

341. The Polymerisation of Styrene by Titanic Chloride. Part III.* Discussion.

By P. H. PLESCH.

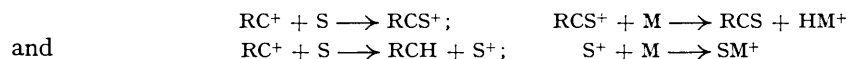
The results presented in Parts I and II are discussed. It is concluded that styrene cannot be polymerised by titanac chloride in the absence of a co-catalyst. Polymerisation induced by this halide and trichloroacetic acid in toluene solution yields low polymers with terminal tolyl groups, *i.e.*, toluene acts as a transfer agent. It is shown that certain alkyl halides and nitrobenzene may act as co-catalysts. Some of the ways in which a solvent may influence cationic polymerisations are discussed. A new nomenclature for various types of transfer reaction is suggested.

IN Parts I and II (preceding papers) some new kinetic and analytical data on the formation of polymers from styrene under the influence of titanac chloride have been presented. These show that there are phenomenological differences between the polymerisations taking place in polar and in non-polar solvents. We therefore discuss these two types of system separately, and then consider, quite generally, some of the possible functions of the solvent in cationic polymerisations.

Non-polar Solvents.—Clark's work (see "Cationic Polymerisation and Related Complexes," ed. P. H. Plesch, Heffer and Sons, Cambridge, 1953, p. 99) has shown that the polymerisation of styrene by boron fluoride in carbon tetrachloride only takes place in the presence of a co-catalyst, such as water. Using the same catalyst and solvent, Brackman and Plesch (*J.*, in the press) obtained the same result with *cis*- and *trans*-stilbene. With alkenes, similar results have been established for some time (for detailed references see *op. cit.*). The present results obtained with styrene and titanac chloride and with hexane and toluene as solvents support the view that styrene can only be made to polymerise by metal halides in the presence of a co-catalyst. The small and variable residual reactivity found in the present work, and previously by Pepper (*Trans. Faraday Soc.*, 1949, **45**, 397, 404) with similar systems, is ascribed to adventitious co-catalyst, probably water. Jordan and Mathieson's claim (*J.*, 1952, 611) that styrene can be polymerised by aluminium chloride without a co-catalyst, cannot be accepted at its face value, and has indeed been severely criticised (*op. cit.*, p. 93). The present work, like that of Williams (*J.*, 1940, 775, Table I, Expts. Nos. 15 and 22) shows once again the importance of an adequate purification technique.

The kinetic results obtained in the present work with toluene as solvent are not sufficient for the deduction of a reaction scheme. However, in conjunction with the analytical and spectroscopic results, they indicate clearly that a co-catalyst is essential, and that the co-catalyst trichloroacetic acid is not incorporated in the polymer. This is in contrast to the results obtained with the system *isobutene*–titanac chloride–trichloroacetic acid–hexane, for which it was found that the co-catalyst is incorporated in the polymer as an end-group (Flett and Plesch, *J.*, 1952, 3355).

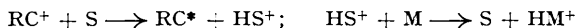
Furthermore, the spectroscopic and analytical evidence presented in Part II shows that the polystyrene chains contain a *p*-tolyl group. The low molecular weight of the polymer and the fact that polymerisation goes to completion indicate that the toluene must be involved in a reaction which terminates the physical, but not the kinetic, chain. For this there are at least two possible processes which may be represented thus:



where RC^+ represents the growing polymer, S the transfer agent (toluene in this instance), RCH and RCS are saturated, dead polymer, and M is the monomer. Both mechanisms represent "solvent transfer;" they are, however, sufficiently distinct to merit special

* Part II, preceding paper.

nomenclature, and it is proposed to designate the first Tr-t (transfer with chain termination by the transfer agent), and Tr-i (transfer with initiation by the transfer agent). A third mode of transfer, without incorporation of the transfer agent in the polymer, may be represented thus :



This may be designated Tr-ps (transfer of a proton by the transfer agent) : RC^* is an unsaturated or cyclised polymer. Kinetic chain transfer without extraneous transfer agent, *e.g.*, proton transfer, will be called Tr-pd (transfer of a proton directly), and may be represented thus : $RC^+ + M \longrightarrow RC^* + HM^+$. Some preliminary evidence for this type of transfer has been provided by several workers (*e.g.*, Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359; Meier, *J.*, 1950, 3656; Flett and Plesch, *loc. cit.*). It has been pointed out in Part II that, for the system under consideration here, it is not possible to decide whether the toluene is incorporated in the polystyrene by the Tr-i or the Tr-t mechanism.

Studies on the isomerisation of paraffins have shown that aromatic substances can act as chain-breakers in carbonium-ion reactions (Pines, Aristoff, and Ipatieff, *J. Amer. Chem. Soc.*, 1949, **71**, 749), but in polymerisations this has not been observed previously. The appreciable basicity of alkylbenzenes, well known from other reactions, suggests that styrene itself, or indeed polystyrene, might react in the same way as toluene. There is no evidence so far that they do, but for polymerisations carried out at high monomer concentrations it is a possibility which must be taken into account. The resulting polymers would be expected to have distinctive rheological properties, because reaction of a growing chain with a phenyl group on a "dead" chain would lead to branching (and a Tr-pd transfer); reaction of a growing chain with the ring of a monomer molecule would lead to what might be called a "perverse" propagation giving the following unit in the chain, $-CH_2-CHPh-C_6H_4-CHMe-CH_2-CHPh-$.

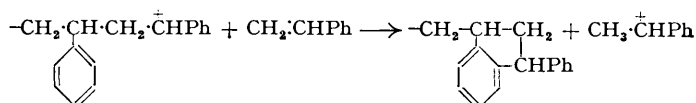
This kind of attack on the phenyl group would only be expected to take place at very high monomer concentrations, and/or with good alkylation catalysts such as aluminium chloride. It has indeed been found by Jordan and Mathieson (*J. Polymer Sci.*, 1952, **9**, 286) that polystyrenes produced with aluminium chloride as catalyst in carbon tetrachloride obey a molecular weight-viscosity relation which differs from that applicable to polystyrenes prepared under the influence of stannic chloride in ethylene dichloride (Pepper, *ibid.*, 1951, **7**, 347). The reason for this might lie in branching or perverse propagation.

In order to shed some light on this question, some polystyrenes prepared from 1.74M-solutions of monomer in ethylene dichloride and in benzene by the action of stannic chloride were obtained by the courtesy of Dr. D. C. Pepper. The spectra of these polymers gave no indication of the presence of disubstituted benzene rings, but they did show a strong absorption band near 1220 cm^{-1} , not found in other polystyrene spectra, which may indicate a quaternary carbon atom. This type of branching in ionically produced polystyrenes must be due to an entirely different process. It may well indicate a hydride-ion transfer reaction analogous to that found for polypropenes by Fontana (*op. cit.*, p. 122); Plesch (*op. cit.*, p. 132) has shown that its occurrence in polystyrenes might be expected. The absence of terminal unsaturation in these polymers is intelligible in terms of the suggested transfer reactions.

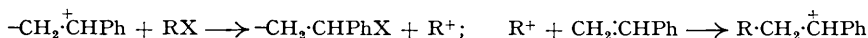
Alkyl Halide Solvents.—With ethylene dichloride as solvent the kinetics of the polymerisation agree qualitatively with those which Pepper established for the same solvent and monomer, but with stannic chloride as catalyst (*loc. cit.*). A reaction scheme similar to that suggested by Pepper therefore seems applicable. The present results differ from his in that the third-order rate constant is about two powers of ten greater than that found by him, and that he found small amounts of water to have no appreciable effect on the rate of polymerisation. Although at this stage no exact significance can be attached to the magnitude of the difference between the rate constants obtained with stannic and with titanichloride, it is in general agreement with other observations which show titanichloride to be the more powerful catalyst (Fairbrother and Seymour, quoted by Plesch, Polanyi, and Skinner, *J.*, 1947, 257; Russell, *op. cit.*, p. 115). The second discrepancy

concerning the effect of water is not easy to explain. It has been discussed in some detail (*op. cit.*, p. 70) without, however, being resolved unambiguously.

The present kinetic results indicate that polymerisation of styrene can be catalysed by titanichloride in ethylene dichloride in the absence of water. However, Pepper's recent discovery, that in this solvent hydrochloric and hydrobromic acid will catalyse this polymerisation (*op. cit.*, p. 75), casts doubt upon this interpretation of the results; it is at least possible that in the present experiments the real catalyst was not the metal halide but adventitious hydrochloric acid contained in the titanichloride solution. The catalysis of cationic polymerisation by hydrogen halides depends upon the cations and anions being separate kinetic entities, and therefore the reaction rate would be expected to be proportional to the $\frac{3}{2}$ power of the monomer concentration and the square-root of the catalyst concentration. This is evidently not the case, and it thus seems very unlikely that in these reactions the real catalyst was hydrogen chloride. It is concluded therefore that chain initiation is due to $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2^+$ ions formed by the interaction of the solvent with the metal halide. The infra-red spectra of the polymers support this conclusion. Spectroscopic results also indicate that polystyrene chains may be started by Et^+ , *iso*- Pr^+ and *tert.*- Bu^+ ions. They also show that all the polymers contain methyl groups; for those prepared in ethylene dichloride this must be ascribed to a Tr-pd reaction. The terminal unsaturation, however, which might be expected to accompany such a transfer reaction is notably absent. This may be explained if it is assumed that the transfer reaction is accompanied by cyclisation:



It is well known that polystyrenes produced by cationic catalysis lack unsaturation; and the cyclisation reaction suggested here has been found by Schöpfle and Ryan for 1:1-diphenylethylene (*J. Amer. Chem. Soc.*, 1930, **52**, 4021), by Bergmann *et al.* (*Ber.*, 1931, **64**, 1493) and Dainton *et al.* (*op. cit.*, p. 80) for α -methylstyrene, and has been suggested for stilbene by Brackman and Plesch (*J.*, in the press; *op. cit.*, p. 103). An alternative reaction which will account for all the observed features involves yet another type of transfer reaction with the solvent, which will be called Tr-ti, because fragments of the solvent act as chain terminator and initiator. For an alkyl halide RX:



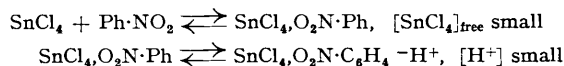
Much more detailed analytical work is required to decide whether, and to what extent, these alternative reactions take place in each particular system. In view of the fact that titanichloride can, like aluminium chloride, catalyse aromatic alkylations (Stadnikoff and Kaschtanoff, *Ber.*, 1928, **61**, 1389; Cullinane, *op. cit.*, p. 89), the solvent fragments identified spectroscopically in the polymer might be due to ring alkylation. That this is not so is shown conclusively by the absence of any absorption bands indicative of disubstituted benzene rings.

The co-catalytic activity of alkyl halides in the polymerisation of styrene by titanichloride links this reaction with the polymerisation of propene by aluminium bromide for which isopropyl bromide is a co-catalyst (Fontana *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3745; *op. cit.*, p. 122) and with the cationic isomerisations of hydrocarbons for which alkyl halides also act as co-catalysts (Pines *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 1742; 1951, **73**, 5738).

Function of the Solvent.—The importance of the dielectric constant of the solvent in ionic polymerisations was first pointed out by Pepper (*Nature*, 1946, **158**, 789; *Trans. Faraday Soc.*, *loc. cit.*) and later by George, Mark, and Wechsler (*J. Amer. Chem. Soc.*, 1950, **72**, 3891, 3896; *J. Polymer Sci.*, 1951, **6**, 525). Both groups of workers (using styrene and stannic chloride) showed that there appeared to be a linear relation between the logarithm of the polymerisation rate and the dielectric constant (D.C.) of the solution, at least over a limited range of D.C. However, a closer examination of Pepper's work,

and a comparison with that of George *et al.*, shows that this relationship, so far from being unique, is a function not only of the polar, but also of the non-polar, component of the solvent mixtures. Pepper's data show that the rate of polymerisation of styrene in a benzene-ethylene dichloride mixture of D.C. 8.5 is over 100 times greater than in a benzene-nitrobenzene mixture of the same D.C. Since it has been shown (Pepper, *loc. cit.*; Overberger *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 5541; *op. cit.*, p. 106) that the polymerisation in these systems is relatively insensitive to traces of water, this difference in rate in the two solvents indicates a more direct participation of the solvent in the polymerisation reaction than had been suspected before. This is supported by a comparison of Pepper's results with those of George *et al.* concerning the effect of D.C. on the polymerisation rate of styrene in benzene-nitrobenzene and in carbon tetrachloride-nitrobenzene, respectively. At corresponding values of the D.C. the rates are consistently very much greater in the latter mixtures than in the former, and so is the slope of the (log Rate)-D.C. plot. Although a detailed comparison of the results of different groups of workers is probably unjustified at present, yet these very large differences suggest strongly that the non-polar component of the solvent mixture may also influence the reaction.

The above-mentioned phenomena may be explained as follows: (1) Ethylene dichloride acts as a co-catalyst, giving a certain concentration of $\text{CH}_2\text{Cl}\cdot\text{CH}_2^+$ ions, but nitrobenzene combines with the catalyst (Reihlen and Hake, *Annalen*, 1927, **452**, 47) and, being in large excess, only leaves very little metal halide free to combine with adventitious co-catalyst; or the nitrobenzene-stannic chloride complex is itself catalytically active, but weak, giving only a small concentration of ions:

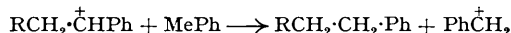


(2) Whereas nitrobenzene appears to be a poor co-catalyst (see *op. cit.*, p. 89), carbon tetrachloride may be a much better one. Unfortunately, there is no direct evidence for this supposition, but there are related phenomena which support it (see *op. cit.*, p. 97), *e.g.*, the addition of carbon tetrachloride to double bonds, catalysed by aluminium chloride.

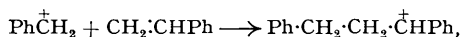
Co-catalysis by nitrobenzene explains very simply why water has little effect on the cationic polymerisations proceeding in this solvent: the mass-action effect would keep most of the metal halide combined with the solvent. It is noteworthy in this context that the co-catalytic activity of aliphatic nitro-compounds is very strong (Schmerling, *Ind. Eng. Chem.*, 1948, **40**, 2072; Russell, *op. cit.*, p. 89), which is intelligible in terms of their pseudo-acidic nature.

The present work, in conjunction with that of other authors, thus shows that in cationic polymerisations a solvent may affect the reaction in the following ways: (1) It may influence (mainly) the initiation and termination steps by electrostatic action (Pepper's dielectric-constant effect). (2) It may form a complex with the metal halide catalyst. This complex may give rise to ions which can initiate polymerisation, *i.e.*, the solvent may act as co-catalyst. If a complex is formed the concentration of free metal halide will be considerably reduced so that a complexing but non-co-catalytic solvent will act as inhibitor. (3) It may act as a transfer agent. Whether a particular solvent can act thus, and the type of transfer which it produces, will depend on the monomer concerned, because the regulating feature in this reaction is the difference between the free-energy changes accompanying the interactions of the polymer ion with the solvent and of the solvent ion with the monomer.

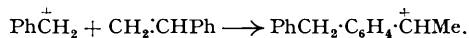
Added in Proof.—Recent work suggests that the polymerisation of styrene in toluene may involve not the tolyl ion as suggested above, but the benzyl ion participating in a Tr-i reaction:



The presence of *para*-disubstitution in the polymer then requires that this should proceed not only by the obvious route,



but also by the "perverse" route



The evidence presented here is consistent with both alternatives.

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