155. *The Cross-linking of Vinyl Polymers by Friedel–Crafts Catalysts. Part I.*

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The production of insoluble cross-linked materials from solutions of various polymers by the action of metallic halides active in Friedel–Crafts reactions is described. Cross-linking occurs by the elimination of a simple molecule HX between two polymer chains; X may be Cl or $CH_3\cdot CO_2$. Except in the special case of polystyrene in solvents containing at least two chlorine atoms per molecule, the solvent probably does not take part in the reaction and the differing efficiencies of various solvents can be related to their dielectric constants.

THE term "cross-linking" is applied to processes whereby the separate molecules of a long chain polymer become linked together by covalencies to give a net-like structure. Such processes are of importance industrially since cross-linking may lead to profound changes in the properties of a polymer; for example a polymer with quite a small degree of cross-linking swells but does not dissolve in liquids which would normally dissolve the polymer quite readily.

Studies of cross-linking can be divided into two categories; in one, polymerization and cross-linking are carried out simultaneously, whereas in the other a polymer is made and cross-linked subsequently. Norrish and Brookman (*Proc. Roy. Soc.*, **1937**, *A*, **163**, 205) carried out investigations of the first type by mixing with the main monomer, such as styrene, small amounts of a second substance, such as divinylacetylene, which can be incorporated in the growing polymer and also lead to cross-linkage. Into the second category come the study of the vulcanisation of rubber, and the work of Baker (*J. Amer. Chem. Soc.*, **1947**, **69**, 1125) on the cross-linking of linear polyesters by free radicals.

It was observed that although the chlorination of polyvinyl chloride in tetrachloroethane solution proceeded smoothly in an all-glass apparatus in the laboratory to give a white soluble product, attempts to carry out the same process on a large scale in an enamelled vessel resulted in the formation of a dark insoluble gel. It was discovered that the gelation and discoloration were due to traces of ferric chloride formed from a small area of exposed iron in the chlorination pot. Similar effects have been reported by Morrison, Holmes, and McIntosh (*Canadian J. Res.*, **1946**, **24**, 179) who have shown that solutions of polystyrene and of polyvinyl acetate in certain solvents give insoluble gels under the influence of ferric chloride. This work has now been extended, allowing conclusions to be drawn concerning the mechanism of the cross-linking reaction.

EXPERIMENTAL.

When solutions of polyvinyl chloride in tetrachloroethane were treated with ferric chloride at 70° in stoppered tubes, considerable darkening occurred and within an hour an insoluble gel had formed. Stannic chloride and aluminium chloride also caused gelation, and of the three catalysts aluminium chloride gave a gel most quickly; sulphur monochloride and phosphorus trichloride were completely ineffective as catalysts, and pure aluminium, iron, and tin caused gelation only if the polymer solution containing the suspended metal was saturated with chlorine. Other polymers containing chlorine which reacted similarly to polyvinyl chloride were chlorinated polyvinyl chloride (% Cl = 65), "halothene" (% Cl = 56), a co-polymer of vinyl chloride and vinylidene chloride (% Cl = 63) and a co-polymer of vinyl chloride, vinylidene chloride, and methyl methacrylate (% Cl = 53, % methyl methacrylate by weight = 11). In all cases the solutions contained about 5 g. of polymer and 1·5 g. of catalyst in 100 ml. of solvent. The speed at which gelation occurred increased with the chlorine content of the polymer.

Solvents other than tetrachloroethane (dielectric constant at 20° = 8·2) used successfully for the gelation of chlorinated polyvinyl chloride with stannic chloride were nitrobenzene (ϵ_{20° = 36·1), ethylene dichloride (ϵ_{20° = 10·5), chlorobenzene (ϵ_{20° = 5·9), bromobenzene (ϵ_{20° = 5·4), ethylene dibromide (ϵ_{18° = 4·9), and amyl acetate (ϵ_{19° = 4·8). Trichloroethane and bis-(2-chloroethyl) ether were also used successfully; values of their dielectric constants are not available, but they are probably quite high. Although the magnitudes of the dielectric constants at 70° will be different from the values quoted above, they are likely to be in the same order; it was observed that the speed at which gelation occurred increased with the dielectric constant of the solvent. Blank experiments with solvents and catalysts led to some darkening, but, except for amyl acetate, this was comparatively slight. Solutions of the polymer in toluene (ϵ_{20° = 2·4) darkened after the addition of stannic chloride and became appreciably more viscous after several hours at 70°, but even prolonged treatment gave no gel; addition of small amounts of tetrachloroethane or of ethylene dichloride to the solution in toluene did not result in gelation.

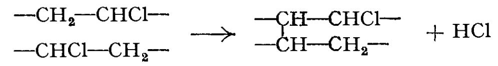
A series of experiments using solutions of 5 g. of chlorinated polyvinyl chloride in 100 ml. of nitrobenzene, and aluminium chloride as catalyst, showed the effect of catalyst concentration upon the reaction. Provided the catalyst concentration exceeded 15 g. for 100 g. of polymer, a dark gel was formed readily at 70°; the gels made with concentrations of catalyst just greater than the critical value were soft, but those prepared with higher concentrations exuded solvent if kept at 70° and were firmer; evidently further cross-linking occurred giving a product containing less solvent in its equilibrium swollen state. For systems containing less than 15 g. of aluminium chloride to 100 g. of polymer, darkening and thickening of the solutions occurred to an extent depending on the amount of catalyst present; systems containing between 10 and 15 g. of catalyst with 100 g. of polymer, though liquid at 70°, formed soft gels on cooling to room temperature. The polymers were recovered by treatment with methyl alcohol and subsequently with steam until no smell of nitrobenzene remained. The products formed with more than 20 g. of aluminium chloride to 100 g. of polymer were black, hard, and brittle; with smaller concentrations of catalyst, a series of products was obtained for which the discoloration decreased and the toughness increased as the amount of catalyst was reduced from 20 g. to 2 g. per 100 g. of polymer. The insolubility of the materials recovered from the gels was confirmed, and it was observed that the materials took up bromine slowly, suggesting unsaturation.

Polyvinyl acetate in nitrobenzene gave a dark insoluble gel at 70° with aluminium chloride; under the same conditions polymethyl methacrylate formed an insoluble gel with considerably less darkening.

Solutions of polystyrene in ethylene dichloride and in bis-(2-chloroethyl) ether formed dark gels fairly slowly with stannic chloride, but in nitrobenzene (the best solvent for the gelation of polymers containing chlorine) no gel was obtained. Polystyrenes chlorinated in the benzene rings behaved similarly to polystyrene, but if substitution was at aliphatic carbon atoms gelation occurred readily.

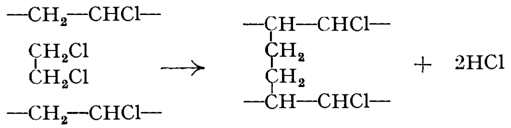
DISCUSSION.

The production of the insoluble gel from solutions of polymers containing chlorine can be formulated as :



$$\begin{array}{l}\mathrm{-CH_2-CHCl-}\\ \mathrm{-CHCl-CH_2-}\end{array}\longrightarrow\begin{array}{l}\mathrm{-CH-CHCl-}\\ \quad|\\ \mathrm{-CH-CH_2-}\end{array}+\mathrm{HCl}$$

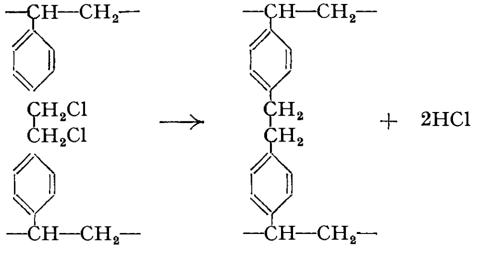
the elimination of hydrogen chloride occurring under the influence of Friedel–Crafts catalysts. Similarly, the cross-linking of polyvinyl acetate in our experiments may be due to the elimination of acetic acid; Marvel and Riddle (*J. Amer. Chem. Soc.*, **1940**, **62**, 2666) suggested that the black insoluble material, formed during attempts to polymerise vinyl acetate with boron trifluoride, was produced by the elimination of acetic acid to give a cross-linked product. The dependence of speed of gelation upon the chlorine content of the polymer can be understood on the mechanism given above. The possibility that the solvent itself is involved in the reaction thus :



$$\begin{array}{l}\mathrm{-CH_2-CHCl-}\\ \mathrm{CH_2Cl}\\ \mathrm{CH_2Cl}\\ \mathrm{-CH_2-CHCl-}\end{array}\longrightarrow\begin{array}{l}\mathrm{-CH-CHCl-}\\ \mathrm{\quad CH_2}\\ \mathrm{\quad CH_2}\\ \mathrm{-CH-CHCl-}\end{array}+2\mathrm{HCl}$$

is rejected because (i) cross-linking occurs most readily in nitrobenzene solution, yet this substance is very inert in Friedel–Crafts reactions (Calloway, *Chem. Reviews*, **1935**, **17**, 327), (ii) gelation cannot be made to occur in toluene solution by adding small amounts of ethylene dichloride or of tetrachloroethane, substances which by themselves are good solvents for the reaction. It seems that the efficiency of a solvent for this reaction depends on some physical property, and our results indicate that it is probably dielectric constant. This agrees with the fact that Friedel–Crafts reactions proceed by an ionic mechanism and also that dielectric constant affects similarly the Friedel–Crafts catalysed polymerisation of α-methylstyrene (Pepper, *Nature*, **1946**, **158**, 789).

Solutions in nitrobenzene of a hydrocarbon polymer such as polystyrene do not gel, because elimination of a molecule such as hydrogen chloride between two polymer molecules is impossible, but polystyrene will gel slowly in ethylene dichloride presumably by a reaction involving the solvent, such as :



Chlorinated polystyrenes do not undergo cross-linking in nitrobenzene solutions if the chlorine is attached to the benzene ring, because such chlorine atoms are inert in Friedel–Crafts reactions. Whether gelation occurs or not in nitrobenzene solution, can be used as a convenient test for the position of chlorine atoms in chlorinated polystyrenes.

Darkening frequently occurs during Friedel–Crafts reactions, but following a suggestion of Marvel and Riddle (*loc. cit.*), the darkening in our experiments may be due in part to conjugation brought about by the elimination of hydrogen chloride or of acetic acid from neighbouring carbon atoms in a polymer molecule. As shown above there was evidence for unsaturation in the cross-linked product. In this connection Boyer (*J. Physical and Colloid Chem.*, **1947**, **51**, 80) has shown that a relationship exists between the extent of discoloration in polymers containing chlorine and the amount of conjugation brought about by the elimination of hydrogen chloride; the same phenomenon is shown by our series of cross-linked products made with varying amounts of aluminium chloride, where the extent of discoloration increases with the amount of catalyst employed. It is unlikely that polymethyl methacrylate is cross-linked by the elimination of methyl formate, and it is probable that a simple molecule such as methyl alcohol is eliminated. Similarly the elimination of methyl formate from neighbouring carbon atoms in a polymer chain is unlikely and so conjugation probably does not occur; this may well account for the slight darkening observed during the cross-linking of polymethyl methacrylate.

Detailed consideration of the mechanism of the reactions described in this paper will be given in a second communication.

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