

Determination of the Molecular Weight Distribution of Polyisoprene by Random Scission

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Synopsis

cis-Polyisoprene in dilute solution in toluene (plus antioxidant) undergoes random scission when exposed to γ -radiation. The possibility of using this scission in a method to assess the width of the molecular weight distribution of the polymer has been explored and found potentially useful in situations where conventional methods provide little information.

INTRODUCTION

The characterization of the products of random scission of a linear polymer can provide information concerning its molecular weight distribution. Nanda and Pathria¹ have shown that the number- and weight-average molecular weights of the original sample and of the products of random scission at differing degrees of degradation can be used to define the molecular weight distribution to a high degree of precision. In this work we took a different approach and examined the possibility of using random scission of a polymer as a quick method of obtaining a measure of the molecular weight distribution.

METHOD

If a polymer of known molecular weight distribution is degraded by random scission, the drop in intrinsic viscosity can be calculated as a function of the number of bonds broken per original "viscosity average" molecule (β). The equations used in the calculations can be found in the literature^{1,2}; the intrinsic viscosity-molecular weight relationship used is that in toluene at 25°C reported elsewhere.³ In Figure 1, we show the variation of the intrinsic viscosity $[\eta]$, expressed as a fraction of the intrinsic viscosity of the original polymer $[\eta]_0$, with β for *cis*-polyisoprene with a "most probable" distribution of molecular weights and with a monodisperse sample of the same polymer. It will be seen that the two types of

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polymer may have intrinsic viscosities differing by as much as 10% at the same β , and this difference forms the basis of our investigation.

To use this correlation, it is necessary to measure β for a given random scission process. This can be done by using a polymer of known molecular weight distribution to establish a relationship between the number of bonds broken and the time of exposure to conditions causing random scission; we have in fact used practically monodisperse *cis*-polyisoprenes produced by anionic catalysis. Random scission was effected by γ -irradiation of dilute

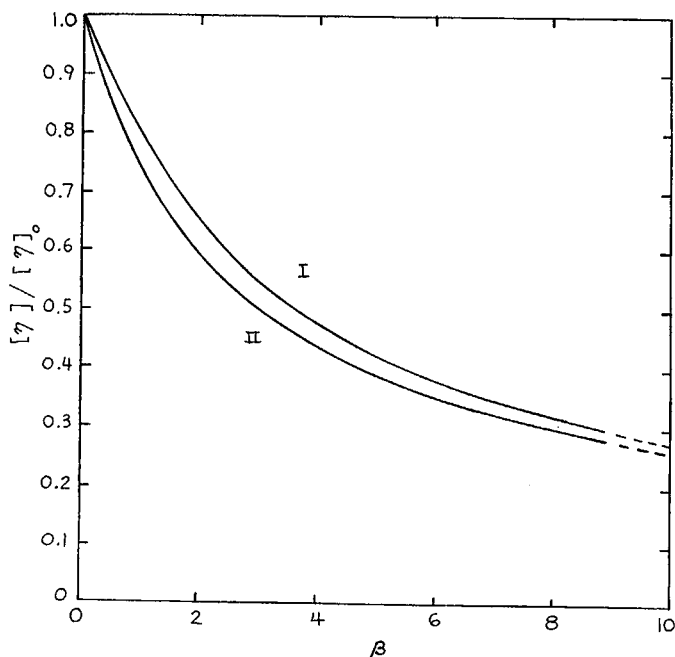


Fig. 1. $[\eta]/[\eta]_0$ vs. number of bonds broken per viscosity average molecule of polyisoprene (β): (I) "monodisperse" initial molecular weight distribution; (II) "most probable" initial molecular weight distribution.

solutions in air. The mechanism of polymer degradation by γ -irradiation in solution is not simple nor well understood.⁴ However, it is known that both polymeric and solvent free radicals are present during the scission reaction. Therefore, to deactivate the polymeric free radicals before they can react with other chains by mutual termination or by grafting to form larger molecules, a free-radical scavenger (e.g., Ionol, a commercial antioxidant) is added before irradiation.

EXPERIMENTAL

Polyisoprenes. Samples of *cis*-1,4-polyisoprene with very narrow molecular weight distributions were prepared in the laboratory using butyllithium initiator in an aliphatic hydrocarbon solvent under an inert

atmosphere, as described by Morton and others.^{7,8,9} Similar samples have been discussed in earlier papers.^{3,5}

Intrinsic Viscosities. Intrinsic viscosities were determined in toluene at 25°C. Modified Desreux-Bischoff viscometers (shear stress 3 g cm⁻¹ sec⁻²) were used, and all values were corrected to zero shear stress by use of a correlation determined with "monodisperse" samples.³

Irradiation. Samples were dissolved in toluene (Analytical Reagent Grade), and Ionol (2,6-di-*t*-butyl-4-methylphenol) was added as a free-radical scavenger. These solutions were exposed in air at room temperature to γ -radiation from a cobalt 60 source. Precautions were taken to ensure that all samples received a known and reproducible radiation dose in a given time; for example, sample tubes could be placed reproducibly in the exposure chamber, corrections were made for decay of the source, and the intensity was checked from time to time, etc.

RESULTS AND DISCUSSION

The results of a study of the weight-average molecular weight and the molecular weight distribution of degraded polyisoprenes produced by the method employed here have been reported elsewhere.⁵ These data show that the reaction is free from branching and crosslinking and that the molecular weight distribution produced is approximately that expected for the random scission of a monodisperse polymer. These results gave assurance that our experimental method was soundly based.

TABLE I
The Random Scission of Polyisoprene II*: The Effect of Ionol Concentration

Ionol concentration, g/dl	[η], dl/g, after exposure for:		
	30 min	60 min	120 min
0.0005	1.00	—	—
0.014	1.60	—	—
0.100	4.01	2.19	—
0.500	5.83	—	—
1.00	6.50	4.50	2.74
10.00	8.04	7.24	4.34

* See Table V. Polymer concentration = 0.1 g/dl.

Before measuring [η] as a function of exposure time, several variables were investigated.

Postirradiation Reaction. The intrinsic viscosity of a degraded polymer was found to decrease slightly when the solution was stored in the dark at room temperature. All measurements reported in this paper were made within 4 hr of exposure; our experiments indicated that [η] decreased less than 1% in this period. In those experiments in which we needed a precise comparison of different samples care was taken to ensure that treatment was identical.

Consumption of Antioxidant. Since commercial rubbers invariably contain a proportion of antioxidant, we did not investigate the degradation of the pure polymer in solution. The effect of the concentration of antioxidant (Ionol) upon $[\eta]$ of the exposed polymer is illustrated in Table I. Since $[\eta]$ is sensitive to the Ionol concentration, especially at low concentration, the question arises as to whether the depletion of Ionol during exposure leads to an increase in the rate of scission of bonds. This was shown to be the case by exposing 90 ml of a solution of Ionol in toluene to γ -irradiation for 1 hr before adding 10 ml polymer solution (which contained 0.1 g/dl Ionol) and exposing again. Table II presents the results of this experiment and compares them with the data of Table I. It is indicated that about

TABLE II
The Random Scission of Polyisoprene II: The Effect of
Exposing the Ionol Solution^a

Ionol concn. in original soln., g/dl	Time of ex- posure of original Ionol Soln., min	[η] of polymer after 60 min addnl. exposure of polymer soln. and Ionol soln. combined, dl/g		Ionol concn. be- fore second ir- radiation (est. ^b from data in Table I), g/dl	Ionol consumed in first 60 min. irradiation (by difference), g/dl
1.0	60	4.33	0.84	}	0.07
1.0	0	4.42	0.91		
0.5	60	3.38	0.38	}	0.08
0.5	0	3.63	0.46		
0.1	60	3.24 ^c	0.055	}	0.035
0.1	0	3.80 ^c	0.09		

^a Volume of original Ionol solution: 90 ml; volume of polymer solution added after first irradiation: 10 ml; concn. of polymer solution added after first irradiation: 0.1 g/dl.

^b By graphical interpolation on the curve relating initial Ionol concentration to $[\eta]$ after the appropriate (60 min or 30 min) irradiation time, to determine what the Ionol concentration must have been to have given the observed $[\eta]$.

^c 30-min exposure.

0.07 g/dl Ionol is consumed during an exposure of 1 hr under our conditions irrespective of the original concentration (except at low concentrations). We assume, therefore, that at high Ionol concentrations, practically all the free radicals, most of which are produced from solvent molecules, are terminated by Ionol. This assumption, taken with the figure of 0.07 g/dl Ionol consumed and the known radiation dosage, gives a G -value of 3 for the production of free radicals from toluene, in agreement with other estimates.⁶

In this work we have used an initial Ionol concentration ($[I]_0$) of 1 g/dl, and we have corrected the exposure time for depletion of Ionol in the following way. By plotting $\log \beta$ (determined from $[\eta]/[\eta]_0$ for the monodisperse polymer) against $\log [I]_0$, it was found that $\beta \propto [I]_0^{-0.35}$ in the region of $[I]_0 = 1$ g/dl, irrespective of exposure time. This finding, together with the

earlier observation that 0.07 g/dl Ionol is consumed in 1 hr, gave the relationship

$$t_c = t \left(\frac{[I]_0 - 0.035t}{[I]_0} \right)^{0.35}$$

where t_c is the exposure time corrected to constant Ionol concentration $[I]_0$. The correction is small when $[I]_0$ is large, e.g., 1% in 1 hr when $[I]_0 = 1$ g/dl.

The irradiation of solutions essentially freed of oxygen by bubbling with argon was investigated. It was found that Ionol concentration was relatively unimportant in this case, but rate of degradation in the absence of oxygen was much slower and the procedure more complicated. Hence, the anaerobic approach was not pursued further.

The effects of oxygen depletion during exposure and the effect of incorporation into the polymer molecules of Ionol residues were not quantitatively investigated. However, the overall success and consistency of the method indicates that these effects are not significant.

Typical data obtained with other antioxidants are given in Table III. The variation of $[\eta]$ presumably reflects the efficiency of the antioxidants as free-radical traps under our conditions. The possible advantage of using *p*-benzoquinone in the scission experiments to obtain more degradation in a shorter irradiation time has not been pursued.

Polymer Concentration. Table IV shows that $[\eta]$ is independent of polymer concentration (within the range 0.02 to 1 g/dl). This finding is

TABLE III
The Random Scission of Polyisoprene II: The Effect of Antioxidant Type^a

Antioxidant	$[\eta]$, dl/g, after 30 min exposure
2,2'-Methylenebis(4-methyl-6- <i>t</i> -butyl phenol)	7.3
2,6-Di- <i>t</i> -butyl-4-methylphenol (Ionol)	5.7
Diphenyl picryl hydrazyl	5.6
<i>p</i> -Benzoquinone	2.6

^a Polymer concentration = 0.1 g/dl; antioxidant concentration = 0.5 g/dl.

TABLE IV
The Random Scission of Polyisoprene II: The Effect of Polymer Concentration^a

Polymer concentration, g/dl	$[\eta]$, dl/g, after 60 min exposure
1.0	4.7
0.5	4.6
0.2	4.8
0.1	4.5
0.05	4.4
0.02	4.6

^a Ionol concentration = 1 g/dl.

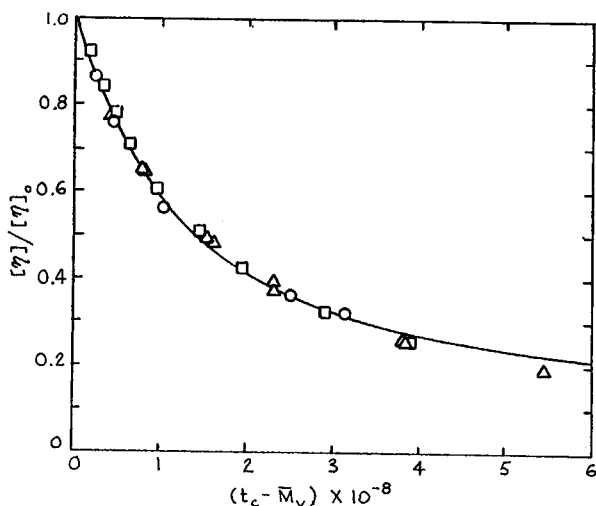


Fig. 2. $[\eta]/[\eta]_0$ vs. product of exposure time and viscosity-average molecular weight.

consistent with our observation that most of the radicals produced are trapped by the antioxidant.

Random Scission of "Monodisperse" Polyisoprenes. Toluene solutions of three samples of *cis*-polyisoprene with narrow molecular weight distributions were irradiated. The intrinsic viscosities and viscosity-average molecular weights are given in Table V, and $[\eta]/[\eta]_0$ is plotted against $(t_c \times \bar{M}_v)$ in Figure 2. The solid curve is calculated for a monodisperse polymer assuming

$$\beta = 2.55 \times 10^{-8} (t_c \times \bar{M}_v).$$

As required by theory, $[\eta]/[\eta]_0$ is independent of initial molecular weight, and this finding is good evidence that we have random scission. At low values of $[\eta]/[\eta]_0$, the points tend to fall below the theoretical line for the polymers of highest molecular weight. This is no doubt due to the fact that we have applied a shear stress correction determined with polymers of narrow molecular weight distribution to polymers with wide molecular weight distributions. Since we know the molecular weight distribution of the degraded polymers, it is possible to calculate a correction for the degraded polymers, but we have not felt it necessary for this study.

TABLE V
The "Monodisperse" Polyisoprenes

Sample	$[\eta]$	$\bar{M}_v \times 10^{-6}$
I	6.13	1.45
II	10.75	3.10
III	20.5	7.6

APPLICATION OF THE METHOD

Mixtures of Polymers. Mixtures of the three "monodisperse" polymers discussed earlier showed a greater drop in $[\eta]/[\eta]_0$ at a given value of β than the polymers themselves. Again, the data are only partially corrected for the effect of finite shear stress and cannot be assessed quantitatively. However, as an example, a mixture of 60 wt. % of sample I with 40 wt.-% of sample III gave $[\eta]/[\eta]_0$ of 0.495 when $\beta = 3.00$, compared with $[\eta]/[\eta]_0 = 0.546$ for the "monodisperse" polymers.

Polymer of Wide Molecular Weight Distribution. Polymer IV was a polyisoprene with a wide molecular weight distribution but a microstructure similar to those of samples I to III. It was fractionated using conventional methods (see, for example, ref. 3), taking the usual precautions, in the following way: 10 g of sample IV was dissolved in 2 liters of toluene and methanol was added to obtain sample IVF1 as a precipitated phase. Sample IVF1 was redissolved and a second fraction was precipitated (IVF11), which was itself redissolved and a third fraction (IVF111) obtained. The fractionation data are given in Table VI, together with the results of their random scission by exposure in toluene solution under the usual conditions. These latter figures have to be compared with $[\eta]/[\eta]_0 = 0.546$ and 0.499 at $\beta = 3.00$ for monodisperse polyisoprene and polyisoprene having a "most probable" distribution, respectively. They illustrate the increased sharpness of the molecular weight distribution of fraction IVF111 brought about by reprecipitation and serve as a reminder of the inefficiency of the single-stage precipitation fractionation.

TABLE VI
Fractionation and Degradation of Sample VI

Sample	Weight, % of original	$[\eta]$, dl/g	$[\eta]/[\eta]_0$ when $\beta = 3.00$
IV	100	4.51	0.510
IVF1	21.0	5.08	0.530
IVF11	10.0	—	—
IVF111	2.6	6.10	0.5403

CONCLUSIONS

We have shown that differences in the weight distributions of molecular weights of polyisoprenes can be detected and assessed by studying the drop in intrinsic viscosity after random scission. If $[\eta]$ and $[\eta]_0$ are measured with care, and if due regard is paid to the effects of shear stress, the method may well provide data in a molecular weight region (say 10^6 and over) where other methods are not easily applied. However, a reproducible method of degrading the polymer is not easily defined; we have investigated γ -irradiation only. The choice between γ -irradiation and more conventional degradation methods would depend on such considerations as availability of facilities and overall time requirements.

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