CONF-950801--21

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Volume 40, No. 3
Preprints of Papers Presented at the
210th ACS National Meeting
Chicago, IL
August 20-25, 1995

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# EFFECT OF TETRALIN ON THE DEGRADATION OF POLYMER IN SOLUTION

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Keywords : polymer, hydrogen donor, thermal degradation, continuous kinetics, solvent effect

## ABSTRACT

The effect of a hydrogen-donor solvent tetralin on thermal degradation of poly(styrene-allyl alcohol) in liquid solution was investigated in a steady-state tubular flow reactor at 1000 psig at various tetralin concentrations, polymer concentrations, and temperatures. The experimental data were interpreted with continuous-mixture kinetics, and rate coefficients determined for the specific and random degradation processes.

## Introduction

Thermolytic degradation of polymers is similar in some respects to other important thermal decomposition processes like petroleum cracking and coal thermolysis. All these processes involve complex mixtures, both as reactants and as products. Polymer degradation usually occurs in a polydisperse mixture, and observing the temporal change of the molecular weight distribution (MWD) caused by degradation affords a means to test kinetic models. Due to the advance of technology in analytical instrumentation, dynamic MWD data can be obtained by gel permeation chromatography (GPC). A continuous-mixture approach is applicable for these cases, since it is based on mass balance equations that govern the temporal change of a distribution function (Aris and Gavalas, 1966; Cheng and Redner, 1990). This approach has been used for a theoretical discussion of polymer degradation (Ziff and McGrady, 1985,1986), for the kinetics of reactions in reversible oligomerization (McCoy, 1993), as a model for coal liquefaction (Prasad et al., 1986), and for coal thermolysis (Wang et al., 1994). Recently, Wang et al. (1995) measured the rates of specific and random scission for the degradation of poly(styrene-allyl alcohol) in t-butanol using the continuous-mixture approach.

There is little information of the effect of hydrogen-donor solvents on the degradation of polymer in solution. Sato et al. (1990) investigated the solvent effect on the thermal degradation of polystyrene at 300-450 C and 2 MPa. They observed that solvents with higher hydrogen donating capability produced less conversion of polystyrene. These experiments indicated that the degradation behavior, and the conversion of the polymer are affected by the solvents. Murakata et al. (1993) investigated the effect of hydrogen-donor solvents on the degradation of poly-α-methylstyrene and observed that there was no effect of the solvent on the degradation mechanism and the conversion of the polymer. The effect of hydrogen-donor solvents has been extensively investigated for coal liquefaction. The literature on this subject, including generally accepted pathways for hydrogen transfer from a donor solvent, was summarized by Chawla et al. (1989).

The objective of this study was to investigate the effect of the hydrogen-donor solvent, temperature, and residence time on the degradation of the poly(styrene-allyl alcohol). The experimental data was obtained by passing the polymer solution through a steady-state flow reactor, and analyzing the products using HPLC-GPC. Continuous kinetics ideas were employed to interpret the experimental data and fundamental data.

## Experiments

The polymer used in this study was poly(styrene-allyl alcohol) (Polysciences, Inc.) of number-average molecular weight 1100. The polymer was pretreated to remove components in the lower molecular weight range, which would interfere with the analysis of the product peaks. A detailed explanation of the pre-treatment is given by Wang et al. (1995). The polymer was pre-treated by dissolving 50 grams of the polymer in 500 ml of t-butanol. The polymer solution was continously stirred using a magnetic stirrer and heated to 40 C on a heating plate. A volume of 1350 ml of distilled water was added drop by drop to this polymer solution. The high molecular-weight polymer precipitated and settled at the bottom. The dried precipitate was blanketed under nitrogen in a closed bottle to avoid oxidation. The MW of the treated polymer was 1640

The experiments were carried out at high pressure, 1000 psig (6.8 MPa), to prevent the vaporization of the solvent, 1-butanol, at high temperatures and to ensure that the reaction of the polymer occurs in the liquid phase. The polymer solution was prepared by dissolving the polymer in 1-butanol at a known concentration in the range of 1-4 g/L. The polymer solution flows through the reactor, a water cooled heat exchanger, two pressure reduction valves placed in series, and finally exits through a rotameter. The flow rate (and hence the residence time of the fluid in the reactor) is controlled by the rotameter. Degradation experiments were carried out at three different polymer concentrations, four different temperatures, and four different tetralin concentrations to study the effects of these parameters on the rate of polymer degradation. At each condition, the experiment was conducted at four different residence times (i.e., four different flow rates). Since the flow rates were measured at ambient conditions, the residence times for each temperature were corrected with the density calculated from Lee-Kesler equation (Lee and Kesler, 1975). After reaching steady state, two 20 ml samples were collected at each residence time for the HPLC-GPC analysis. Experiments of 1-butanol and 10 to 50% tetralin, in the absence of polymer, were conducted at 150 to 200 C to investigate interactions between the solvents. The GPC analysis of samples from these experiments indicated no products.

The significant difference of these experiments compared to pyrolysis experiments in gas or vacuum is that all the reactions take place in the liquid phase, and thus the residence time for both the reactants and products is the same. Further, the mild temperatures limit the amount of random chain scission and eliminate repolymerization.

Before analyzing the effluent sample by GPC, one needs to concentrate the sample and dissolve the reactant and products in tetrahydrofuran. Hence, 20 ml of the effluent sample is concentrated to 4 ml by evaporating the 1-butanol under vacuum at 353 C. The molecular weight distribution of the effluent samples was determined by gel permeation chromatography using PLgel columns (Polymer Labs) in a high performance liquid chromatograph (Hewlett Packard 1050). For this purpose, two columns packed with crosslinked poly(stryene-divinyl benzene) of 100 and 500 A pore size, respectively, were used in series after a guard column. Tetrahydrofuran (THF, HPLC grade, Fisher Chemicals) was continuously pumped through the columns at a constant flow rate of 1 ml/min. A sample of 100 microliters was injected at the start of each run and the ultraviolet detector was used to measure the absorbance of the compounds in the effluent samples. The wavelength of 254 nm was chosen since this wavelength provided the maximum absorbance of the reactant and products. The molecular weight corresponding to the retention time in the columns was calibrated with polystyrene samples obtained from Polymer Lab. The calibration procedure is described in detail by Wang et al. (1995).

## *Mechanism*

The mechanism of degradation of polymer is similar to that of Wang et al. (1995). The thermal degradation of the polymer is of two kinds: random scission at any position along the polymer chain, and specific scission leading to specific products. Both types of scissions occur in the degradation of poly(styrene-allyl alcohol), as seen from Figure 1, which is the MWD plotted as concentration distribution (g/L MW) versus Log$_{10}$ MW. The figure shows three distinct peaks in the molecular weight range 100-500 indicating specific scission products. The higher MW range peak shifts to a lower MW range relative to the feed polymer indicating random scission.

Though only three distinct peaks are observed in the figure, we expect the formation of styrene, since it was observed by Wang et al. (1995). The styrene peak should appear at a MW of 104. However, since tetralin and styrene have comparable MW of 132 and 104, respectively, the peaks of these two compounds are superimposed. Lacking a method to distinguish styrene from tetralin, we therefore removed this peak from the chromatogram and its subsequent analysis. The remaining peaks in the effluent chromatograms were approximately of MW 162, 222, and 486, respectively, and are proposed to be the oligomer of an allyl alcohol and a styrene molecule (SA), and an oligomer of two allyl alcohols and one styrene molecule (ASA), and a trimer of SA ($(SA)_3$). Any allyl alcohol (A) produced during the degradation would evaporate during the sample preparation.

## *Theoretical Model*

The theoretical model is similar to the one proposed by Wang et al. (1995). The MWD of the feed polymer is described by a gamma distribution. The parameters of the gamma distribution are obtained by calculating the zeroth, first, and the second moments of the experimental peak. This gamma distribution is used as the initial MWD in the kinetics model.

A continuous mixture can be defined as a mixture of a very large number of different-size polymer molecules, whose distribution can be expressed by a continuous index such as the molecular weight. We consider that all the degradation products are dissolved in solution, that no repolymerization reactions occur, and that the flow reactor can be treated as a steady-state plug-flow reactor. Model equations based on continuous kinetics for polymer degradation were developed by Wang et al. (1995).

## Results and Discussion

For the degradation of poly(styrene-allyl alcohol) in a solvent of pure t-butanol, both random and specific scission of the polymer occurred at 130-200 C and 1000 psig (Wang et al., 1995). However, in the present case of 1-butanol solvent, no degradation of the polymer was observed at these conditions in the absence of tetralin. This suggests that t-butanol was involved in the reaction, possibly as a hydrogen donor. Sato et al. (1990), on the other hand, reported decreased degradation of several polymers in presence of hydrogen donors. These results indicate the significance of the solvent effect in thermolytic degradation reactions, and the importance of continued investigation along these lines.

An experimental MWD and model simulation are presented in Figure 2. As explained earlier, a peak of styrene has been removed since the peak of tetralin is superimposed on it. The three distinguishable peaks, SA, ASA, $(SA)_3$, are the products of specific chain scission. The same products (S, SA, ASA, $(SA)_3$) are produced with either t-butanol or 1-butanol plus tetralin.

The parameters in the model are the parameters of the gamma MWD describing the feed polymer and the rate coefficients for specific and random degradation. The rate coefficients for specific degradation are determined from the equation (Wang et al., 1995):

$$q = k_i\, p\, t \tag{1}$$

where p is the feed concentration (mol/L), t is the residence time, and q is the concentration of the specific product (mol/L). These concentrations are the zeroth moments of their MWDs divided by MW. Since the zeroth moment is the area under the curve, the area of each specific product peak was determined by numerical integration using the trapezoidal rule. The slope of the line gives the rate coefficient for specific degradation, $k_i$. The rate coefficients for random degradation are obtained by fitting the experimental MWD data of random degradation with gamma distribution parameters, using the relationship derived by Wang et al. (1995).

The dependence of the specific and random degradation rate coefficients on the temperature, concentration of the polymer, and concentration of the hydrogen-donor solvent (tetralin) are shown in the Tables 1-3. The rate constants are independent of polymer concentration, confirming that the reactions for both specific and random degradation are first-order. This is consistent with the assumption of Wang et al. (1995).

The activation energies for random and specific degradation are extracted from the temperature dependence of the rate coefficients (Figure 3) and are given in Table 4. The dependence of the rate constants on the concentration of tetralin were modeled by the following equation:

$$k = k_t C_t / (1 + \kappa C_t) \tag{2}$$

where k is the rate constant and $C_t$ is the vol% of tetralin. Parameters $k_t$ and $\kappa$ are obtained by plotting the inverse of the rate versus the inverse of tetralin concentration and are given in Table 5. Tetralin is essential for the degradation of the polymer at this temperature and pressure. A tetralin concentration of 25% produces rate coefficients nearly an order of magnitude higher than the rate coefficients obtained by Wang et al. (1995), who degraded the same polymer using t-butanol without tetralin. However, the activation energies for the specific and random degradation of the polymer by 1-butanol and 25% tetralin are comparable to the activation energies for the specific and random degradation of the polymer by t-butanol.

## Acknowledgement

The financial support of Pittsburgh Energy Technology Center Grant No. DOE DE-FG22-94PC94204, and of the University of California UERG is gratefully acknowledged.

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**Table 1.** Rate coefficients (1/sec) for specific and random degradation of the polymer at various temperatures and at a constant polymer concentration of 2 g/L and a tetralin concentration of 25%.

| Temperature | k for SA ($\times 10^3$) | k for ASA ($\times 10^3$) | k for $(SA)_3$ ($\times 10^3$) | $k_r$ ($\times 10^4$) |
|---|---|---|---|---|
| 130 | 1.68 | 2.52 | 3.36 | 0.22 |
| 150 | 1.89 | 3.09 | 4.05 | 2.1 |
| 170 | 3.9 | 4.68 | 5.85 | 18 |
| 200 | 5.95 | 6.43 | 7.14 | 130 |

**Table 2.** Rate coefficients (1/sec) for specific and random degradation of the polymer at various polymer concentrations and at a constant temperature of 150 C and a tetralin concentration of 25%.

| Polymer Conc. (g/L) | k for SA ($\times 10^3$) | k for ASA ($\times 10^3$) | k for $(SA)_3$ ($\times 10^3$) | $k_r$ ($\times 10^4$) |
|---|---|---|---|---|
| 1 | 1.73 | 3 | 4.2 | 2.3 |
| 2 | 1.89 | 3.09 | 4.05 | 2.1 |
| 4 | 1.75 | 2.89 | 3.9 | 2.3 |

**Table 3.** Rate coefficients (1/sec) for specific and random degradation of the polymer at various tetralin concentrations and at a constant temperature of 150 C and a constant polymer concentration of 2 g/L.

| Tetralin Conc. | k for SA ($\times 10^3$) | k for ASA ($\times 10^3$) | k for $(SA)_3$ ($\times 10^3$) | $k_r$ ($\times 10^4$) |
|---|---|---|---|---|
| 5 % | 0.58 | 1.6 | 1.78 | 0.4 |
| 10 % | 0.8 | 2.3 | 2.5 | 1.0 |
| 25 % | 1.89 | 3.09 | 4.05 | 2.1 |
| 50 % | 2.09 | 3.57 | 4.9 | 2.5 |

**Table 4.** Activation energies for specific and random degradation

| Specific Product | Activation energies (kcal/mol) |
|---|---|
| SA | 7.5 |
| ASA | 5.2 |
| $(SA)_3$ | 4.4 |
| Random degradation | 33.1 |

**Table 5.** Parameters for the dependence of rate coefficients of polymer degradation on tetralin concentration.

| Specific Product | $k_t$ ($\times 10^4$) (1/sec/vol%) | $\kappa$ (1/vol%) |
|---|---|---|
| SA | 1.33 | 0.043 |
| ASA | 5.59 | 0.138 |
| $(SA)_3$ | 4.96 | 0.085 |
| Random degradation | 1.07 | 0.012 |

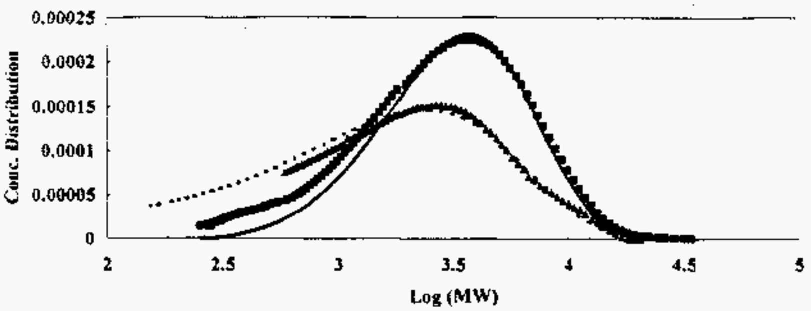

Figure 1. The MWD before and after thermal degradation (■: chromatograph before degradation, —— . Gamma Distribution fit ; ▲ : chromatograph after degradation at 150 C, 25% tetralin, and residence time of 42.51 min. , ...... : Gamma Distribution fit).

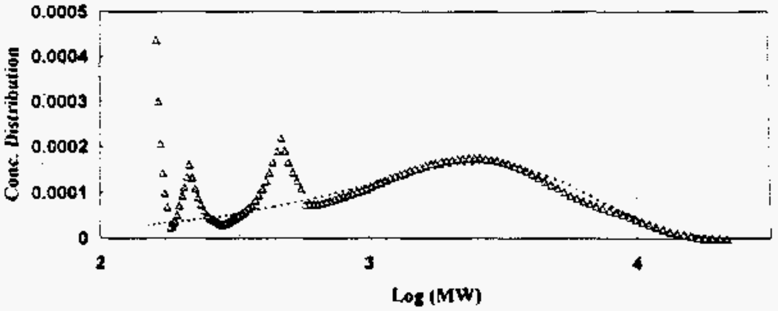

Figure 2. Comparison of experimental results of MWD with model simulation at 150 C, 25% tetralin and at a residence time of 42.51 minutes (Δ . experimental data; ...... : Gamma Distribution fit).

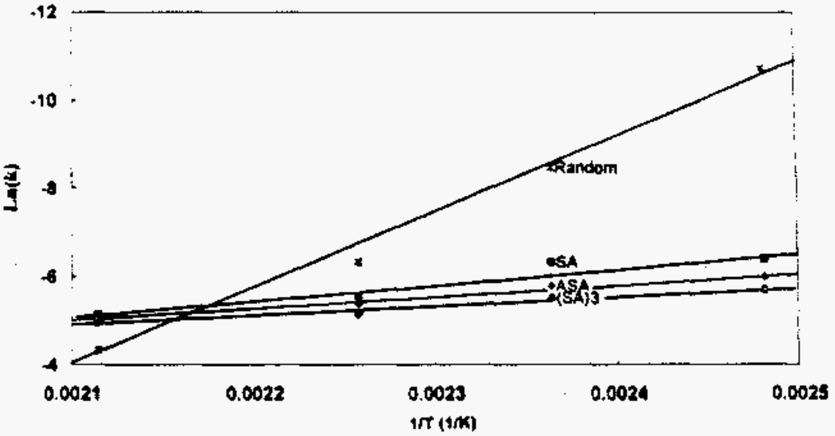

Figure 3. Arrhenius plot of the degradation coefficients versus temperature to determine the activation energies of the specific scission and random degradation.