

## MECHANISTIC MODELING OF THE PYROLYSIS OF ETHYLENE BRIDGED POLYMERS

K.R. Squire, P.R. Solomon, M.B. DiTaranto and R.M. Carangelo

Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108, USA

Recently, Solomon and King reported a tar formation model applicable to the pyrolysis of softening bituminous coals (1). Their theory combined the random cleavage of weak bonds (similar to a concept used by Gavalas and coworkers (2)) with transport of depolymerization fragments by vaporization and diffusion (like Unger and Suuberg (3)). It predicted char and tar yields and molecular weight distributions and provided several insights into the role of donatable hydrogen and the dependence of product distributions on reaction conditions.

The Solomon and King (SK) theory was developed using model polymers which contain functional groups representative of coal structure. Polymers were studied because coal is generally insoluble, heterogeneous, and chemically complex and is, therefore, difficult to use in validating models. Several types of bridging groups between the aromatic rings in these polymers were considered; it was found that ethylene bridges decompose in the same temperature range where coal evolves tar while oxymethylene bridges cleave at temperatures which are too low and methylene bridges at temperatures which are too high (1,4,5). From these studies it's been found that ethylene bridged polymers are quite valuable in elucidating the mechanisms of tar formation since they have simple, well established chemical structures and melt and produce tars under conditions similar to those where softening bituminous coals form tar. Studies on lignins have also shown that cleavage of oxyethylene and ethylene bridges both play important roles in the formation of tar during pyrolysis of lignins (6).

Although the SK tar formation model has been found to provide reasonable predictions for tar and char yields and for the molecular weight distributions of tars, it contains three significant conceptual problems:

- 1) Reaction yields were controlled in this model by an adjustable parameter which determined how many donatable hydrogens were available for capping the arylmethylene radicals formed when ethylene bridges cleave. This parameter has been found to vary with reaction conditions and not predictable a priori.
- 2) The effect of product olefinic bridges on the bond breaking distributions was not included. The presence of unbreakable double bonds in the oligomer chains should make it less likely that monomers and dimers will form.
- 3) It is difficult to extend the SK model to include realistic chemical mechanisms since the actual concentrations of ethylene and olefinic bridges are not monitored. Attempts to correct this problem have led to excessive computer run-times.

In this paper, a revised version of the SK model is presented which can predict product yields and molecular weight distributions directly from initial polymer structures. In this model all three of these problems have been eliminated. In addition, this new model has been solved using Monte Carlo techniques, is more efficient computationally than the SK model, and can potentially be expanded to detailed simulations of extremely complex polymers such as coal. Furthermore, since this model predicts product spectra directly from polymer structures without use of adjustable parameters, it can be used to investigate the validity of alternative pyrolysis mechanisms. Simulations using this model suggest that ipso substitutions by H radicals occur during thermal decomposition of ethylene bridged polymers and that radical recombination reactions play an important role in determining the molecular weight distributions of pyrolysis tars.

## EXPERIMENTAL

Poly(p-xylylene), 1, was purchased from Frinton Laboratories. As a byproduct of di-p-xylylene (p-cyclophane) synthesis, this polymer was very impure and contaminated with the dimer. It was purified by Soxhlet extraction in toluene for two days.

Poly(1,4-dimethylenenaphthalene), 2, as prepared at Iowa State University using an adaptation of Golden's synthesis for poly(dimethylenedurene) (7). This synthesis was accomplished using phenyllithium to couple the bis(bromomethyl) derivatives which were prepared from dimethylnaphthalenes using N-bromosuccinimide and benzoyl peroxide in  $\text{CCl}_4$ . The degree of polymerization (DP), defined as the number of monomer units in a polymer molecule, is estimated to be 64 (MW = 10,000). Additional use of these polymers as models for coal chemistry was recently described by Squires et al. (8).

Several pyrolysis experiments, including slow heating rate and flash pyrolyses, were carried out on these ethylene bridged polymers using an apparatus which employs an electrically heated grid within an infrared cell to provide on-line, in-situ analysis of evolved products by Fourier Transform Infrared (FT-IR) spectrometry. Details of these experiments have been described previously (1,10). Field Ionization Mass Spectrometry (FIMS) were performed at SRI International and have been described by St. John and coworkers (11).

## THEORY

The original SK tar formation model considered the molecular weight distribution,  $Q_i$  in the reacting polymer and the molecular weight distribution,  $N_i$  of the tar, where  $Q_i$  and  $N_i$  are the molar quantities of the polymeric component with  $\text{DP}=i$  in the reacting polymer and in the tar. The rate of change of  $Q_i$  was written as:

$$dQ_i/dt = (dF_i/dt) - (dB_i/dt) - (dN_i/dt) \quad (1)$$

where  $dF_i/dt$  was the rate of formation for the component with  $\text{DP}=i$  from the decomposition of components with  $\text{DP} > i$  in the reacting polymer;  $dB_i/dt$  was the rate of disappearance by decomposition of the component with  $\text{DP}=i$  in the reacting polymer; and  $dN_i/dt$  was the rate of transport of fragments with  $\text{DP}=i$  from the particle as tar or gas.

The terms of  $dF_i/dt$  and  $dB_i/dt$  were the rate of creation and destruction of oligomers with  $\text{DP}=i$  through the cleavage of weak bonds. The cleavage of these weak bonds was assumed to be a first order process with a rate constant  $k$ , i.e., the rate at which bonds break was  $k$  times the number of breakable bonds. It was further assumed that all bonds in a given oligomer were equivalent and were breakable. Thus, since there were  $(i-1)$  bonds in the polymeric component with  $\text{DP}=i$ , and the breaking of any one of them would remove that component from the distribution parameter  $Q_i$ , the rate of destruction for the component  $i$  was written as

$$dB_i/dt = (i-1)kQ_i \quad (2)$$

Similar arguments were also used to write down the rate at which component  $i$  was created from oligomers with  $\text{DP}=j > i$  (see Eqs. 3 and 4 of Ref. 1).

From Eqs. 1 and 2 it can be seen that this model only kept track of the molar quantities of tar and polymer oligomers; the actual concentrations of ethylene or olefinic bridges were not monitored. Instead, it was assumed that a  $\text{DP}=i$  oligomer always contained  $(i-1)$  breakable ethylene bridges.

Since weak ethylene bridges were not explicitly removed when they donated hydrogens to "cap" free radicals, another parameter was necessary to determine the extent of reaction. In the SK model, the extent of reaction was controlled by an adjustable parameter,  $F_{\text{pqb}}$ , defined as the fraction of weak bonds (ethylene bridges) whose resulting free radicals could be stabilized by donatable hydrogens. The total number of cleaved bonds was continuously monitored during a pyrolysis simulation and, when it

got larger than  $F_{pdb}$ , the reaction was said to have completed. Thus,  $F_{pdb}$  directly controlled char and tar yields in the original SK model. Unfortunately, this parameter varied from polymer to polymer and also depended upon reaction conditions. It could not be predicted from just a knowledge of the polymer's structure and reaction conditions.

This formulation for tar formation led to simple equations which were easy to solve and also produced reasonable predictions for tar molecular weight distributions (1,4). However, it is clearly incorrect to assume that a  $DP=1$  oligomer always contains (1-1) breakable bonds, because as the depolymerization reaction proceeds, many ethylene bridges are converted to olefinic bridges following their use as hydrogen sources. Towards the end of tar formation it is entirely possible that a  $DP=1$  oligomer would contain no breakable ethylene bridges. In a more realistic model the actual numbers of both olefinic and ethylenic bonds need to be monitored.

To take into account the effect of olefinic bridges it is necessary to keep track of the number of oligomers with no double bonds, with 1 double bond, with 2 double bonds, etc. This means that for each  $DP=m$  oligomer, the concentrations of  $m$  double bond combinations need to be monitored. To follow the depolymerization of a polymer with initial chain length  $n$ , the concentrations of approximately  $(n^3)/2$  different oligomers need to be followed. The time evolution of each of these oligomer concentrations is described by a separate differential equation. Thus, even this simple model improvement leads to a dramatic increase in the computational effort necessary to solve it! To avoid solving these complex networks of coupled differential equations, a new approach to the modeling of tar formations has been developed.

The essential problem of modeling polymer pyrolyses is simply that each modified oligomer is technically a new chemical species. As more complex oligomers are treated, the number of differential equations describing the time evolutions of these oligomers rapidly proliferates and becomes computationally unmanageable. An alternative approach is to use Monte Carlo modeling techniques.

In a Monte Carlo simulation, separate differential equations for the concentrations of individual modified oligomers are not explicitly solved. Instead, a small representative sample of polymer molecules is symbolically constructed in the memory of a computer. A bonding array is used to keep track of each monomer's identity, which substituents are attached to a given monomer, and how the monomers are connected to each other. The first four columns of this array are pointers indicating how monomers are attached to other monomers or substituents; the next four columns indicate the bonds involved in each attachment; and the last keeps track of each monomer's identity (e.g. benzene or naphthalene rings). A separate row is stored in this array for each monomer included in the simulation. Pyrolysis is simulated by statistically changing the bonding patterns stored in this array according to the kinetic and vaporization rate laws of the tar formation model.

In the current configuration, 25-40 polymer molecules can be simulated during a single run so that approximately 1200 ethylene bridges are being decomposed. Each monomer can be connected to as many as four other monomers or ring substituents. Up to fifty different monomers and twenty bond types can be used to construct the polymers for each simulation. For example, unreacted polymer 1 would be simulated using only benzene monomers, ethylene bridge connections between monomers, and methyl end groups for the terminal monomers of each polymer chain. As the pyrolysis simulation proceeded, new bond types would be introduced (e.g. olefinic bridges between monomers) to describe the gradual decomposition of the polymer.

Vaporizations are simulated by removing an oligomer from the computer's memory, by adding its mass to the running tar yield, and by putting a count in the appropriate bin of a file describing the molecular weight distribution of the evolving tar. For example, when a molecular weight 312 trimer from polymer 1 vaporizes (composition: 3 benzene monomers, 2 terminal methyl groups, 1 olefinic bridge, 1 ethylene bridge), all its pieces would be removed from the bonding arrays, 312 atomic mass units would be

added to the tar yield, and a single count would be added to bin 312 of the tar's molecular weight distribution file.

A typical simulation proceeds as follows: A series of random numbers are chosen to determine which "global" reactions occur. In the current configuration, oligomer evaporations and a complex network of reactions describing the decomposition of ethylene bridges are the "global" reactions. The random numbers are compared with normalized reaction velocities to see if the pending reaction will occur. If the random number is larger than the velocity, then the program branches to a subroutine which performs the appropriate reaction "chemistry" on the oligomer arrays. If the random number is smaller than the velocity, then the next reaction is tested until the list is exhausted. After every twenty iterations through the reaction list, time is incremented using the observed concentration changes and reaction velocities. The simulation continues until a preset time is reached or no further changes in the bonding arrays are occurring.

The reactions which have been included in the mechanism for ethylene bridge decomposition are presented in Fig. 1. In Step 1, ethylene bridges homolytically cleave to form two arylmethylene radicals. This step is assumed to be rate-limiting and its kinetic rate constants are in good agreement with predictions based upon thermochemical kinetics calculations (5).

The arylmethylene radicals can then react in six ways: they can abstract hydrogens from unreacted ethylene bridges (Step 2) or butylene bridges (Step 3), they can substitute for ethylene bridges (Step 4) or aromatic methyl groups (Step 5), and they can recombine with other arylmethylene radicals (Step 6) or with ethylene bridge radicals (Step 7). Which of these pathways occurs during a given pass through the "chemistry" subroutine is determined by comparing a random number with a set of normalized branching probabilities. In the current program fixed branching probabilities are used to determine how the decomposition proceeds, but in a future model we plan to calculate the individual velocities of the reactions in Fig. 2 using rate constants and steady state radical populations. In these simulations, branching probabilities will be the normalized ratios of these reaction rates.

Steps 2-5 lead to new radicals which continue to react while 6 and 7 produce stable bonds and terminate the reaction. The butylene bridge radicals of Step 3 are assumed to spontaneously decompose via a  $\beta$ -elimination reaction into an ethylene bridge radical and an olefinic bridge, Step 11. The arylethyl and methyl radicals produced in Steps 4 and 5 are assumed to stabilize via abstraction of hydrogens from unreacted ethylene bridges, Steps 15 and 16. Thus, all four of the reactive pathways for arylmethylene radicals eventually form an ethylene bridge radical.

In this model, ethylene bridge radicals are allowed to react in three ways: they can disproportionate (Step 8), they can recombine to form butylene bridges (Step 9), or they can decompose via a  $\beta$ -elimination reaction into a hydrogen radical and an olefinic bridge (Step 10).

The hydrogen radicals formed in Step 10 can then react in three ways: they can abstract hydrogens to stabilize (Step 12), they can substitute for ethylene bridges (Step 13), or they can substitute for aromatic methyl groups (Step 14). The arylethyl and methyl radicals formed in Steps 13 and 14 are assumed to stabilize via hydrogen abstractions from unreacted ethylene bridges, Steps 15 and 16. Thus, all the reactions of hydrogen radicals lead to the formation of new ethylene bridge radicals to replace the ones lost when Step 10 formed H radicals.

This complex network of reactions is an extension of the mechanisms proposed by Stein (12) and Poutsma (13) for the pyrolysis of diphenylethane. In the current Monte Carlo model, these reactions are carried out on the polymer bonding arrays each time the simulation determines that an ethylene bridge has decomposed. Figure 2 is a flow diagram which shows how the "chemistry" is carried out by the simulation.

as predicted by the SK model. With 90% recombination of end radicals (Fig. 5c) the increase in high molecular weight oligomer counts is sizeable, while recombinations of bridge radicals (5d) make high molecular weight oligomers less abundant.

Comparing the experimental FIMS data for polymer 1, Fig. 5a, with these simulated spectra it is apparent that even higher end radical recombination frequencies are necessary to reproduce this polymer's uneven oligomer patterns. Clearly, however, recombinations of bridge radicals can not be contributing to the observed maximum in this polymer's FIMS data.

To understand why recombinations of end radicals lead to increased populations of high molecular weight oligomers while recombinations of bridge radicals decrease their populations, we need to consider the counting statistics for each type of radical: for end radicals the probability of a radical occurring on an oligomer is independent of chain length (they occur only at the ends of chains) while for bridge radicals the probability of a radical occurring on an oligomer increases with chain length (more bridges increase the number of sites where a radical can occur).

When two end radicals recombine, oligomers can be lost in the formation of larger oligomers or they can be formed from smaller ones. For the DP = i oligomer, the terms appearing in the time derivative would be:

$$R_i = \sum_{j=1}^{i-1} f_{i-j} f_j - f_i \sum_{j=1}^a f_j \quad (3)$$

Here the f's are the probabilities of forming each radical oligomer and a is the largest oligomer which can recombine. The first term is due to formations from smaller oligomers and the second is due to losses in the formation of larger oligomers. From the SK tar model we know that roughly equal numbers of each size oligomer are formed by the homolytic bond cleavage reaction (Fig. 5b), so we conclude that  $f_i$  is, to first approximation, a constant and is independent of the degree of polymerization. Putting  $f_i = c$  into equation 3 the result is:

$$R_i = c^2(i-a-1) \quad (4)$$

Thus, recombinations of end radicals decrease the rate of formation of all oligomers but they affect the time derivatives of large radicals less than those of small ones. The net effect is a shift in the tar mass spectrum towards longer chain length oligomers.

When end radicals recombine with bridge radicals, a different result is found. Now the terms appearing in the time derivative are products of the probability of finding end radicals, f's, and the probability of finding radical bridges, g's.

$$R_i = \sum_{j=1}^{i-2} g_{i-j} f_j + \sum_{j=2}^{i-1} f_{i-j} g_j - f_i \sum_{j=2}^a g_j - g_i \sum_{j=1}^a f_j \quad (5)$$

The f's are still independent of the degree of polymerization, i.e.,  $f_i = c$ . However, the g's are proportional to the number of bridges in an oligomer or  $g_i = b(i-1)$ . When these probabilities are inserted in Eq. 5, the sums are slightly more difficult but can still be carried out. We find that

$$R_i = bc(i^2 - (3+a)i + 2 + a - \frac{a(a-1)}{2}) \quad (6)$$

This contribution to the time derivatives is quadratic in the degree of polymerization and reaches a minimum at  $i = (a+3)/2$ . For our simulations, recombinations can occur for at least 40 oligomers (the starting degree of polymerization) so this minimum occurs at a DP of at least 21. Inserting  $a = 40$  and some typical values of i into this formula we find:

$$R_1 = -781 bc \quad R_5 = -928 bc \quad R_{10} = -1068 bc \quad R_{15} = -1158 bc \quad (7)$$

Thus, for recombinations between end and bridge radicals, the contributions to the

rates of formation of the oligomers with  $DP < 21$  are all negative and get more negative with increasing chain length. These terms result in the formation of relatively fewer midsized oligomers when these recombinations occur than when no recombinations occur.

Similar calculations for recombinations of two bridge radicals can also be carried out and yield a cubic equation for  $R_1$ . This cubic is negative in the range  $DP = 1$  to 15 and gets more negative with increasing oligomer chain lengths. Thus, recombinations of bridge radicals also result in the formation of relatively fewer midsized oligomers during pyrolysis of these ethylene bridged polymers.

Both kinds of recombination reactions are probably important in pyrolyses of ethylene bridged polymers, lignins, and coals. The maximum in the FIMS data of polymer 1 seems to be caused by recombination of end radicals while rapid mass drop-offs are observed in the FIMS spectra of lignins (6), lignites (1), and ethylene bridged methoxybenzene polymer (5). Examples of these FIMS spectra will be presented during the talk.

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#### REFERENCES

1. Solomon, P.R. and King, H.H., *Fuel*, **63**, 1302, (1984).
2. Gavalas, G. R., Cheong, P. H. and Jain, R. "Ind. Eng. Chem. Fundam.," **20**, 113 and 122 (1981).
3. Unger, P. E. and Suuberg, E. M. "Eighteenth Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, PA, (1981), 1203.
4. Solomon, P.R., "Synthesis and Study of Polymer Models Representative of Coal Structure", Gas Research Institute Annual Report for Contract #5081-260-0582. GRI Accession #GRI-83/0171 (April, 1983).
5. Squire, K.R., Solomon, P.R., DiTaranto, M.B., "Synthesis and Study of Polymer Models Representative of Coal Structure", Gas Research Institute Annual Report for Contract #5081-260-0582. GRI Accession #GRI-84/0083 (May, 1984).
6. Squire, K.R. and Solomon, P.R., "Characterization of Biomass as a Source of Chemicals", NSF Final Report under Contract No. CPE-8107453, (1983).
7. Golden, J.H., *J. Chem. Soc.* (1961), 1604-1610.
8. Squires, T.G., Smith, B.F., Winans, R.E., Scott, R. and Hayatsu, R., "International Conference on Coal Science", Pittsburgh, PA, Proceedings, p. 292, (1983).
9. Golden, J.H., *J. Chem. Soc.* (1961), 3741-3738.
10. Solomon, P. R. and Hamblen, D. G., "Chemistry and Physics of Coal Utilization, AIP Conference Proceedings No. 70, Amer. Inst. Phys., New York (1981), pg. 121.
11. St. John, G.A., Buttrill, S.E., Jr., and Anbar, M., "Field Ionization and Field Desorption Mass Spectroscopy Applied to Coal Research, in "Organic Chemistry of Coal", (Ed. J. Larsen, ACS Symposium Series, 71, pg. 223, (1978).
12. Stein, S.E., "New Approaches in Coal Chemistry", (Ed. Blaustein, B.D., Bockrath, D.C., and Friedman, S.), Am. Chem. Soc. Symposium Ser. 169, Washington, DC, pg. 208, (1981).
13. Poutsma, M.L., *Fuel*, **59**, 335, (1980).

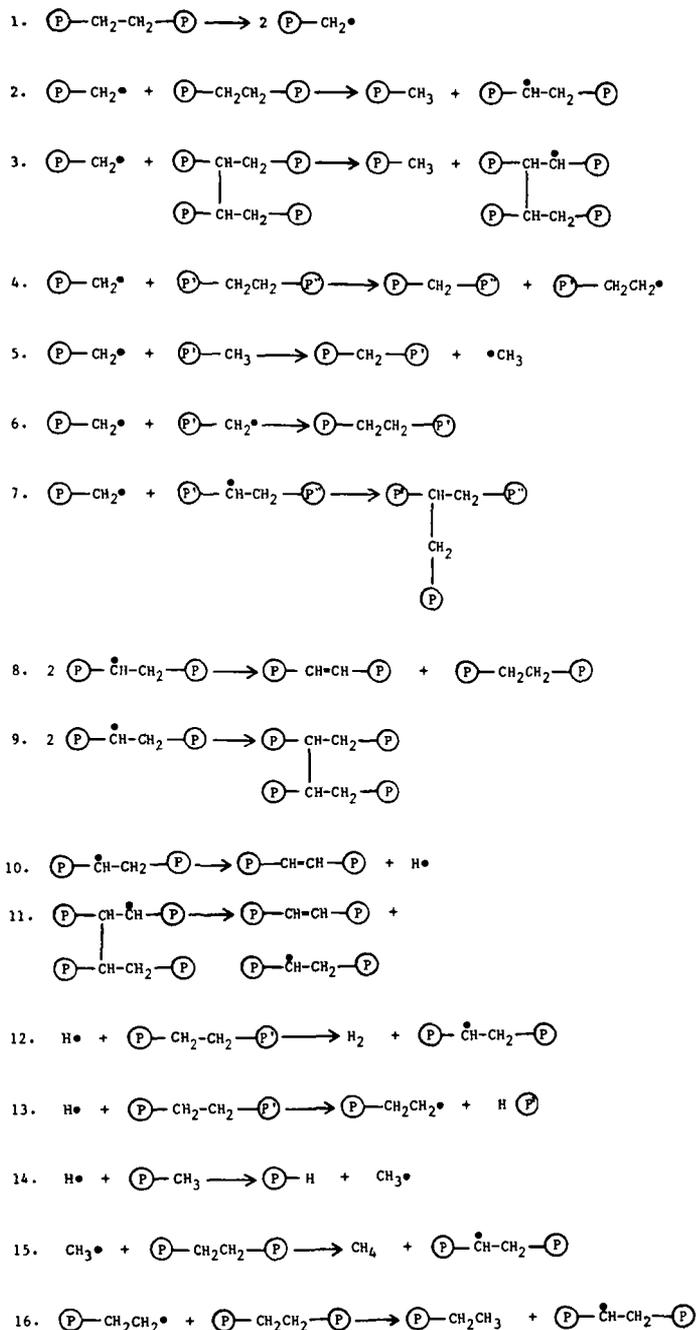


Fig. 1 Proposed Mechanism for the Decomposition of Ethylene Bridges.



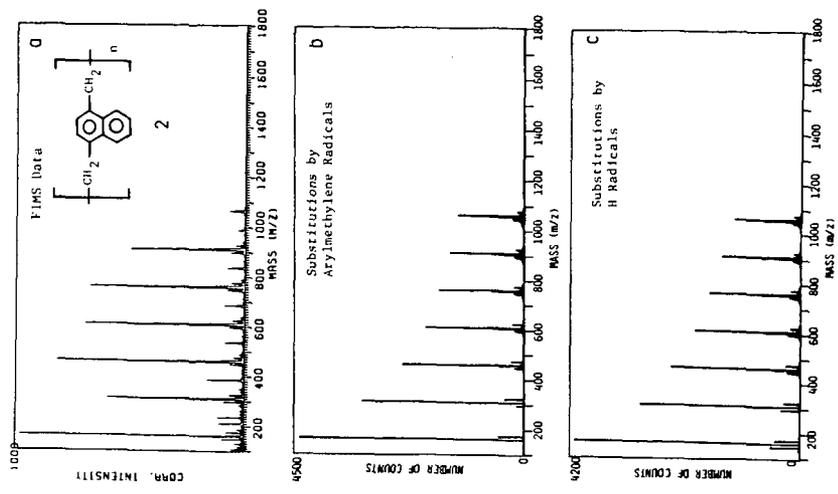


Figure 4. Monte Carlo Simulations for Polymer 2.

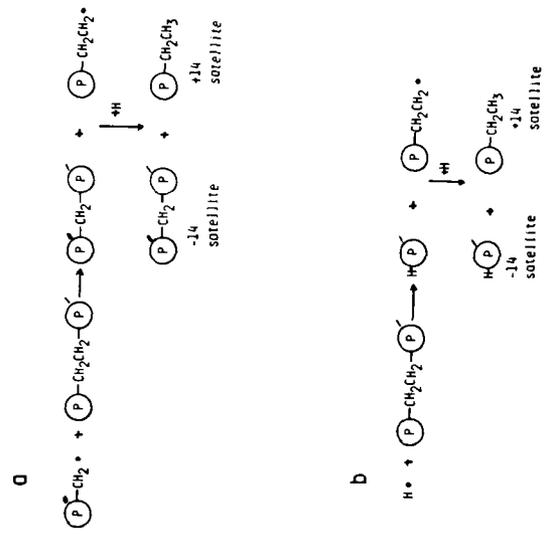


Figure 3. Mechanisms for Ipso Substitution Reactions. a) Substitutions by Arylmethylene Radicals. b) Substitutions by H Radicals.

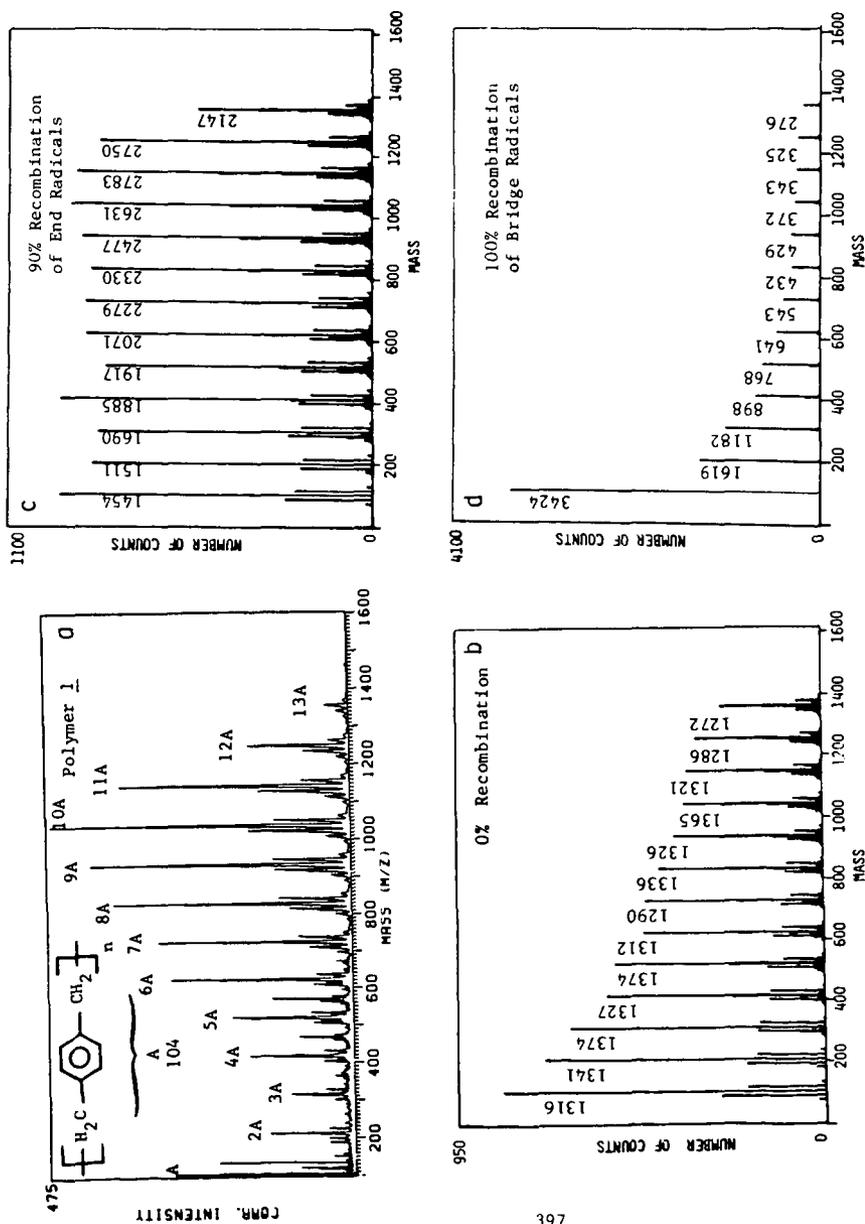


Fig. 5 Monte Carlo Simulations for Polymer 1.