

Polymer Degradation. V. Changes in Molecular Weight Distributions During Sonic Irradiation of Polyisobutene

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Synopsis

Gel permeation chromatography was used to follow changes in the molecular weight distribution of a polyisobutene, initial $\bar{M}_v = 466,000$, during degradation induced by sonic irradiation. Seven samples taken at times of 200-163,500 sec. were studied. In general, a steady decrease in molecular weight was observed, although a bimodal distribution was present after 20,000 sec. irradiation. Various measures of inhomogeneity, \bar{M}_w/\bar{M}_n , U , etc., were examined. The function, σ_n/\bar{M}_w , where σ_n is the standard deviation of the number distribution, is considered as a measure of the relative distribution. It is shown to be almost constant throughout the degradation.

The energy-induced degradation of polymers is well known.¹⁻⁵ Studies on the changes in molecular weight distributions during degradation are not common, however, due to the tedious nature of determining such distributions. The advent of gel permeation chromatography has simplified measurement of molecular weight distributions. This paper presents results obtained in this manner to define changes in distribution during sonic irradiation of a polyisobutene solution.

Experimental

A commercial polyisobutene of viscosity-average molecular weight, \bar{M}_v , 466,000 (supplied by Enjay Chemical Company) was dissolved in 1,2,4-trichlorobenzene at slightly above room temperature. The concentration was 9.06 g./100 cc. of solution. A relatively large amount of this solution, 174.5 g., was irradiated in a Raytheon magnetostrictive oscillator, Model DF-101. This oscillator has a nominal power input rating of 250 w. at 10 kc./sec. It was thermostated with tap water through the cooling jacket which maintained the average bulk temperature in the range 35-39°C. Irradiation was carried out at full power. At various time intervals shown in Table I, small samples, about 1 cc., were withdrawn.

Molecular weight moments and distributions were determined using a modified gel permeation chromatograph manufactured by Waters As-

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TABLE I
Results from Gel Permeation Chromatography

Sample	Irradiation time, sec.	Concentration, wt.-% for GPC measurement	Molecular weights computed from GPC		
			\bar{M}_n	\bar{M}_v	\bar{M}_w
0-252	0	0.2	249,000	466,000	506,000
2-246	200.2	0.2	183,000	367,000	401,000
5-243	2,000	0.5	177,000	335,000	368,000
6-247	5,000	0.5	142,000	272,000	300,000
7-250	10,000	0.5	110,000	202,000	222,000
8-251	20,000	0.5	35,500	98,800	110,000
9-249	65,080	0.5	21,800	40,100	43,700
10-248	163,550	1.13	11,500	19,000	20,600

sociates, Framingham, Massachusetts. The solvent was 1,2,4-trichlorobenzene, flow rate about 1 ml./min., and temperature 150°C. Details of the calibration and computation procedures have been described elsewhere.^{6,7} Concentrations at which measurements were made (Table I) were sufficiently low so that no significant concentration dependence was present.

Results and Discussion

Table I lists number-average, viscosity-average, and weight-average molecular weights, \bar{M}_n , \bar{M}_v , and \bar{M}_w , respectively, as a function of irradiation time. The molecular weights progressively decrease to an \bar{M}_w of about 20,600 at 1.63×10^5 sec. There is no reason to believe that this is a limiting value, as the irradiation was arbitrarily terminated. There is an appreciable amount of degraded material with molecular weight below 2000. This is additional support to our previous conclusion that for polyisobutene no lower limit below which degradation cannot take place exists.³ This conclusion is in disagreement with a considerable body of earlier work; see, for example, the summary by Allen et al.⁸ Importantly, the presence of the low molecular weight materials also indicates degradation below the molecular weight concentration range necessary for entanglement conditions, again contrary to previously expressed hypotheses.⁹

A fundamental question in all degradation experiments and theories is the change in the molecular weight distribution. Arguments have been advanced that degradation will (a) narrow or (b) widen the resulting distribution.^{10,11} A good deal of the data consists simply of \bar{M}_w/\bar{M}_n ratios, not complete distributions. The measurement of \bar{M}_n with good accuracy is difficult. In addition, there is no direct evidence that the mechanism for sonically induced degradation is the same as that for degradation induced mechanically.

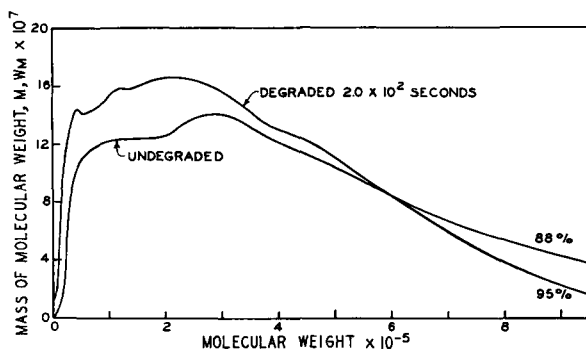


Fig. 1. Differential molecular weight distribution for undegraded polyisobutene and after irradiation for 2.0×10^2 sec.

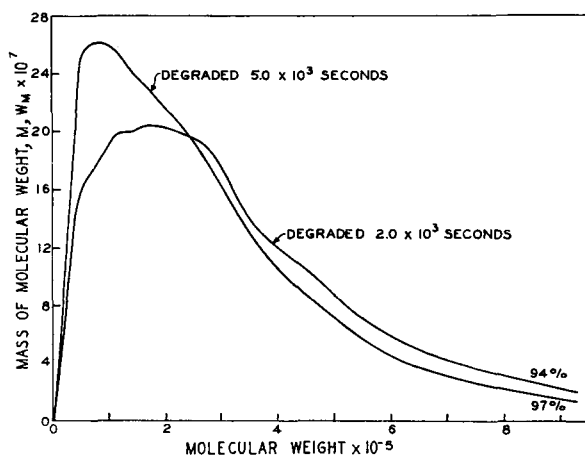


Fig. 2. Differential molecular weight distribution of polyisobutene after irradiation for 2.0 and 5.0×10^3 sec.

Figures 1-4 show differential molecular weight distributions for the starting polymer solution and seven fractions irradiated for times given in Table I. In general, the curves decrease in a regular fashion. An exception is found for the sample irradiated for 20,000 sec., in which a bimodal distribution is observed. While such distributions have been reported before,³ there is no ready explanation for the singular behavior of this sample.

Table II gives a number of computed molecular weight ratios. The ratio of decrease of number- and weight-average molecular weights compared to the original molecular weight designated by a zero subscript, \bar{M}_n/\bar{M}_{n0} , respectively, is regular. Significantly, the overall aspect indicates that \bar{M}_n/\bar{M}_{n0} and \bar{M}_w/\bar{M}_{w0} are about the same. This would indicate that there is little change in molecular weight distribution. The inhomogeneity factor, U , defined by $U = (\bar{M}_w/\bar{M}_n) - 1$ also shows little change

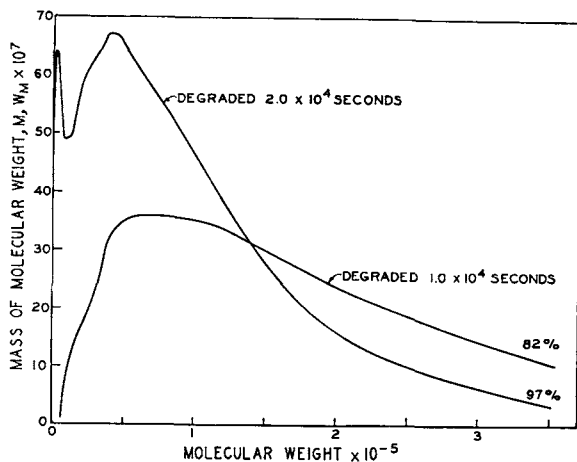


Fig. 3. Differential molecular weight distribution of polyisobutene after irradiation for 1.0 and 2.0×10^4 sec.

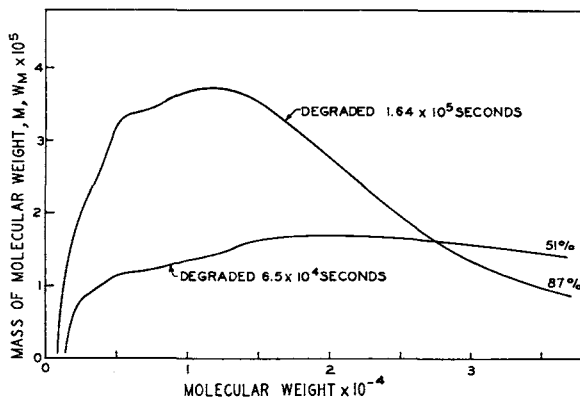


Fig. 4. Differential molecular weight distribution of polyisobutene after irradiation for 6.5×10^4 and 1.64×10^5 sec.

except for the value at 20,000 sec., where the markedly different U reflects the bimodal distribution. Table II also contains values for σ_n , the standard deviation of the number distribution, and a quantity proportional to the number of bonds broken, $[(1/\bar{M}_n) - (1/\bar{M}_{n0})]$. These values are used for computations reported in Table III.

A parameter σ_n/M , where M may be either \bar{M}_n or \bar{M}_w is presented in Table III. This has the advantage of being a convenient method of looking at the relative distribution as a function of molecular weight. The values for σ_n/\bar{M}_n are relatively constant, those for σ_n/\bar{M}_w remarkably so. This indicates that the distribution as defined is neither narrowing or widening but remaining constant. Also listed in Table III is the function, $[(1/\bar{M}_n) - (1/\bar{M}_{n0})]/t$, where t is irradiation time, which is a measure of

TABLE II
 Computed Molecular Weight Ratios

Sample	Ir-radiation time, sec.	\bar{M}_n/\bar{M}_{n0}	\bar{M}_w/\bar{M}_{w0}	U	σ_n	$\left(\frac{1}{\bar{M}_n} - \frac{1}{\bar{M}_{n0}}\right) \times 10^5$
0	0	1.000	1.000	1.034	253,000	
2	200.2	0.735	0.792	1.192	200,000	0.145
5	2,000	0.710	0.728	1.084	184,000	0.164
6	5,000	0.572	0.593	1.109	150,000	0.300
7	10,000	0.444	0.493	1.009	111,000	0.504
8	20,000	0.143	0.218	2.101	51,400	2.415
9	65,080	0.088	0.086	1.005	21,800	4.185
10	163,550	0.046	0.041	0.791	10,200	8.293

 TABLE III
 Computed Distribution Parameters

Irradiation time, sec.	σ_n/\bar{M}_n	σ_n/\bar{M}_w	$\left(\frac{1}{\bar{M}_n} - \frac{1}{\bar{M}_{n0}}\right)/t \times 10^9$
0	1.016	0.500	—
200.2	1.093	0.499	7.25
2,000	1.040	0.500	0.820
5,000	1.056	0.500	0.600
10,000	1.009	0.500	0.540
20,000	1.448	0.467	1.208
65,080	1.000	0.499	0.642
163,550	0.887	0.495	0.517

the rate of bond breaking. While there is considerable scatter, the indicated energy input is relatively constant.

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Résumé

La chromatographie par perméation sur gel a été utilisée pour suivre les changements de distribution du poids moléculaire de polyisobutène initialement $\bar{M}_v = 466.000$ au cours de la dégradation induite par irradiation sonore. Sept échantillons pris à des temps de 200–163.500 secondes ont été étudiés. En général, une décroissance stationnaire du poids moléculaire a été observée bien qu'une distribution bimodale soit présente après 20.000 secondes d'irradiation. Des mesures de variation d'inhomogénéité, \bar{M}_w/\bar{M}_n , U , etc., ont été observées. La fonction σ_n/\bar{M}_w , où σ_n est la déviation standard de la distribution est une mesure de la distribution relative. On le montre être presque constant au cours de toute la dégradation.

Zusammenfassung

Die Änderung der Molekulargewichtsverteilung eines Polyisobutylens mit anfänglich $\bar{M}_v = 466000$ während des durch Bestrahlung hervorgerufenen Abbaus wurde mittels Gelpermeationschromatographie verfolgt. Sieben, nach Dauern von 200–163500 Sekunden entnommene Proben wurden untersucht. Im allgemeinen wurde eine stetige Molekulargewichtsabnahme beobachtet, allerdings trat nach einer Bestrahlungsdauer von 20000 Sekunden eine bimodale Verteilung auf. Verschiedene Inhomogenitätsmaße \bar{M}_w/\bar{M}_n , U etc. wurden angewendet. Die Funktion σ_n/\bar{M}_w , wo σ_n die Standardabweichung der Häufigkeitsverteilung ist, wird als ein Mass der relativen Verteilung betrachtet. Sie erweist sich während des ganzen Abbaus als fast konstant.

Received August 5, 1966

Prod. No. 1470