

pared by inducing crystallization in the melt at 150°C. under 2000 atm. for 2 hr. and then slowly cooling. The difference in density between the compression-molded and the pressure-crystallized samples seems to persist up to the melting point at the same slow rate of heating (Fig. 4).

Some highly significant observations were made during this experiment. When the temperature was increased from 137 to 150°C. over a 7-hr. period, the pressure-crystallized sample continued to exhibit several small (1–2 mm. in diameter) translucent spots. After an elapsed time of 16 hr., at 150°C. these spots became less defined, and disappeared almost completely when the temperature was further increased to 152°C.

When this experiment was ended at 161°C., the sample was left to cool in the bath and was found to have recrystallized to the original pressure-crystallized density of 0.978 g./cm.³. Since such a high density is not ordinarily obtainable under atmospheric pressure in a short time interval, the result suggests that some "memory" of the previous crystalline state had still persisted for several hours at 10–20°C. above the melting temperature. Dilatometric measurements show that the melting point of this sample is essentially the same ($\pm 0.5^\circ\text{C}$.) as that of the compression-molded sample, but a more sensitive measurement would conceivably have revealed the existence of order in this presumably nonequilibrium melt.

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Moisture Permeability of Polymers. Effect of Symmetry of Polymer Structure

In order to be able to correlate water vapor permeability with polymer structure, it is necessary that one be able to measure the permeability of polymeric films as completely amorphous structures or to calculate the permeability of the amorphous regions based on data obtained with partially crystalline films which include a large number of the inter-

esting polymeric structures. In a previous paper,¹ it has been shown for polyethylene terephthalate, nylon 610, and polyethylene (at densities above about 0.94 g./cc.) that the water vapor permeability P for a given polymeric structure varied directly as the square of the amorphous volume fraction X_a , i.e., $P = P_a X_a^2$, in which P_a is the permeability of the film as a completely amorphous structure. This relation also appears to hold for other hydrophilic polymers such as nylon 6 and nylon 66; these data will be reported at a later date. It is the purpose of this letter to show the utility of this relation in the isolation of some interesting effects of short-chain branching on the water vapor permeability of vinyl-type polymers. The water vapor permeabilities were determined as previously reported¹ at a 53-mm. Hg vapor pressure differential at 39.5°C. and reported, for thicknesses of 1.0 mil, in units of grams/100 m.²/hr.; such data are readily converted to more conventionally used permeability units, i.e., cc. (STP)/sec./cm.²(area)/mm. (thickness)/cm. Hg (vapor pressure differential), by multiplying by 0.166×10^{-8} .

The particular polymeric structures of interest are those from 1-substituted and 1,1-disubstituted vinyl monomers in which the substituted group is the nonpolar methyl group in one case and the polar chlorine atom in another case. These polymers are shown in Table I and represent two structural

TABLE I
Effect of Structure on Water Vapor Permeability

Polymer	Water vapor permeability P_a , g./100 m. ² /hr./mil	Comments
Polyethylene	200–220	P_a calculated (see ref. 1)
Polyisobutylene	90	P_a measured*
Polypropylene	420	P_a calculated from film with 2% crystallinity
Polyvinyl chloride	~300	P_a estimated from data as described in this letter
Polyvinylidene chloride	~30	P_a calculated as described in this letter.

* Morgan² reports value of 76 g./100 m.²/hr./mil.

series: (1) polyethylene, polypropylene, and polyisobutylene; and (2) polyethylene, polyvinyl chloride, and polyvinylidene chloride. The value of the water vapor permeability of the linear polyethylene structure is that calculated in a previously reported work.¹ Before considering the data, some comments on the structures *per se* and their water vapor permeabilities should be made. The water vapor permeability of polyisobutylene was determined on a completely amorphous structure and that of polypropylene on structures with less than 10% crystallinity. Also, both structures are linear, having been prepared with coordination-type catalysis in the case of polypropylene and in a low temperature, ionic-catalyzed polymerization in the case of polyisobutylene. In the case of the polyvinyl chloride and polyvinylidene chloride structures, however, the situation is substantially different. Polyvinylidene chloride homopolymer is highly crystalline and insoluble; it was necessary to arrive at the permeability of this homopolymer by extrapola-

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.²/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.²/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.²⁻⁴ In Morgan's work,² values as high as 368 g./100 m.²/hr./mil were reported, while in the work of others,^{3,4} 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.²/hr./mil and as low as 85 g./100 m.² 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.⁵ 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.²/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.²/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., respectively⁶). 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.²/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

Horikx¹ 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 fraction² and elasticity end correction³ 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