

tion of data obtained on three copolymer series with vinyl chloride, acrylonitrile, and methacrylonitrile, containing up to 96 wt.-% vinylidene chloride. For highly annealed film samples, the permeability composition curves extrapolated to a water vapor permeability of 4-6 g./100 m.<sup>2</sup>/hr./mil for a 100% vinylidene chloride sample. In the calculation of the amorphous permeability, a crystalline content was assumed to be 60%; hence, the amorphous permeability was calculated to be about 30 g./100 m.<sup>2</sup>/hr./mil. This polymer is reportedly quite linear. The permeability of polyvinyl chloride films has been studied by the author as well as many others.<sup>2-4</sup> In Morgan's work,<sup>2</sup> values as high as 368 g./100 m.<sup>2</sup>/hr./mil were reported, while in the work of others,<sup>3,4</sup> values of 90 to 115 were obtained at 40°C. The author has obtained values on extruded films and well-dried cast films as high as 205 g./100 m.<sup>2</sup>/hr./mil and as low as 85 g./100 m.<sup>2</sup> hr./mil, as a function of annealing conditions at elevated temperatures (to 150°C.). Under such conditions, crystallization is believed to occur; such crystallization has been observed also by Kovacs.<sup>5</sup> Such a study was made in order to arrive at an estimate for the water vapor permeability of the polyvinyl chloride structure. In Morgan's data, it appears that his value (368) may be high, since it was the author's experience that it is difficult to remove all of the solvent (dimethylformamide) used to prepare his films; another possible explanation is that the polymer he used was considerably branched. Interestingly, for chlorinated polyethylenes containing 46.6 and 64.0% chlorine, Morgan reports film permeabilities of 252 and 334 g./100 m.<sup>2</sup>/hr./mil, respectively. These films were characterized as being amorphous. Hence, it appears reasonable the amorphous permeability of polyvinyl chloride would be between 250 and 330 or about 300 g./100 m.<sup>2</sup>/hr./mil, and the highest value obtained in this work may be representative for a film containing about 18% crystalline polymer. This would also mean that the lowest permeability value obtained is representative of polyvinyl chloride with about 45% crystallinity. That such a high degree of crystallinity could exist in PVC is not unreasonable to the author in view of its mechanical properties. However, it is obvious that the least dependable structure in the comparison in this letter is that of polyvinyl chloride and the quantitative aspects of its comparison with other structures are probably only semiquantitative.

However, two conclusions may be readily drawn from these data: (1) Short chain branches or pendant groups or atoms substituted in an unsymmetrical manner on a linear polyethylene molecule, as represented by polypropylene and polyvinyl chloride structures, lead to an increase in water vapor permeability. (2) Such branches or atoms substituted in a symmetrical manner, represented by the linear structures of polyisobutylene and polyvinylidene chloride, lead to a decrease in permeability, not only from that of the unsymmetrical, monosubstituted structures but also from that of the unsubstituted structure itself (linear polyethylene). It is particularly striking that the water vapor permeabilities of polyisobutylene and polyvinylidene chloride films are considerably lower than those of the corresponding monosubstituted structures, i.e., polypropylene and polyvinyl chloride, by a factor of 5-10. Since one would expect the progressive and orderly substitution of chlorine on polyvinyl chloride leading to the polyvinylidene chloride structure would increase the solubility of water vapor in the polymer, the much lower permeability of amorphous poly-

vinylidene chloride would appear to be a result of a much lowered diffusion coefficient due to the structural configuration and packing in the amorphous areas. The parallel decrease in permeability from that of polypropylene to that of polyisobutylene, in which the chemical constitution is constant, would also support this above conclusion. It would not be unreasonable to explain the higher permeability of polypropylene compared to polyvinyl chloride as a result of the larger van der Waal radius of the methyl group compared to that of the chlorine atom (2.0 Å. vs. 1.8 Å., respectively<sup>6</sup>). It should be noted that the quantitative difference between the permeability of these two structures, if polyvinyl chloride is linear, should reflect differences in both the size and the polarity of the methyl group and the chlorine atom. Interestingly, the calculated amorphous water vapor permeability of polyvinyl fluoride films prepared in this laboratory is about 250 g./100 m.<sup>2</sup>/hr./mil, and hence there appears to be some correlation of water vapor permeability data with the size of the pendant atom or group. Permeability data on polyvinyl bromide films would certainly be interesting in comparison with those on polypropylene, since the bromine atom and the methyl group are about the same in size and any differences should be a result of the polar nature of the bromine atom.

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#### Directed Scission in Rubber Vulcanizates

Horikx<sup>1</sup> has introduced a method of investigation of degradation of rubber vulcanizates in which comparison is made between the amount of soluble material cut from the main network and the equilibrium swelling of the remaining insoluble gel, different relationships between these quantities being characteristic of different sites for the scission reaction. Horikx gave appropriate theoretical treatments for the two cases of cutting at random along the polymer chains of the vulcanizate and of crosslink scission, but for the third important case of scission of chains at points adjacent to the crosslinks he gave only a very approximate approach. Recent theoretical treatments of sol fraction<sup>2</sup> and elasticity end correction<sup>3</sup> make a treatment of this case of "directed scission" an easy matter.

Starting with a vulcanizate containing originally only tetrafunctional branch points (crosslinks) distributed, as also are the chain ends, randomly through the polymer, we

consider the case in which all the four chains meeting at a crosslink may with equal probability be cut at points immediately adjacent to the crosslink. After a fraction  $\beta$  of the vulnerable bonds have been cut, the functionality of some of the branch points will have been reduced, the number  $X_r$  of functionality  $r$  per unit weight of polymer being

$$X_r = X \binom{4}{r} \beta^{4-r} (1 - \beta)^r \quad r = 0, 1, \dots, 4 \quad (1)$$

where  $X$  is the total number of crosslinks per unit weight. Defining  $\alpha_r$  as the probability that a branch point of functionality  $r$  is encountered on proceeding along a chain segment chosen at random we have

$$\alpha_r = rX_r / (E_0 + 4X) \quad (2)$$

$E_0$  being the original number of chain ends. The reasoning used previously<sup>2</sup> gives for the fraction  $s_1$  of the chain ends in the sol and for the weight fraction of sol  $s$

$$s_1 = 1 - (\alpha_2 + \alpha_3 + \alpha_4) + \alpha_2 s_1 + \alpha_3 s_1^2 + \alpha_4 s_1^3 \quad (3)$$

and

$$s = s_1^2 \quad (4)$$

Using the criterion<sup>3</sup> for elastically active chain segments that a cut in one would not increase the amount of sol gives for the number  $\nu$  of effective chains per unit weight of total polymer

$$\begin{aligned} \nu &= 1/2[4X_4(1 - s_1)^4 + 3X_4s_1(1 - s_1)^3 + 3X_3(1 - s_1)^3] \\ &= 2X(1 - s_1)^3(1 - \beta)^3(1 + 2s_1)(1 - \beta) + 3\beta \end{aligned} \quad (5)$$

The number  $\nu'$  of effective chains per unit weight of gel is

$$\nu' = \nu / (1 - s) \quad (6)$$

For illustration, Figure 1 shows  $s$  plotted against the fractional decrease in effective chains in the gel  $(\nu_0' - \nu')/\nu_0'$  for a hypothetical network with initially no free ends both for directed scission and for random scission. The number of effective chains and the sol fraction in the latter case being given<sup>2,3</sup> by the equations

$$\nu = 2X(1 - s_1)^3(1 + 2s_1) \quad (7a)$$

$$s = s_1^2 \quad (7b)$$

$$s_1 = (1 - \alpha) + \alpha s_1^2 \quad (7c)$$

$$\alpha = 4X / [(E_0 + 4X)(1 + c)] \quad (7d)$$

$c$  being the average number of cuts per chain segment. For this hypothetical network, crosslink scission never leads to the formation of sol.

The figure also includes similar curves calculated by use of the method of Flory<sup>4</sup> instead of the method of allowing for free ends developed by the present author. In the case of random scission, eqs. (7b)–(7d) still apply<sup>1,3</sup> but

$$\nu = 2X(1 - s_1)^2(1 + s_1) \quad (8)$$

Directed scission results in a network with branch points of different functionalities, and it is not immediately obvious how the Flory calculation of number of effective chains

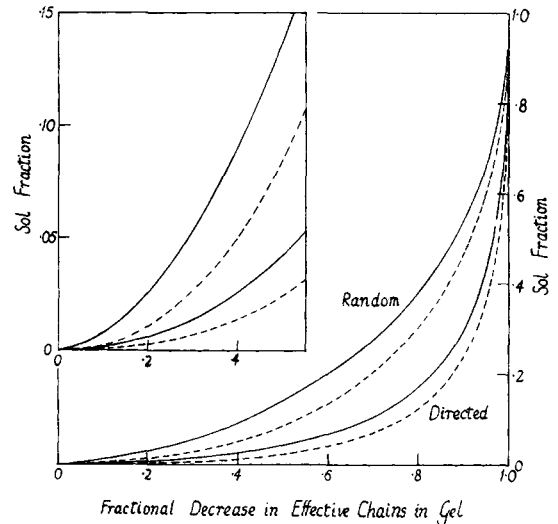


Fig. 1. Illustrative curves for directed scission and random scission of vulcanizate initially without free ends: (—) obtained by use of end correction developed by present author; (---) obtained by Flory end correction.

should be applied in such a situation. In fact,  $\nu$  was obtained in this case by constructing in place of the network produced by directed scission an elastically equivalent network produced by random scission. This can be done because  $\nu$  is determined by the number of chain segments running between two crosslinks which are not cut. The fact that a chain already cut may be cut again has an effect on the sol fraction  $s$  but cannot change  $\nu$ . Again, scission of a chain attached at one end to a crosslink will change  $s$  but not  $\nu$ . Two networks, initially similar, one of which undergoes random scission and one directed scission, still have the same number  $\nu$  of effective chains if the fraction of chain segments between two crosslinks cut at least once is the same in both cases, regardless of the fact that the number cut more than once will be different as also will be the number cut among segments joined at only one end to crosslinks. Thus, to calculate  $\nu$ , eqs. (8), (7c), and (7d) are used, with  $c$  obtained from

$$2\beta(1 - \beta) = c / (1 + c) \quad (9)$$

[Use of eq. (7a) instead of eq. (8) with eqs. (9), (7c), and (7d) gives the same result as obtained above through eq. (5).] The sol fraction  $s$  must, however, be calculated from eqs. (1)–(4) and  $\nu'$  then obtained by eq. (6).

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