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SIMULATION OF MOLECULAR WEIGHT DISTRIBUTION AFTER POLYMER BREAKDOWN. II. DEGRADATION OF *cis*-POLYISOPRENE BY ULTRASOUND AND OZONOLYSIS

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ABSTRACT

cis-Polyisoprene was degraded by two different methods, ultrasound and ozonolysis. Monte Carlo simulation of the molecular weight distribution after breakdown gave very poor fits to the observed data when the extent of degradation was estimated from number-average molecular weight data. Much improved fits were obtained when the degradation index was estimated by a least-squares method.

INTRODUCTION

The breakdown of polymer molecules and its simulation have been extensively studied [1-8]. In the course of some of our work, we studied the degradation of *cis*-polyisoprene both by exposure to ultrasound and by ozonolysis. In simulating degradations of this kind, consideration must be given to two probabilities: first one must consider the probability, P, that a molecule of a given molecular weight will be "selected" from the overall molecular weight distribution (MWD) to undergo cleavage reaction. This will, of course, depend to some extent upon the number of molecules of that molecular weight present at any one time. It may also depend, however, upon the molecular weight itself. For example, Bueche [1] showed that this probability was proportional to exp (MW) for the mechanical degradation of rubber. It has also been suggested that there is some minimum molecular length below which no further scission occurs [9-12]. The second consideration is the site of scission along a polymer chain. Again, Bueche [1] showed the probability Q of scission to be greatest near the center of the molecular chain. This was corroborated by Glynn et al. [7] in studying the ultrasonic degradation of narrow molecular weight polystyrene.

In this paper we describe our experience in simulating the MWDs of *cis*-polyisoprene degraded by ultrasound and ozonolysis. We also demonstrate a novel procedure for estimating parameters in Monte Carlo models.

EXPERIMENTAL

The *cis*-polyisoprene used was commercially available NATSYN 400, obtained from the Goodyear Tire and Rubber Company. It was purified by dissolving in hexane, coagulating in methanol, and drying *in vacuo* at 50°C for 2 days. Polymer solutions were prepared at 4% (wt/vol) concentration in heptane. Ozonolysis reactions were performed at 25°C using the procedure described by Ho [13]. Ultrasonation experiments were performed at room temperature using a Branson SONIFIER W-350 apparatus equipped with a microtip, set at 50 W, 20 kHz. MWD data were obtained using a Hewlett Packard Model 1090 GPC.

RESULTS AND DISCUSSION

The MWDs arising from the ultrasonic experiments are shown in Fig. 1. From the MWD data it is possible to calculate the number of chain scissions that have occurred. Glynn et al. [7] used the relation $DI = (\bar{M}_{n,0}/\bar{M}_n) - 1$, where $\bar{M}_{n,0}$ is the number-average molecular weight of the polymer before degradation and $\bar{M}_n$ is that after degradation. The parameter DI (degradation index) indicates the number of scissions which have occurred per molecule present in the original material. These experimental values are shown in Table 1 in the column labeled "calculated."

The DI values arising from the ultrasonic experiments were used in simulating the MWDs by the Monte Carlo procedure described by Glynn et al. [7] and using the same assumptions: i) the probability of a molecule undergoing scission is directly proportional to the number of molecules of that particular molecular weight; ii) the most likely site for scission is nearest the center of the molecule, as defined by a Gaussian probability distribution; iii) molecules below a certain threshold molecular weight do not undergo further

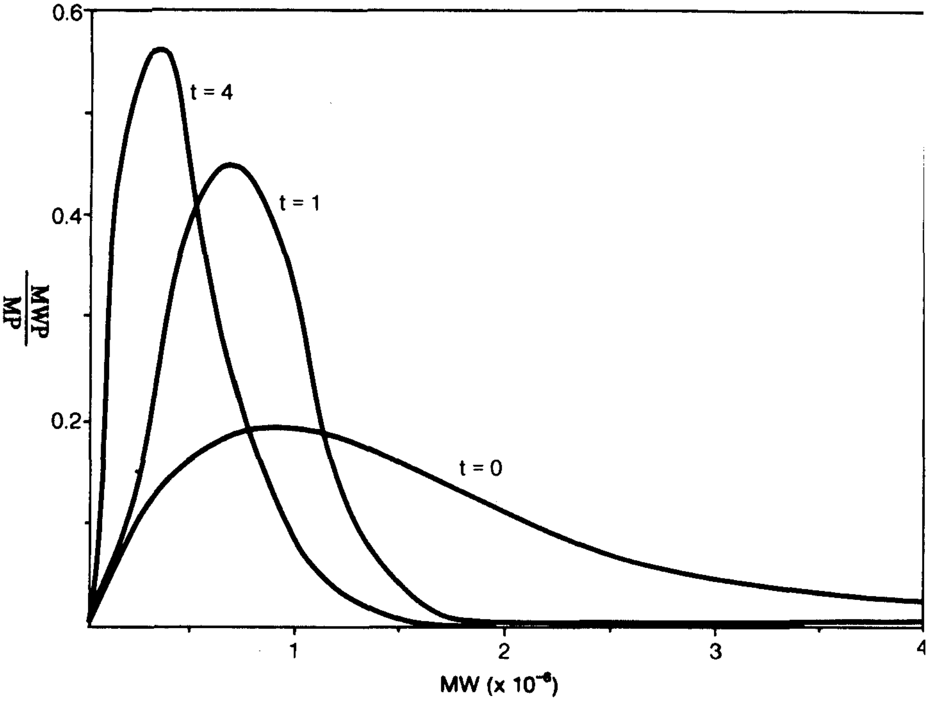

FIG. 1. MWDs arising from ultrasonation experiments. The numbers indicate the irradiation time in hours.

scission. We have assumed that neither crosslinking nor recombination of two fragments arising from two distinct original molecules occurs. The *DI* values calculated from the MWDs gave rise to very poorly fitting simulated MWDs when the above model was applied, as shown in Figs. 2 and 3. We felt that, although Glynn et al. had used narrow molecular weight polystyrene, the model should still be applicable to the polyisoprene case.

The discrepancy probably arose from the much broader original MWD in our case. The problem then became one of attempting to estimate a "better" value of *DI*. Our previously described least-squares procedure [14] was employed and gave significantly different values for *DI* (Table 1), and marked improvements in the fit to the observed distributions (Figs. 2 and 3). Ultra-

TABLE 1. Degradation of Polyisoprene

	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	*DI* Calculated	*DI* Estimated
Original polymer	292 000	2.45	–	–
Ultrasonation:				
0.5 h	224 000	1.42	0.3	0.78
1.0 h	177 000	1.56	0.65	1.45
2.0 h	165 800	1.43	0.76	1.68
4.0 h	140 900	1.42	1.09	2.09
Ozonolysis:				
2 min	17 016	24.7	16.2	0.47[a] 0.52[b]
4 min	14 459	35.9	19.9	0.94
5 min	12 000	13.2	23.3	1.08[a] 1.02[b]
6 min	8 000	12.6	35.5	1.16

[a] *P* proportional to MW and number of molecules at MW, *Q* random scission.

[b] *P* proportional to number of molecules at MW, *Q* random scission.

sonation tended to narrow the MWD, as judged by $\bar{M}_w/\bar{M}_n$. Presumably, preference for center breakage contributes to this by producing a gradual shift in the MWD toward lower weights.

Ozonolysis, however, produced broad, bimodal distributions for which the $\bar{M}_n$ data appeared to be of limited value (Table 1). The calculated *DI*s were extremely high. In simulating the ozonolysis case, we did not have any prior information about the Monte Carlo model. The following assumptions were invoked: a) The probability that a polymer molecule reacts, *P*, is proportional to both the number of molecules of that molecular weight and to the molecular weight itself (based on the premise that the probability that a molecule of ozone encounters a polymer molecule of a given molecular weight depends up-

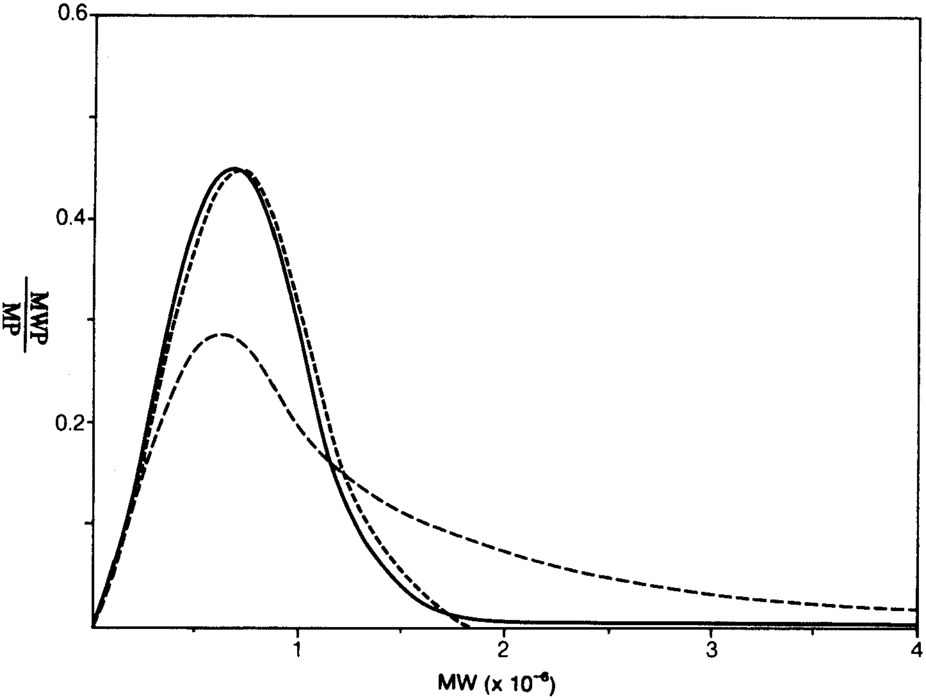

FIG. 2. Results of simulation at $t = 1$ h. The "calculated" *DI* of 0.83 (— —) is compared with the estimated *DI* of 1.45 (- -). The observed MWD is shown as the solid line.

on the number and size of such species); b) once a particular molecule has been "selected" for reaction, the site for scission is random (based on the assumption that no discrimination between olefinic bonds in ozonolysis); c) the lower limiting molecular weight is that of the monomer unit since ozone will be consumed as long as olefinic bonds are present.

The simulations produced estimated *DI* values much different from those calculated from $\bar{M}_n$ data (Table 1). In addition, trials were run in which *P* was proportional only to the number of molecules and independent of molecular weight. The results of these simulations are compared in Fig. 4. With both simulations providing reasonably good fits to the observed MWDs, it is evident, and not unreasonably so, that one may estimate either the

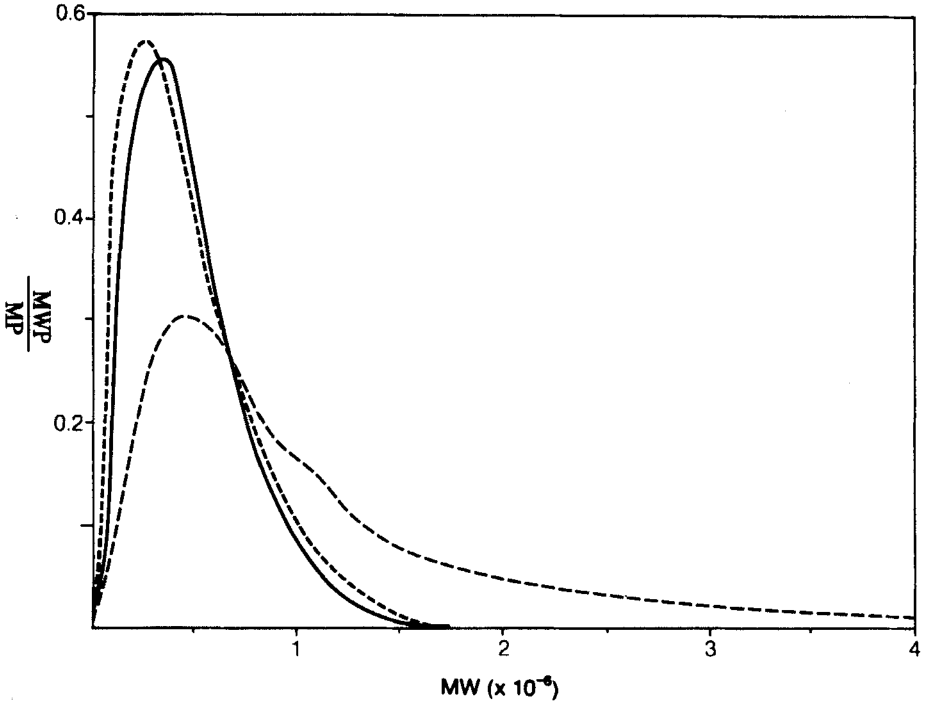

FIG. 3. Results of simulation at $t = 4$ h. The "calculated" *DI* of 1.296 (— —) is compared with the estimated *DI* of 2.09 (- -). The observed MWD is shown as the solid line.

Monte Carlo model or the parameter of interest but not both. Further work would be required to differentiate among various mechanistic models, as defined by the assumptions.

The vast differences between the *DI* values calculated from the $\bar{M}_n$ data and those estimated by simulation warrant further comment. In the case of ultrasonation, the Monte Carlo model has been fixed by the assumptions that have been applied successfully to the ultrasonation of other polymers [7]. There is no reason for us to believe that they do not apply in the polyisoprene case. The discrepancy must arise then, in the method of calculating *DI*. For narrow MWDs, the reciprocal of $\bar{M}_n$ can provide an estimate of the number of polymer molecules per unit mass. As one goes to broader MWDs, this estimate deteriorates significantly as the tails of the distribution begin to affect

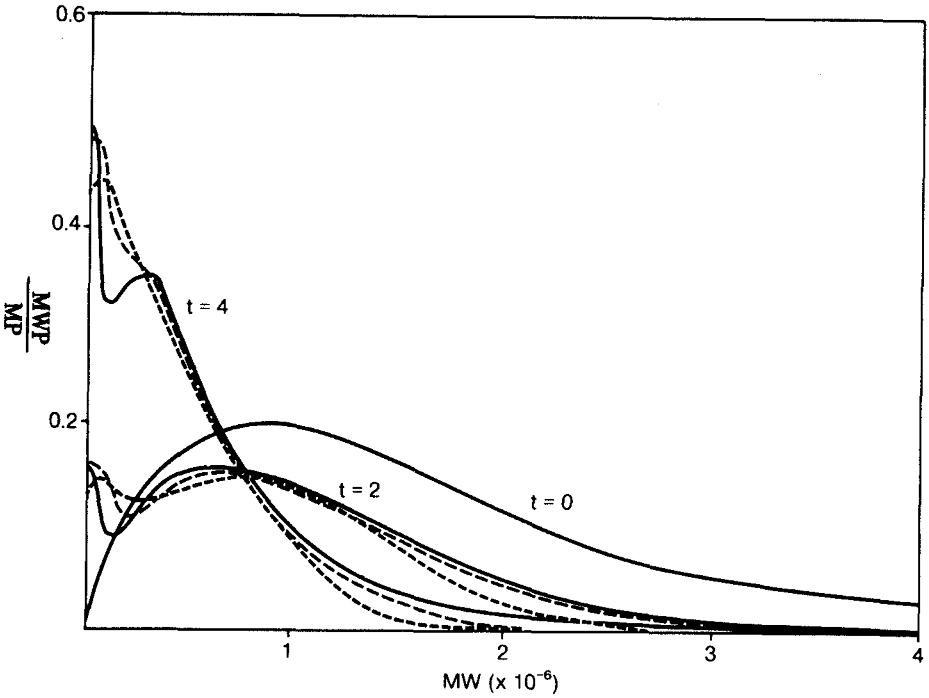

FIG. 4. Ozonolysis results. Numbers indicate reaction time in minutes. The solid lines represent observed MWDs. Simulations with P + MW (- -) and P independent of MW (— —) are shown.

the accuracy with which one can measure $\bar{M}_n$. This effect is most pronounced in the ozonolysis cases where the bimodality of the MWD makes estimation of the number of molecules difficult. The ozonolysis case is complicated by several additional factors. First, the analytical insensitivity to small molecules can have a profound effect on the determination of the MWD. Second, these small molecules contain carboxylic acid groups which may adversely affect the detector sensitivity.

CONCLUSIONS

We have used a novel parameter estimation procedure to simulate the breakdown of polyisoprene by ultrasound and ozonolysis. The procedure gave values for the degradation index significantly different from those calculated from the MWD data. These estimated values of *DI* gave much better fits to the observed MWDs when used in Monte Carlo simulations. In the case of ultrasonation, the favored sites for scission were located toward the center of the molecule in a Gaussian type of distribution. A purely random scission model was adequate for the ozonolysis results but model discrimination was not possible.

The procedures described here should prove useful in handling other systems which are described by Monte Carlo models.

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