

Fig. 7. Fiber photographs of the stretched samples: (a) stretched α form; (b) stretched β form.

other bands characteristic of the α or β form except those at 1325 and 1315 cm^{-1} are observed. The crystallization-sensitive bands common to both forms are observed at 1050, 897, 698, 601, 527, and 428 cm^{-1} . The band at 1017 cm^{-1} becomes strong in its intensity when the sample is melted, and it corresponds to the amorphous band at 1027 cm^{-1} studied by Hatano and Kambara.³

Infrared dichroisms were measured on the stretched sample of α form (α -S) and of the β form (β -S); these are shown in Figure 6. α -S was prepared by stretching the film to a length four times the original length in a glycerine bath at 150°C. and keeping it in the bath for 4 hr. β -S was prepared by stretching the quenched sample to a length five times the original, at room temperature. Remarkable differences in dichroic nature between the α and β forms are not found. The orientation character along the molecular chain of both structures may be considered to be the same. The identity period of the α form is the same as that of the β , or about 4.8 Å; it was determined from the fiber photographs shown in Figure 7. However, no details concerning the molecular structure of either form were found in the present study.

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Inhibitor Technique for Chemical Stress Relaxation

For rubber networks undergoing random oxidative scission, the number of moles of cuts $q(t)$ that have been produced up to time t can be measured by stress relaxation at constant extension using the equation:¹

$$q(t) = -N_0 \ln f(t)/f(0) \quad (1)$$

In eq. (1), N_0 is the number of moles of network chains per cc. of the rubber network, $f(t)/f(0)$ is the ratio of stress at time t to stress at time zero. The subject of this note is to show how $q(t)$ is affected by the presence of an antioxidant (inhibitor).

We have measured $q(t)$ by means of eq. (1) in a rubber network produced by photocopolymerizing very thin films (9 mils) of ethyl acrylate with small amounts (2 mole-%) of tetraethylene glycol dimethacrylate. N_0 is obtained from the concentrations of both monomers and polymer density. The value of N_0 for the film studied here is 4.42×10^{-4} moles/cc. This value of N_0 correctly predicted the measured value of the elastic modulus by use of the equation of state for rubber elasticity.

Stress relaxation measurements were carried out at $140 \pm 0.5^\circ\text{C}$. in the absence and in the presence of an antioxidant (inhibitor), namely 2,6-di-*tert*-butyl-*p*-cresol.

The curves for $q(t)$ in the absence of inhibitor and $q_i(t)$, which is the scission in the presence of inhibitor at various levels, are shown in Figure 1. It is clear that the inhibitor affects the curve for $q(t)$ vs. t essentially by producing an induction period t_i which depends on the amount of inhibitor used.

We define $q(t_i)$ as the number of cuts produced in the uninhibited sample after a length of time t_i . In Table I we present data for inhibitor concentration, [Inh], in moles per cc.; t_i produced by [Inh]; $q(t_i)$ corresponding to [Inh]; and finally $q(t_i)/[\text{Inh}]$. This quantity $q(t_i)/[\text{Inh}]$ is a fundamental property of the system which tells how many scissions are suppressed by each inhibitor molecule. It is a quantity that should have wide applicability for the scission of numerous polymer networks.

It is very interesting to note that $q(t_i)/[\text{Inh}]$ is very close to unity in the particular case reported here. This means that one inhibitor molecule suppresses one scission in this system. This is a significant finding which emphasizes the value of our new method.

Each inhibitor molecule is also believed to suppress two radical chains.² If this is true our present finding would mean that there is one effective scission per two kinetic

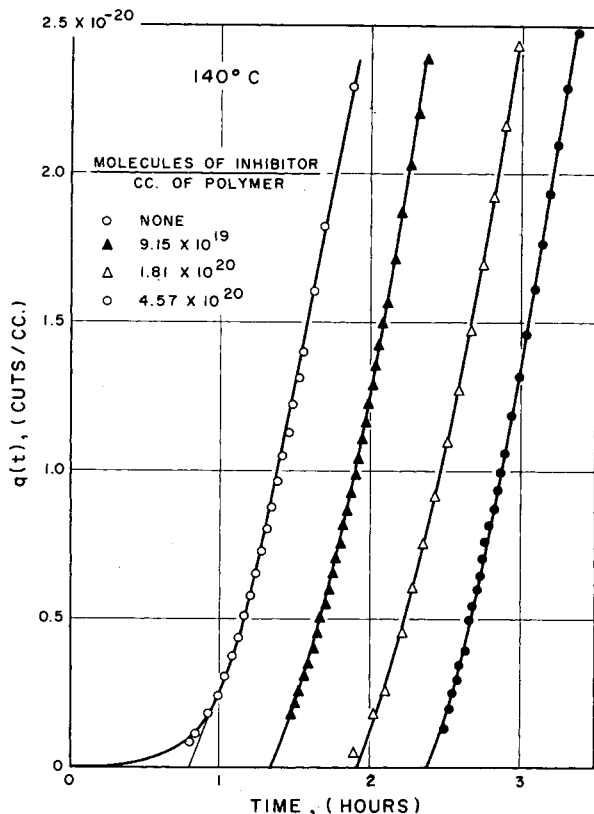


Figure 1.

TABLE I

[Inh], moles/cc. $\times 10^4$	t_i , hr.	$q(t_i)$, moles of cuts	
		$\times 10^4$ cc.	$q(t_i)/$ [Inh]
0	0	0	1
1.52	1.3	1.31	0.86
3.0	1.8	3.5	1.17
7.6	2.4	7.25	0.95

chains. This is not inconsistent with our previous hypothesis that scission occurs in the termination step of the oxidative chain reaction; namely, there is scission at the step at which two RO_2 radicals react with each other.^{3,4}

We have studied $q(t)$ vs. t at various levels of N_0 and conclude that scission is occurring randomly throughout the network with slight preference for the crosslinks. This is very reasonable in terms of the chemical structure. For low values of N_0 , $q(t)$ defined by eq. (1) is essentially independent of N_0 . The value of N_0 discussed in this paper is within this range. This means that the overall scission can be regarded as random on this range.

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Determination of Isotacticity in Polypropylene

It has been suggested by a number of workers¹⁻⁵ that certain absorption bands in the infrared spectrum of polypropylene are indicative of the helical configuration. The bands in question are at 1167, 997, and 841 cm^{-1} . These absorptions are due to a combination of vibrational modes, one mode being characteristic of the methyl group in the helical chain configuration. With proper annealing, essentially all the isotactic chains can be made to exist in the helical structure. The helical content in an annealed polypropylene sample should then effectively be a measurement of the isotactic content.

Infrared methods of measuring isotacticity in polypropylene have previously been proposed for the 1167 and the 997 cm^{-1} bands.^{3,4} However, with respect to materials of isotactic content of less than 90% there is considerable disagreement between results of the two methods. A third method, based on the 841 cm^{-1} band, was developed. All three methods utilize the 974 cm^{-1} band as an internal thickness measurement. This band is linear, with thickness between 1 and 5 mils, and is essentially independent of isotacticity. In Table I are listed the ratios of the absorbancies of the 1167, 997, and 841 cm^{-1} bands to the 974 cm^{-1} band for the standards chosen as 100% and 0% isotacticity.

The assumption is made, in all three methods, that the change in absorption ratio is linear with the change in isotactic content. Good agreement is obtained among the three methods near the 100% and 0% isotactic levels, indicating little difference in the standards chosen for them. However, considerable disagreement occurs between the extremes, and in order to determine which one, if any, of the three methods gives a valid measure of isotacticity an independent determination was chosen.

According to Flory's theory⁶ the composition of a random copolymer consisting of crystallizable and noncrystallizable units may be calculated from the melting point by means of the following equation:

$$1/T_m - 1/T_m^{\circ} = (-R/\Delta H_1) \ln N_1$$

In terms of polypropylene the helical segments are the crystallizable units and the atactic segments are the noncrystallizable units. The melting point of the pure crystal-