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SCISSION SITE OF POLYMER CHAIN IN DILUTE SOLUTION
UNDERGOING AN EXTENSIONAL FLOW FIELD

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ABSTRACT

The scission site of polystyrene ($\bar{M}_w = 300,000$; $\bar{M}_w/\bar{M}_n = 1.14$) in dilute toluene solution undergoing extensional flow was studied using gel permeation chromatography. Three chromatograms for mid-point scission, 66.7% midpoint and 33.3% quarter point scission, and random scission were matched to the chromatogram of the degraded solution. The result showed that the second of the three chromatograms fitted best, which certainly ruled out the possibility that the polymer chain was fully extended before scission and that weak linkage was the site of chain scission.

INTRODUCTION

One of the important types of laminar flow in the study of macromolecular hydrodynamics is an extensional flow, the streamline of which is shown in Figure 1. It is generated by flowing fluid in a cylinder through a small orifice as seen in Figure 2. When a linear flexible polymer chain is subjected to an extensional flow field, it would feel a tensile force along the direction of the flow exerted on it by the surrounding solvent molecules as shown in Figure 3. Left to itself in a non-flow field, it would attain a random-flight configuration due to the Brownian motion as shown in Figure 4. The object of this study was to use gel

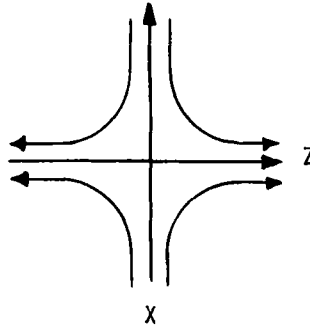


FIGURE 1
Streamline of an Extensional Flow Field on X-Z Axes

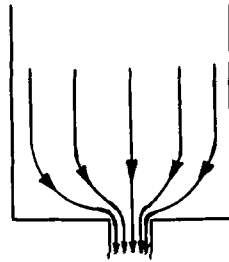


FIGURE 2
Streamline of Flow Through an Orifice

permeation chromatography (GPC) to find the location of breakage on the polymer chain when it was subjected to an extensional flow field. The understanding of which would help to elucidate the mechanism of chain scission in this type of flow.

FRESH AND DEGRADED POLYMER SOLUTION

Table 1 presents the homologous series of polystyrenes obtained from the Pressure Chemical Company. Only PS11 in toluene at a

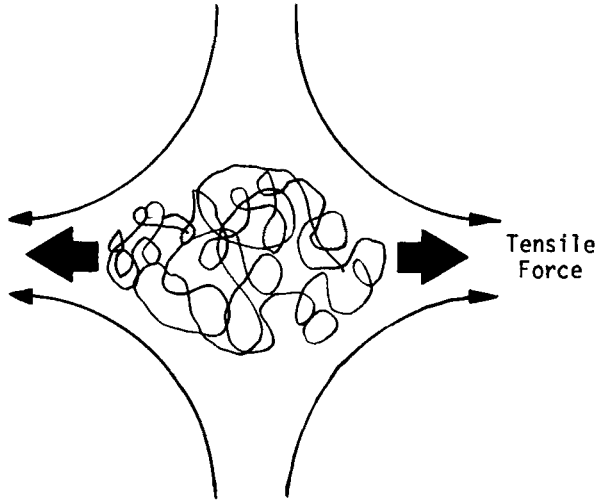


FIGURE 3
A Polymer Chain in an Extensional Flow Field

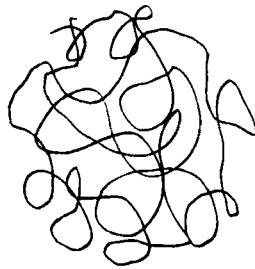


FIGURE 4
A Polymer Chain in a Non-Flow Field

concentration of 0.05 wt% was degraded in the extensional flow field. To degrade the polymer, 14 cc of its solution is filled into a 3/4" diameter cylinder, then it is pushed at a constant speed by a hydraulically driven piston through 0.51 mm diameter

TABLE 1

List of the Homologous Series of Polystyrenes

Polymer Code	PS8	PS20	PS14	PS11
Manufacturer's Batch No.	1c	3b	13a	6a
\bar{M}_w	188,000	390,000	643,000	800,000
\bar{M}_w/\bar{M}_n	1.09	1.10	1.24	1.14

orifice. The degraded solution is collected in another cylinder attached to the orifice as shown in Figure 5.

GPC

The GPC instrument used is Waters Associates model ALC/GPC244 high pressure liquid chromatograph. The set of columns used is 10^4 \AA , 10^5 \AA , 10^6 \AA , 10^6 \AA μ Styragel[®] columns. Filtered toluene is used as carrier solvent. It is operated at 2 ml/min flow rate, and 2 cm/min chart speed. 1/2 cc sample injection size is used throughout this work.

MATHEMATICAL TREATMENT

Breakage at Midpoint

Define a_0 to be the number of the original polymer molecules of molecular weight M_0

a_1 to be the number of M_0 polymer left undegraded

n_i to be the number of degraded polymer of M_i

\bar{M}_n to be the number-average molecular weight of the degraded polymer.

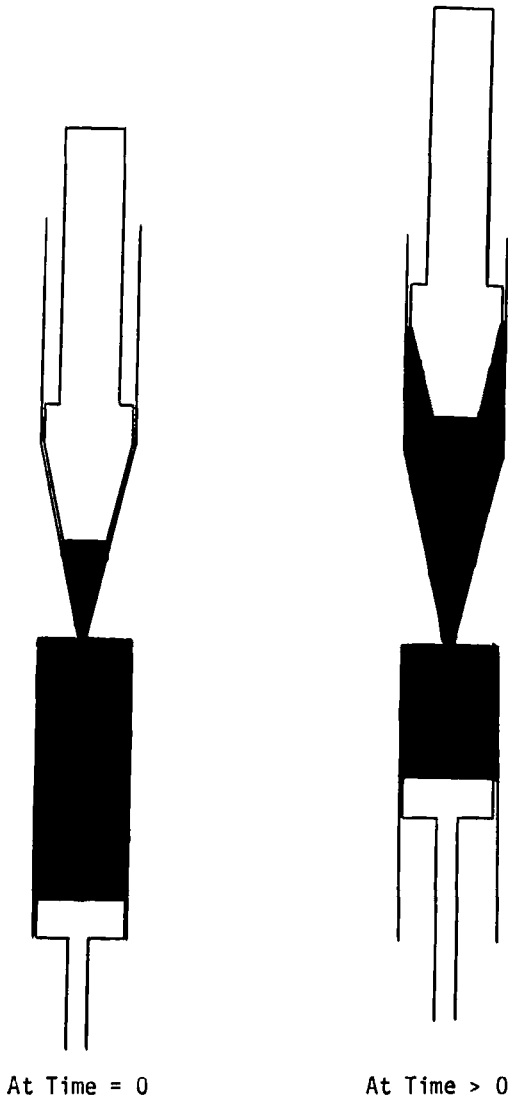


FIGURE 5
An Apparatus Used to Generate an Extensional Flow Field

Therefore,

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\text{Total Weight}}{\sum n_i}$$

$$M_0 = \frac{\text{Total wt.}}{a_0}$$

so
$$\frac{M_0}{\bar{M}_n} = \frac{\sum n_i}{a_0}$$

Assume one molecule to break only once.

$$\text{Number of } M_0 \text{ polymer degraded} = a_0 - a_1$$

$$\text{Number of } 1/2 M_0 \text{ polymer produced} = 2(a_0 - a_1)$$

Hence,

$$\sum n_i = a_1 + 2(a_0 - a_1) = 2a_0 - a_1$$

and
$$a_1 = a_0 \left(2 - \frac{\sum n_i}{a_0} \right) = a_0 \left(2 - \frac{M_0}{\bar{M}_n} \right)$$

$$W(M_0) = \text{Wt. of remaining polymer of } M_0 = \frac{a_1 M_0}{N_{AVO}} = a_0 \left(2 - \frac{M_0}{\bar{M}_n} \right) \frac{M_0}{N_{AVO}}$$

$$\begin{aligned} W\left(\frac{1}{2}M_0\right) &= \text{Wt. of product polymer of } \frac{1}{2}M_0 = 2(a_0 - a_1) \frac{M_0}{2N_{AVO}} \\ &= a_0 \left(\frac{M_0}{\bar{M}_n} - 1 \right) \frac{M_0}{N_{AVO}} \end{aligned}$$

Therefore,

$$W(M_0) : W\left(\frac{1}{2}M_0\right) = \frac{2 - \frac{M_0}{\bar{M}_n}}{\frac{M_0}{\bar{M}_n} - 1}$$

Breakage with 66.7% Probability at Midpoint and 33.3% Probability at Quarter Point

Since there are two quarter points and one midpoint on a given chain, one half of the number of M_0 polymer degraded would occur at the midpoint while the other half of the degraded polymer would occur at either of the two quarter points.

$$N(M_0) = \text{number of remaining polymer of } M_0 = a_1$$

$$N\left(\frac{1}{2}M_0\right) = \text{number of generated polymer of } \frac{1}{2}M_0 = a_0 - a_1$$

$$N\left(\frac{3}{4}M_0\right) = \text{number of generated polymer of } \frac{3}{4}M_0 = \frac{a_0 - a_1}{2}$$

$$N\left(\frac{1}{4}M_0\right) = \text{number of generated polymer of } \frac{1}{4}M_0 = \frac{a_0 - a_1}{2}$$

Therefore,

$$\sum n_i = a_1 + (a_0 - a_1) + \left(\frac{a_0 - a_1}{2}\right) + \left(\frac{a_0 - a_1}{2}\right) = 2a_0 - a_1$$

and
$$a_1 = a_0 \left(2 - \frac{M_0}{M_n}\right)$$

$$W(M_0) = \text{Wt. of remaining polymer of } M_0 = a_0 \left(2 - \frac{M_0}{M_n}\right) \frac{M_0}{N_{AVO}}$$

$$W\left(\frac{1}{2}M_0\right) = \text{Wt. of generated polymer of } \frac{1}{2}M_0 = a_0 \left(\frac{M_0}{M_n} - 1\right) \frac{M_0}{2N_{AVO}}$$

$$W\left(\frac{3}{4}M_0\right) = \frac{a_0}{2} \left(\frac{M_0}{M_n} - 1\right) \frac{3}{4} \frac{M_0}{N_{AVO}}$$

$$W\left(\frac{1}{4}M_0\right) = \frac{a_0}{2} \left(\frac{M_0}{M_n} - 1\right) \frac{1}{4} \frac{M_0}{N_{AVO}}$$

Therefore,

$$W(M_0) : W\left(\frac{3}{4}M_0\right) : W\left(\frac{1}{2}M_0\right) : W\left(\frac{1}{4}M_0\right) = \frac{3\left(2 - \frac{M_0}{\bar{M}_n}\right)}{\left(\frac{M_0}{\bar{M}_n} - 1\right)} : 3 : 4 : 1$$

Random Breakage

Define A: Chromatogram of original fresh polymer

B: Chromatogram of the polymer solution undergoing an extensional flow

C: Chromatogram of part of A that remains undegraded

D: Chromatogram of part of A that is degraded, so $D = A - C$

E: Chromatogram of the degraded product from D, so

$$B = C + E$$

F: Chromatogram of the most-probable distribution with the same \bar{M}_n as E

G: Chromatogram of the polymer solution with random scission, so $G = C + F$

The procedure to produce a chromatogram of polymer randomly degraded is described by the following:

1. Normalize the area of A and B
2. From the value of M_0 of A and \bar{M}_n of B, calculate the fraction of the fresh polymer that is degraded, i.e.,

$$\left(\frac{a_0 - a_1}{a_0}\right) = \frac{a_0 - a_0\left(2 - \frac{M_0}{\bar{M}_n}\right)}{a_0} = 1 - \left(2 - \frac{M_0}{\bar{M}_n}\right) = \left(\frac{M_0}{\bar{M}_n} - 1\right)$$

3. Use this fraction to calculate C from A
4. Subtract C from B to get E
5. Calculate F from E by using the two following equations (1)

$$\bar{x}_n = \sum xp^{x-1}(1-p)$$

and
$$\bar{x}_n = \frac{1}{(1-p)}$$

where x = number of mer units in a polymer chain

p = the probability of continuation of the chain

\bar{x}_n = number-average of mer units per polymer chain

6. Combine F to C to get G

RESULT AND DISCUSSION

Two chromatograms of PS11 degraded at $\bar{V}_{\text{orifice}} = 11,850$ cm/sec and 11,530 cm/sec are presented in Figure 6 and 7. \bar{V}_{orifice} is the average velocity of the flow at the orifice. In both cases the chromatograms of 66.7% midpoint and 33.3% quarter point scission fit those of the degraded solutions best. The fact that scission does not occur exclusively at midpoint certainly rules out the possibility that the polymer chain is extended fully when it is degraded. Because if the polymer is fully extended in an extensional flow, the tensile force exerted on the polymer chain will be largest at the midpoint of the polymer chain, thus the most likely place to break. Also, the polymer chain does not break randomly. This result rules out the possibility that bond scission is due to weak linkages, because weak linkages, if present, should appear randomly on the polymer chain.

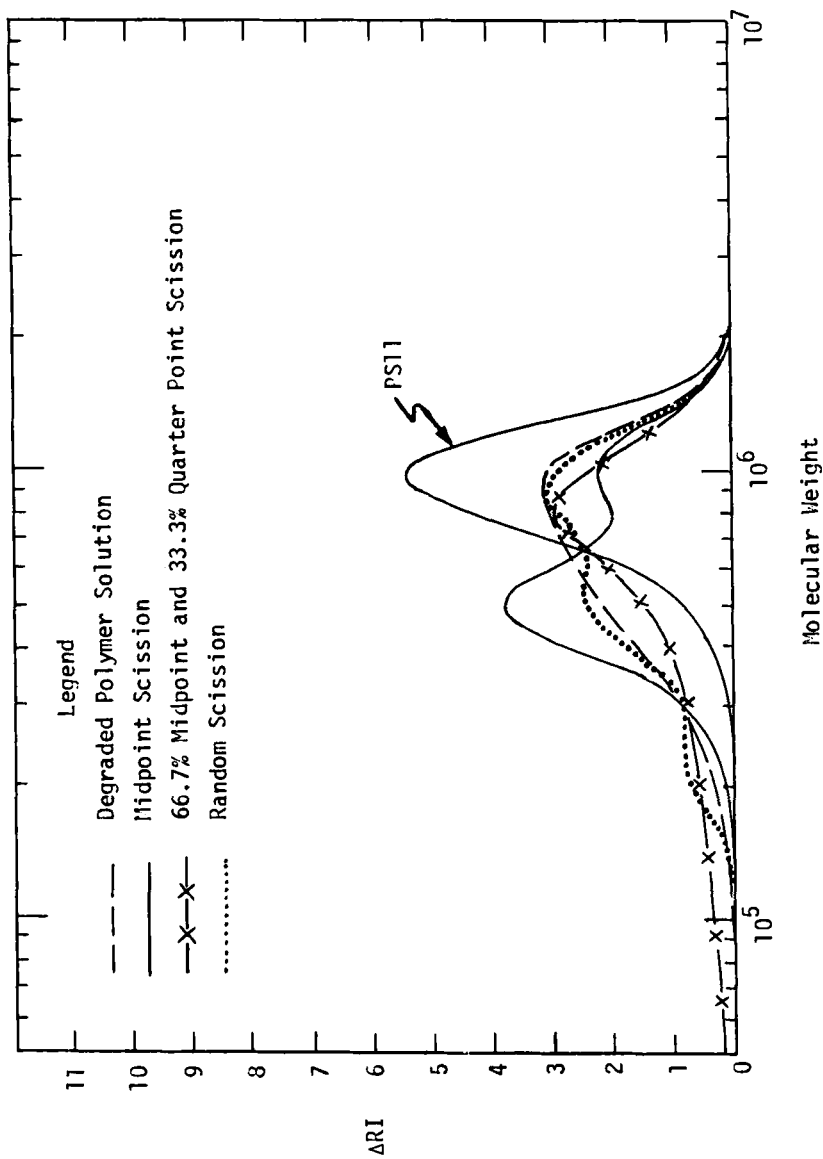
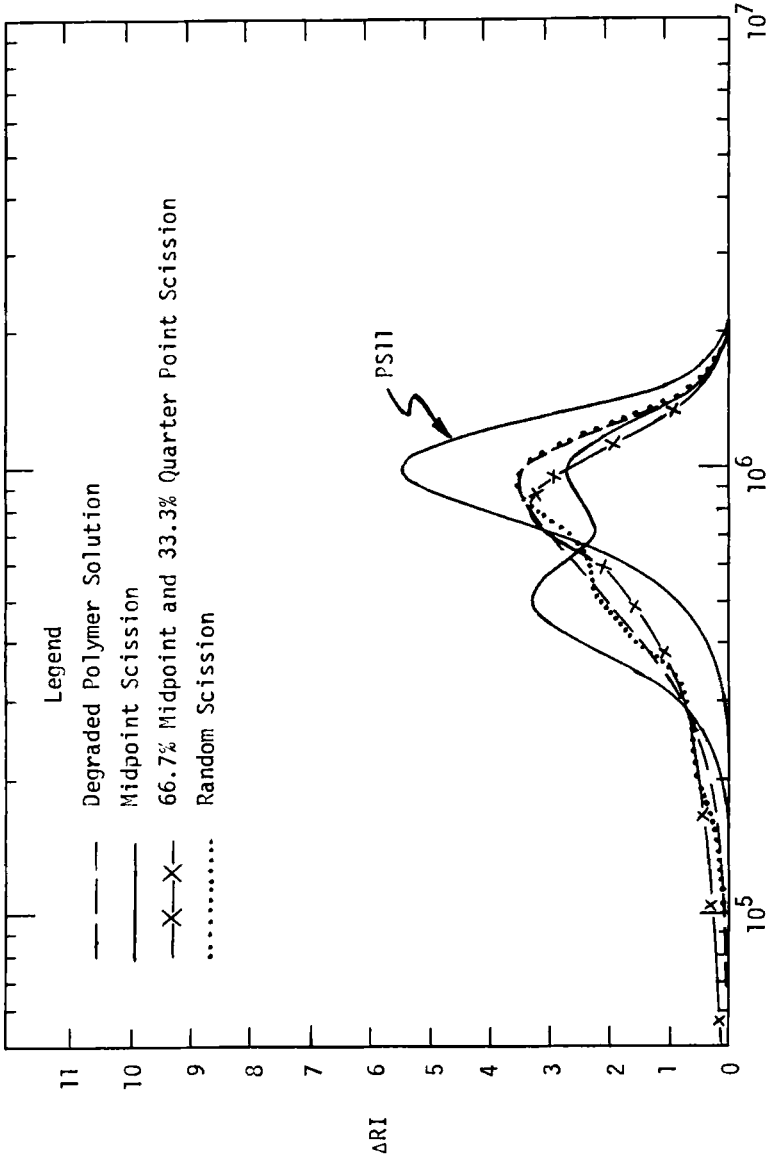


FIGURE 6
 GPC Chromatograms of Different Assumed Scission Sites as Compared
 to the Chromatogram of Degraded Polystyrene Solution at $V_{\text{orifice}} =$
 11850 cm/sec



Molecular Weight

FIGURE 7

GPC Chromatograms of Different Assumed Scission Sites as Compared to the Chromatogram of Degraded Polystyrene at $\bar{V}_{orifice} = 11530$ cm/sec

REFERENCE

- (1) Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1971, p. 325.