

Thermolysis of Polystyrene

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SYNOPSIS

Styrene was recovered from polystyrene (molecular weight of 138,000) by thermolysis in a nitrogen atmosphere at temperatures between 368 and 407°C. The results were independent of the initial weight of polystyrene, which was varied between 30 and 480 g. Up to 90% of the polystyrene was converted to liquid products. The liquid products had a styrene concentration as high as 90% and the styrene yield increased with temperature. Above 390°C, the residue left in the reactor (less than 30% of initial polystyrene charge) consisted mainly of styrene monomer, dimer, and trimer (MW of 190). The kinetics support a first-order reaction with regard to the rate of production of volatiles. The activation energy was estimated to be 166.5 kJ/mol. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Various studies regarding the thermal degradation of polystyrene have previously been reviewed.¹ These studies were carried out under a variety of conditions, including atmospheric pressure, vacuum, and a broad range of reaction temperatures, reaction times, and initial charges. Also, the use of catalysts has been investigated. This has led to a range of yields and product qualities. For example, reaction conducted under vacuum produced large amounts of dimer and trimer in the liquid fraction.²⁻⁶ The addition of catalysts increased the variety of products obtained. Many of these were present in low concentrations, but there was an overall decrease in molecular weight.⁷⁻⁹ In all the studies, both higher temperatures and longer reaction times resulted in an increase in the amount of the liquid fraction^{2,3,5-10} and a decrease in the molecular weight of the residue.^{2,5-7} Many of these experiments were done with very small samples (micrograms and milligrams), and none of them had an initial charge greater than 25 g.

The goal of our research is to develop a practical process to convert waste polystyrene into high yields of styrene monomer. The first step is to scale-up from the microgram and milligram experiments re-

ported in the literature. At the same time, it would be advantageous to avoid expensive factors such as vacuum and/or high temperatures. Therefore, this work has been carried out at moderate temperatures and under atmospheric pressure.

EXPERIMENTAL

Materials

The polystyrene used was the powder form of STY-
RON 688 supplied by Dow Chemical Canada Inc. The number average molecular weight (M_n) and polydispersity index (M_w/M_n) were 138,000 and 2.6, respectively.

Reactors

Two experimental arrangements were used, differing only in the capacity of the reactor vessels. The first reactor (samples weighing 30 to 120 g) was a 500-mL flat bottom vessel covered with a four-necked lid. Mixing was achieved with a paddle connected to a motorized shaft. The vessel was fitted with a flat flask heating mantle (Series STM) from Glas-Col with a controller (Model BS5001J1) from Omega Engineering Inc. Thermocouples, type J, also from Omega Engineering Inc., were used to monitor the melt and still temperatures. The volatiles were condensed and collected in a rotating vessel with six

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Table I Mass Balance for Experiments

Reaction Time (min)	Temperature (°C)	Charge (g)	Yields (% wt of PS)		Losses	
			Residue	Liquid	(g)	(% wt PS)
30	371	30	68	30	0.71	2.4
30	373	30	55	42	0.72	2.4
30	371	60	66	32	1.31	2.2
12	388	60	42	57	0.25	0.4
31	391	60	17	82	0.95	1.6
30	391	60	15	83	1.23	2.0
30	407	60	15	84	0.98	1.6
12	368	120	87	12	0.97	0.8
34	368	120	48	51	1.08	0.9
20	378	120	43	56	0.83	0.7
9	382	120	66	33	1.02	0.9
23	384	120	36	64	0.00	0.0
33	388	120	29	70	1.02	0.9
40	394	120	13	86	0.72	0.6
28	395	120	19	80	1.18	1.0
21	401	120	7	92	1.22	1.0
33	373	480	60	40	1.20	0.2
31	381	480	49	51	1.06	0.2
32	390	480	27	73	0.00	0.0
34	395	480	11	89	0.00	0.0

50- or 100-mL receiving flasks. Ten liquid fractions were obtained by rotating the receiving flasks during the experiment. This allowed the collection of sequential samples of the liquid during a reaction.

The larger reactor was similar to the above except that the vessel and heating mantle had a capacity of 2 L, allowing a charge between 120 and 480 g of polystyrene. This also required a longer condenser and still.

Procedure

Prior to an experimental run, the reaction vessel and the individual flasks on the rotating receiving vessel were weighed. The system was purged for 15 min with nitrogen. The nitrogen flow was then lowered to a constant flow rate of 5 mL/min, and the heating mantle and mixer were turned on.

From 10 to 20 min was needed for the polymer to reach the desired temperature. An average reaction (melt) temperature was calculated for the constant region of the temperature profile. The average standard deviation in the reaction temperature observed for all experiments was 5°C. The reaction time refers to the length of the experiment starting after the still temperature reached the specified value. In this study, the reaction temperature range considered was 370–420°C, the maximum reaction

time was 45 min, and the initial polystyrene charges varied from 30 to 480 g.

The liquid fractions (condensed volatiles at room temperature) obtained in the collection flasks and cold trap were analyzed by gas chromatography (Hewlett Packard 5890A with a flame ionization detector) and gas chromatography–mass spectroscopy (Varian 3500 gas chromatograph with capillary column and Finnigan 700 mass spectrometer with ion trap detector). Cryoscopy and nuclear magnetic resonance (NMR) were used to determine the molecular weight of the residue. The cryoscope used was Cryette WR, model 5009, with bromoform as the solvent. The NMR analysis was performed using a Varian XL-300 NMR spectrometer.

Results

Two types of products were recovered and weighed after each experiment. These were the condensed volatile fraction, or liquid fraction, in the collection flasks and the residue in the reaction vessel. Mass balances are shown in Table I. On average, the relative losses were equal to 3.7% for experiments with an initial charge of 30 g, 1.6% for a charge of 60 g, 0.9% for 120 g, and 0.11% for an initial charge of 480 g of polystyrene (PS). The average absolute

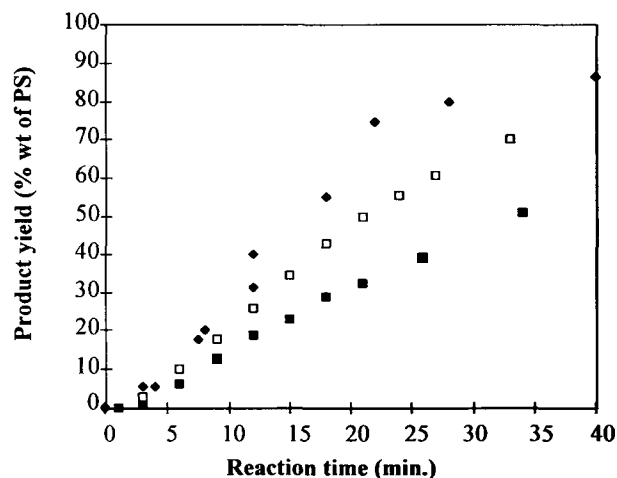


Figure 1 Liquid yield as a function of time for different temperatures: (■) 368°C; (□) 387°C; (◆) 394°C.

loss was about 0.93 g and was independent of the size of the initial charge.

Liquid Products

The total liquid yield from the various experiments is listed in Table I. Figure 1 shows the liquid yield as a function of reaction time with different melt temperatures (368, 387, and 394°C). Figure 2 shows the liquid yield as a function of the melt temperature and initial charge of polystyrene (30, 60, 120, and 480 g) for a reaction time around 30 min.

All the major components in the liquid products were identified. Styrene, styrene dimer, styrene trimer, toluene, α -methylstyrene, ethylbenzene, and 1,3-diphenylpropane account for more than 94 mol % of each of the liquid fractions obtained.

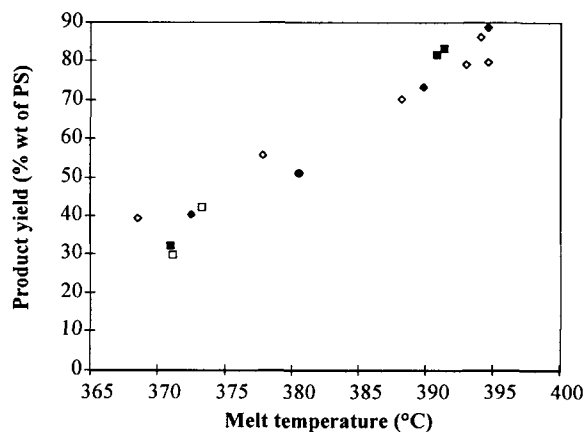


Figure 2 Liquid yield as a function of temperature for 30 min reaction time: (□) 30 g; (■) 60 g; (◇) 120 g; (◆) 480 g.

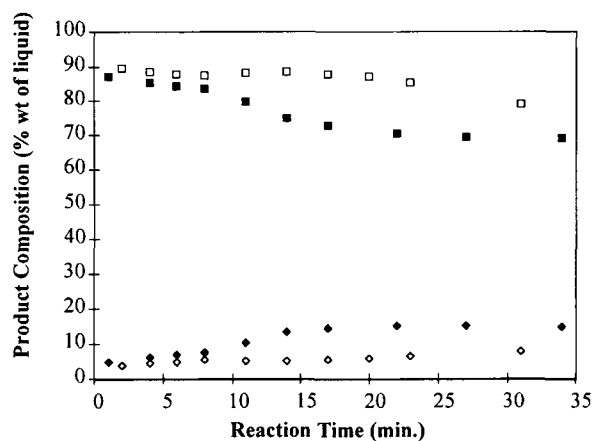


Figure 3 Liquid composition as a function of time at different temperatures: (□) styrene at 381°C; (■) styrene at 395°C; (◇) dimer at 381°C; (◆) dimer at 395°C.

Figure 3 shows the change in composition of the liquid product as a function of the reaction time at two temperatures (381 and 395°C). The components shown are styrene and styrene dimer, which were the most abundant components. The composition in each case is the fraction of the component in the total liquid collected up to a particular time. The smallest styrene concentration obtained was about 70% (wt of styrene/wt of liquid product). It can also be seen that the styrene concentration was lower and the dimer concentration was higher at higher temperature.

The cumulative concentration of styrene monomer and dimer was plotted as a function of melt or reaction temperature, for two different charges (120 and 480 g), in Figure 4. The compositions indicated for each compound are the fraction in the total liquid

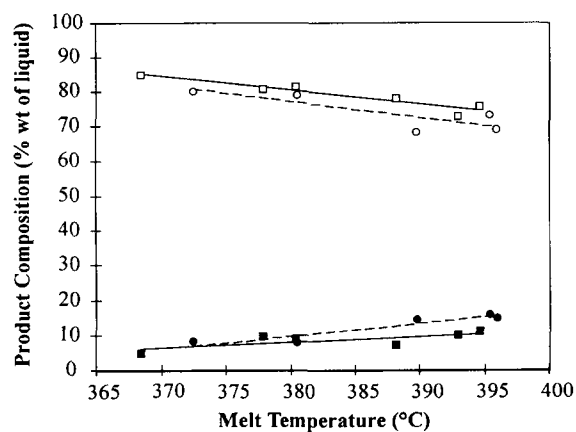


Figure 4 Liquid composition as a function temperature: (□) styrene 120 g; (○) styrene 480 g; (■) dimer 120 g; (●) dimer 480 g; (---) regression 120 g; (--) regression 480 g.

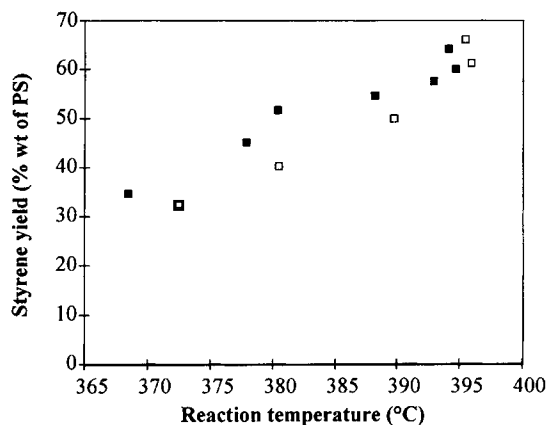


Figure 5 Styrene yields as a function of temperature for 30 min reaction and for different charges: (■) 120 g; (□) 480 g.

collected in a complete run. These represent the concentration of product that would have been collected if a single collection vessel was used for the entire reaction.

Figure 5 shows the styrene yield (wt of styrene/wt of initial PS) as a function of reaction temperature for a reaction time of 28 to 34 min for different charges (120 and 480 g). The maximum styrene yield observed was 67% after reacting 480 g of polystyrene for 34 min at 395°C.

Residue

The data for the amounts of residue remaining in the reaction vessel at the end of each run are tabulated in Table I. The values of residue yield (wt of residue/wt of initial PS) versus melt temperature for different times and charges are shown in Figure 6.

Figure 7 gives the molecular weight of the residue, measured by cryoscopy, as a function of the liquid yield.

DISCUSSION

Material Losses

The losses from the system were negligible as well as consistent and reproducible among experiments. The magnitude of these losses seems to be independent of reaction charge, temperature, and time, which implies that the losses are not due to the formation of noncondensable gases. Otherwise, the losses would be proportional to the reaction charge. In fact, the losses seem to depend on sys-

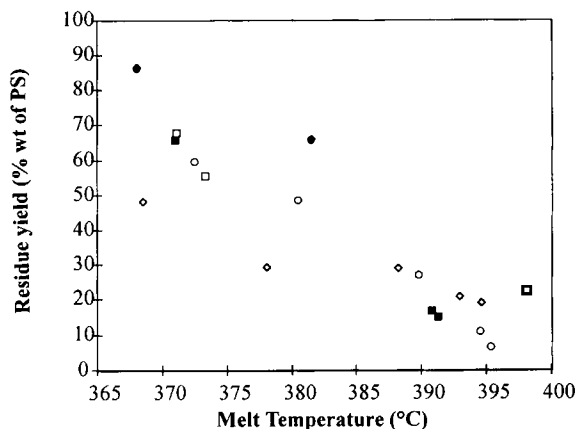


Figure 6 Residue yields as a function of temperature for 30 min reaction and for different charges: (□) 30 g; (■) 60 g; (◇) 120 g; (◆) 120 g, 9–12 min; (○) 480 g.

tem design. Losses are probably due to residual product in the system since not all the liquid could be recovered, as some material was left in the glass connections, etc.

Liquid Products

Previous work^{5,7,9,11,12} has indicated that the yield of the liquid product increases with an increase in temperature. This is supported by the results of this work (Fig. 2). The size of the initial charge of polystyrene in the reactor did not have a significant effect on the yield of liquid products (Fig. 2).

The scale used in this work was orders of magnitude larger than the scale used by previous researchers, since most of the literature data were based on experiments with thin films. To compare

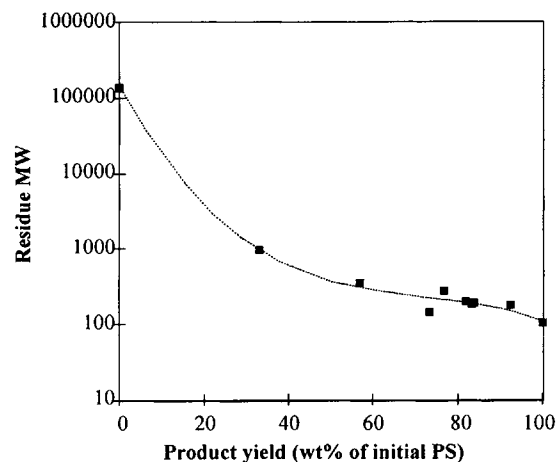


Figure 7 Cryoscopic molecular weight of residue as a function of liquid yield (■) measured, (--) fitted.

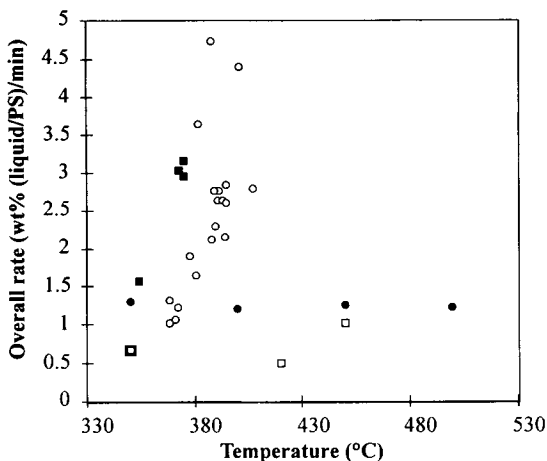


Figure 8 Overall rate of liquid production as a function of temperature from different sources: (■) Madorsky,⁵ (□) Ide et al.,⁹ (●) Ide et al.,⁷ (○) this work.

the quantity of liquid produced by thermolysis of polystyrene in the current work with results reported in the literature, the overall rate of liquid production, as a function of temperature, was evaluated (Fig. 8). In general, this work resulted in comparable or larger amounts of the liquid fraction per unit time. A similar observation can be made, if only the amount of recovered styrene is considered, instead of the total liquid produced. The conversion rates obtained in this work are comparable or superior to values reported in previous work done on a smaller scale and at higher temperatures (350–1200°C).^{2-5,7,9}

Although overall yield is important, it is also important to consider the quality of the condensate. Styrene yield appears to depend on reactor scale (Fig. 5) because of the variation in the quality of the liquid product. In earlier studies, large amounts of dimer and trimer (as high as 25% of each) were obtained in a mixture with the styrene recovered in the condensed liquid fraction.^{2,3,5-10} In this work, the quality of the condensed volatiles (i.e., styrene concentration) is much better than any of the earlier reports (Fig. 9).^{4,5,7,9,13} This is true at all reaction temperatures and at all times throughout the reaction.

An obvious application for the recovered liquids is to complete the cycle by polymerization to form polystyrene. In such a case, the dimers and trimers of styrene could be useful in the mixed feedstock. The second largest component in the product was the dimer. If the styrene, dimer, and trimer concentrations are added together, then the total would account for 85 to 95% (wt % of liquid) of the product

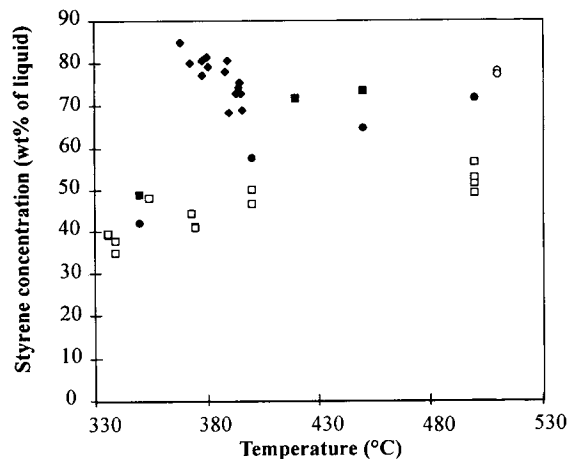


Figure 9 Styrene concentration as a function of temperature from different sources: (■) Ide et al.,⁹ (□) Madorsky,⁵ (●) Ide et al.,⁷ (○) Ohtani et al.,¹³ (◆) this work.

(Fig. 10) and all of this could be suitable for polymerization.

It has been suggested that the dimer is formed, in the reaction zone, by combination of the newly formed monomer units.¹⁴ Therefore, a longer residence time should cause a decrease in the amount of monomer, because it is converted to dimer. This is consistent with the results of the present work. Although the cumulative concentration of styrene in the liquid product is high, there is a decrease in quality with reaction time (e.g., Fig. 3). After 35 min, the concentration of the side products and oligomers becomes appreciable.

In Figures 4 and 9, it is seen that by increasing the temperature from 368 to 395°C, the styrene concentration decreased from 85 to 75% (wt styrene/wt liquid) for the smaller reactor (120 g) and from

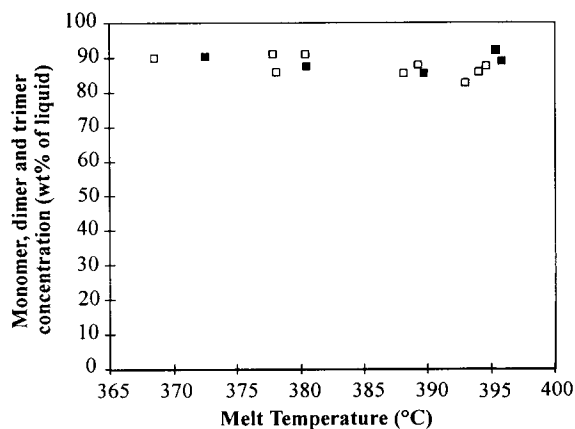


Figure 10 Summation of monomer, dimer and trimer concentration of styrene as a function of temperature with different initial charges: (□) 120 g; (■) 480 g.

80 to 68% for the larger reactor (480 g). An increase in dimer concentration, from around 5 to 10–15%, was observed for the same 27°C increase in temperature. Therefore, the size of the initial polystyrene charge in the reactor appears to influence the concentration of styrene or dimer obtained in the liquid fraction. The styrene concentration was about 5% lower for the larger charge in the temperature range studied. The dimer concentration was 5% higher for the larger charge at the higher melt temperatures, but it was not affected by the size of charge at the lower temperatures. The liquid products from side reactions (i.e., toluene, α -methylstyrene, ethylbenzene, and 1,3-diphenylpropane) were produced in concentrations which were independent of the temperature range studied. They did not appear to be affected by oligomerization reactions after being formed in the reaction vessel.

The decrease in styrene concentration at higher temperatures may be explained as follows. When higher temperatures (and/or reduced pressures) are used, larger quantities of the larger, less volatile fragments are obtained in the liquid fraction. On the other hand, at lower temperatures, the less volatile dimer (Fig. 4), trimer, etc., tend to remain in the reaction vessel. The smaller monomer molecules are more volatile. Therefore, they tend to be dominant in the vapor space above the reactor, and subsequently they are removed and collected in the product vessel.

An important observation was that although the amount of polystyrene in the initial charge did not affect the quantity of liquid product (Fig. 2), it did affect the quality of the condensed liquid products (Fig. 4). These results may be attributed to the higher evaporation rates in the case of the smaller charges. The net effect is that the styrene monomer produced in the reactor would experience a longer residence time in the larger reactor used in conjunction with the larger charges. Thus, the formation of dimer and trimer was enhanced in the larger batches, and the concentration of styrene in the condensed product was reduced.

Residue

In every case, the amount of residue left after treating polystyrene was small, since most of the product appeared in the liquid fraction. An increase in reaction temperature resulted in a decrease in the amount of residue (Fig. 6). As indicated above, there was no significant variability of liquid yield with different initial charges. Consequently, the residue yield was also independent of initial charge. These

results are comparable to the results reported by other researchers.^{5,7,9,11,12}

The pattern of average molecular weight reduction obtained in this work (Fig. 7) is in good agreement with results reported by previous workers.^{2,3,5-7} The molecular weights decreased rapidly up to 15–20% of liquid product yield, followed by a more gradual decrease. However, the actual molecular weight reduction obtained in this work was greater than levels reported by other workers. The final molecular weight of the residue was only 180 in this work, compared to 5000 reported by other workers.^{2,3,5-7} The work of Ide et al.⁷ has shown that initiation of the depropagating chain reaction yielding monomer occurs both by random scission and at chain ends. Hence, the depolymerization reactions involve a combination of random scission and chain end scission. Therefore, the molecular weight decreases at the same time as monomer is being produced. Initially, the molecular weight decreases rapidly, but as the reaction proceeds, the decrease becomes more gradual because the production of unsaturated chain ends increases, and random scission becomes less important.

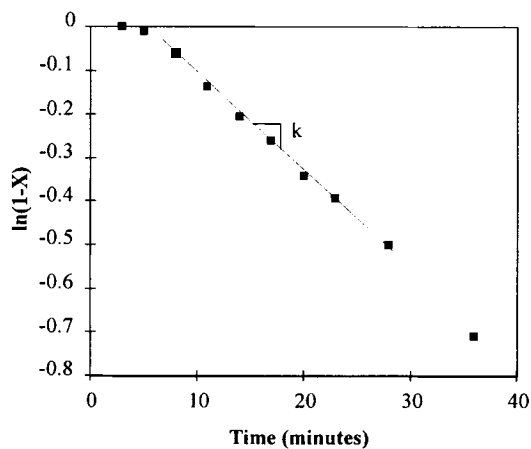
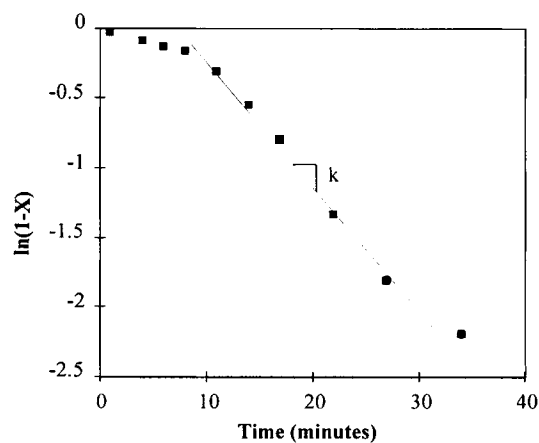
KINETICS

Table II summarizes some of the kinetic data reported by previous researchers and also indicates that polystyrene depolymerization reactions have been described according to zero or first-order kinetics, based on the weight loss, monomer generation, or other characteristic variables. Interestingly, it has been observed that the value of the activation energy is independent of the order of the reaction.¹⁵ In some instances, it has been assumed that zero order prevails at the beginning of the reaction, while first order is applicable in the later stages. At the beginning of the reaction, random scission is dominant, whereas β -scission becomes important later in the reaction.^{15,16} First-order kinetics were found more representative in this work, indicating that random scission is negligible.

Figure 1 shows an example of volatile yield as a function of time for three reaction temperatures. These and all other reaction data were found to fit first-order kinetics. Examples of plots of $\ln(1 - X)$ versus reaction time (where X is the volatile yield) are shown in Figures 11 and 12. In most cases, there was evidence of a short initial anomaly, which could be attributed to random scission or heatup effects. However, it is possible to ignore this early part for a first-order kinetic treatment of subsequent data. It can be seen that for most of the reaction time,

Table II Comparison of Activation Energies for Polystyrene Thermal Degradation

Authors	Conditions	Charges	Activation Energies (kJ/mol)
Jellinek, 1949 ¹⁹	348–398°C up to 180 min vacuum	20 mg	Monomer 187 zero order
Madorsky, 1952 ^b	335–365°C up to 440 min vacuum	5–6 mg	Weight lost 226–243 zero order
Wall et al., 1966 ²²	<350°C vacuum	5–10 mg	Weight lost 205
Richard and Salter, 1967 ²³	260–290°C vacuum	0.1 g	Weight lost 180
Cameron and Kerr, 1968 ¹⁷	280–320°C vacuum	0.1 g	205
Kokta et al., 1973 ²¹	40°C/min nitrogen	Up to 3 mg	Weight lost 138–231 zero first order
Dickens, 1980 ¹⁵	350–405°C nitrogen and vacuum	Up to 50 mg	Weight lost 188 order independent
Cameron et al., 1984 ¹⁸	280–300°C up to 600 min vacuum	Thin films	Molecular weight 227– 232 zero order
Carniti et al., 1989 ²⁴	350–420°C up to 8000 min vacuum	200 mg	Free radical 185 first order
Carniti et al., 1991 ²⁰	330–410°C up to 60 min nitrogen	200 mg	Weight lost 195 first order
Marc, 1992 ¹¹	330–410°C up to 60 min nitrogen	3 g	Monomer 181 first order
This work	365–395°C up to 40 min nitrogen	120–480 g	Volatile 166.5 first order

**Figure 11** First order model, $\ln(1 - X)$ versus reaction time, at $T = 368^\circ\text{C}$, initial charge of 120 g.**Figure 12** First order model, $\ln(1 - X)$ versus reaction time, at $T = 396^\circ\text{C}$, initial charge of 480 g.

the first order model provides an excellent fit of the data.

The slopes of the plots of $\ln(1 - X)$ versus reaction time gave the rate constants (k) for the different temperatures. The maximum slope was employed, in order to avoid the heat-up stage and to concentrate on data in the β -scission region. The values of k are reported in Table III. The Arrhenius plot of $\ln k$ versus $1/T$ is given in Figure 13, where T is the absolute reaction temperature. The activation energy was found to be 166.5 kJ/mol ($R = 0.896$).

The activation energy obtained in this work is comparable with previously reported values^{6,11,15,17-25} as shown in Table II. Depolymerization of polystyrene activation energies varied between 138 and 243 kJ/mol. They show much variation because the values depend on a number of factors, such as, purity of initial polymer, method of preparation, molecular weight, heating rate, set up of the apparatus, conversion and mechanism applied to the polymer degradation, and hence the method of treating the data. The activation energy obtained in this work should be more reliable because of the larger initial charge used. With a larger charge, larger volatile samples are collected, therefore reducing relative errors in measurement of weight and concentration. Moreover, larger samples provide the opportunity to follow the generation of product with time and to obtain more accurate analysis of the product as a function of time.

CONCLUSION

Under the conditions employed in this study, polystyrene can be thermally treated in order to obtain

Table III Rate Constants for Experiments

Temperature (°C)	Charge (g)	k
368.5	120	0.0226
377.9	120	0.0476
380.4	120	0.0542
388.2	120	0.0424
389.3	120	0.0492
393.0	120	0.0609
394.1	120	0.0827
394.7	120	0.0629
395.9	480	0.0984
395.4	480	0.0982
389.8	480	0.0568
380.5	480	0.0365
372.5	480	0.0214

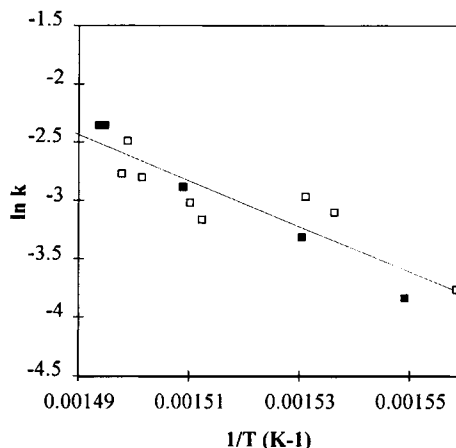


Figure 13 Arrhenius plot for volatile yield with melt temperatures and different charge: (□) 120 g; (■) 480 g.

styrene monomer, dimer, and trimer as the main products. High conversions of polystyrene to styrene (up to 70% styrene yield) were obtained at moderate conditions (368–395°C, nitrogen atmosphere). Thermolysis was achieved using an initial charge, which was several orders of magnitude larger than charges reported in the literature, but yielding comparable results. The conditions used generated a better quality product than that reported for reactions at higher temperatures. The concentration of side products could be further reduced by using shorter reaction times. Only a small amount of residue remained in the reactor, but even this had a low molecular weight. The kinetic analysis supports the assumption of first-order kinetics based on the rate of volatile generation. The estimated activation energy was 166 kJ/mol, which is in the range of other values reported in the literature.

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