropylene in the presence or absence of water in the same range of temperatures and times used in the degradation of PS. The preliminary results indicate that in this case, the presence of water under subcritical conditions has a negligible effect, if any, on the course of the reaction. However, such results have to be confirmed by working with polypropylene adsorbed on an appropriate support in order to ensure, like for PS, a good water-polymer phase contact.

CONCLUSIONS

In conclusion, we can confirm that if PS degrades in the presence of liquid water under subcritical conditions, the degradation mechanism can be highly modified. We think that the ability of water to act as a hydrogen donor and a deep contact between the two phases can saturate the macroradicals formed by hydrogen abstraction from polymer chains. If the concentration of these macroradicals decreases, also inter- and intramolecular hydrogen transfers between or along the macromolecules decrease and therefore all the secondary reactions derived from these transfers are limited. The final result is an increase in the unzipping reaction and, consequently, an increase in the production of monomer and a decrease in the formation of byproducts. Obviously, if styrene is not immediately extracted from the reaction mixture, it undergoes the hydrogenation to ethylbenzene, decreasing the monomer recovery.

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