

# Crosslinking and Scission in Radical-Promoted Functionalization of Polyethylene

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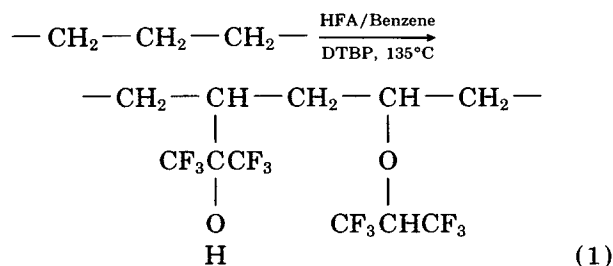
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## SYNOPSIS

We reported earlier on grafting hexafluoroisopropanol groups onto polyethylene through the reaction of polyethylene with hexafluoroacetone and di-*t*-butyl peroxide. The modified polyethylene was partially crosslinked. In this work, we adapted the Charlesby-Pinner Equation to estimate the ratio of chain scission to crosslinking in the reaction.

## INTRODUCTION

In the course of the grafting reaction [eq. (1)] of polyethylene with hexafluoroacetone, using peroxide as initiator, the modified polymer became partially crosslinked.<sup>1</sup> The crosslinking reactions were caused by free radicals since an increase in the amount of peroxide in the reaction increased the gel content in the modified samples.



It is well documented<sup>2,3</sup> that when a polymer is exposed to gamma irradiation the polymer either crosslinked or fragmented via a radical intermediate. The ratio of the two processes can be estimated by the Charlesby-Pinner equation [eq. (2)]:

$$S + S^{1/2} = \frac{G(s)}{2G(x)} + \frac{9.65 \times 10^5}{M_{no}G(x)} \frac{1}{R}, \quad (2)$$

where

$G(s)$  is the number of chain scission per energy unit, usually 100 eV;

$G(x)$  is the number of crosslink per energy unit, 100 eV;

$R$  is the radiation dose in Mrad;

$S$  is the percent of soluble polymer in the network; and

$M_{no}$  is the initial number average molecular weight of the polymer (g/mol).

Since both gamma irradiation and organic peroxide generate free radicals, the Charlesby-Pinner equation can be adapted to study the sol/gel phenomena of our reaction. The procedure is presented in this communication.

## EXPERIMENTAL

### Chemical Modification of Polyethylene

Modified polyethylene samples were prepared with different amounts of di-*t*-butyl peroxide according to the procedure by Schlecht et al.<sup>1</sup>

### Solvent Extraction

The modified polyethylene samples were measured into a preweighed thimble in a soxhlet extractor. The samples were extracted with toluene for 48 h under nitrogen. The swollen gel material in the

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**Table I** Total Amount of Free Radical Generated as a Function of Time

No.	DTBP (mmole)	Time (h)	Radical Dose <sup>a</sup> ( <i>R</i> )	<i>S</i> + <i>S</i> <sup>1/2</sup>
1	3.27	24	3.0E20	0.85
2	6.53	22	2.9E20	0.75
3	3.27	20	1.4E20	1.26
4	3.27	12	1.0E20	1.71
5	3.27	6	6.0E19	1.79
6	1.08	17.5	4.3E19	1.88
7	3.27	3.5	3.8E19	1.97
8	3.27	2	2.3E19	1.99

<sup>a</sup> Radical dose is expressed as number of radicals per gram of polyethylene,  $2I_0[1 - \exp(-kt)]$ , with  $k = 6.19 \times 10^{-5} \text{ sec}^{-1}$  for DTBP decomposition<sup>4</sup> at 135°C in benzene.

thimble was then dried to a constant weight in a vacuum oven (0.1 mm Hg) at 80°C.

## RESULTS AND DISCUSSION

The major difference between gamma irradiation and the organic peroxide system is the rate of radicals generated. The rate of free radical generation by peroxide decreases with time (*t*) for a given initiator concentration (*I*<sub>0</sub>) while that by gamma irradiation is constant. To apply the Charlesby–Pinner equation to the present case, we define dose as the accumulated amount of radicals generated at a given time, which can be calculated from the known rate of decomposition of di-*t*-butyl peroxide. Equation (3) results, with *A*<sub>0</sub> and *B*<sub>0</sub> having the units of number of conversions per radical generated, instead of conversion per energy unit.

$$S + S^{1/2} = \frac{A_0(s)}{2B_0(x)} + \frac{1}{M_{no}B_0(x)2I_0[1 - \exp(-kt)]}, \quad (3)$$

where

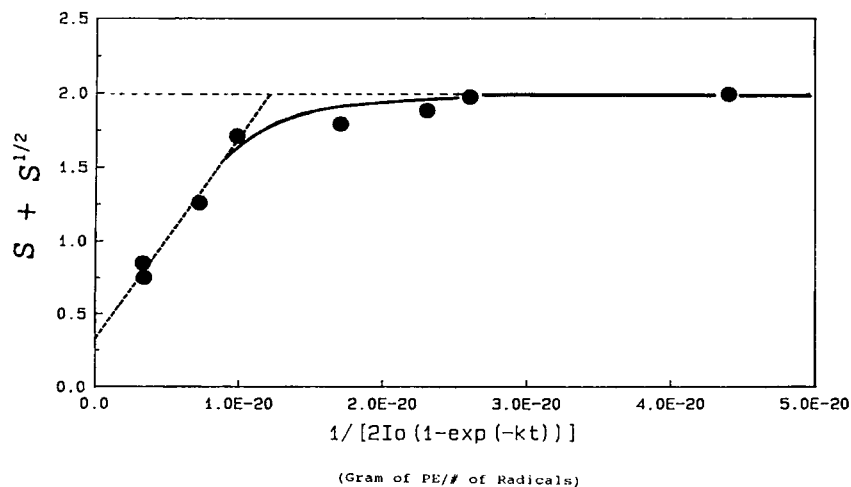
*A*<sub>0</sub>(*s*) is the number of chain scissions per radical;  
*B*<sub>0</sub>(*x*) is the number of crosslinks per radical;

*I*<sub>0</sub> is the initial free radical initiator concentration, and  $2I_0[1 - \exp(-kt)]$  is the total number of radicals generated at time (*t*) per gram of polymer;

*k* is the rate constant of decomposition of the initiator; and

*t* is time in seconds.

Table I lists the soluble fractions of the products of the radical-promoted functionalization at differ-



**Figure 1** Charlesby pinner plot.

ent reaction times. From the extrapolated intercept of the plot of  $S + S^{1/2}$  vs. the reciprocal of radical dose (Fig. 1), the ratio of cleaved to crosslinked units in our reaction was calculated as  $0.33 \pm .1$ , in excellent agreement with the value obtained in gamma irradiation studies.<sup>2,3</sup>

In addition to the ratio of chain scission to crosslinking, the modified Charlesby-Pinner equation provides an estimate of the reaction time at which gelation begins. According to the linear extrapolation of the ascending portion of the curve in Figure 1, the gel point should occur after reaction for 6 h. Experimentally, a completely soluble material could be obtained only for reaction times of 2 h or less. The departure of the sol fractions from their theoretical values may be attributed, at least in part, to the nonrandom molecular weight distribution of the polyethylene sample.<sup>2</sup>

## REFERENCES

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