147. *The Cationic Polymerization of Styrene. Part II.*[1] *Spectra of Polymerizing Systems.*

By D. O. Jordan and F. E. Treloar.

Solutions of styrene and stannic chloride or aluminium chloride in 1,2-dichloroethane or carbon tetrachloride are coloured and polymerization takes place. It is shown that this colour is due to the presence of the 1-phenylethyl cation and the styrene polymer ion. This confirms the suggested mechanism for the polymerization of styrene by such catalysts.

In Part I,[1] it was shown that the 1-phenylethyl ion can exist in both 1,2-dichloroethane and carbon tetrachloride. The methods described there have been extended in order to investigate the coloured solutions formed when styrene is polymerized by using Friedel–Crafts halides as catalysts in an attempt to discover the nature of the intermediates present.

Experimental.—Materials. Styrene, 1-phenylethyl chloride, 1,2-dichloroethane, carbon tetrachloride, and stannic chloride were purified as in Part I.[1] Aluminium chloride was prepared from aluminium and silver chloride by a modification of the method of Wallace and Willard [2] or as described in Part I. The two samples gave similar spectroscopic results.

Solutions were made up and measured, as described in Part I, for organic solvents.

Results.—The spectra of the coloured solutions formed when styrene is polymerized by aluminium chloride in carbon tetrachloride and 1,2-dichloroethane are shown in Fig. 1. The

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[1] Part I, Jordan and Treloar, preceding paper.

[2] Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.

absorption maxima occur at 4200 and 4450 Å in carbon tetrachloride and 4100 Å in 1,2-dichloroethane. To elucidate the nature of the last peak, the spectrum of the system styrene–1-phenylethyl chloride–stannic chloride–1,2-dichloroethane was studied. The solutions immediately developed an intense yellow colour and polymerization occurred as shown by precipitating the polymer with methanol at various times. The results of the measurement of the absorption spectra for a typical experiment are shown in Fig. 2. In solutions containing both styrene and 1-phenylethyl chloride, a peak immediately developed at 4100 Å closely similar to that shown in Fig. 1 for the system styrene–aluminium chloride–1,2-dichloroethane. The value of this maximum remained constant for at least 12 hr. and thereafter gradually decreased. A solution containing the same concentration of 1-phenylethyl chloride, but no styrene, gradually developed the 4400 Å peak characteristic of the 1-phenylethyl ion. A solution containing only styrene at the same concentration as in the mixed solution immediately developed a very pale yellow colour; the maximum was hard to define but occurred at about 4100 Å.

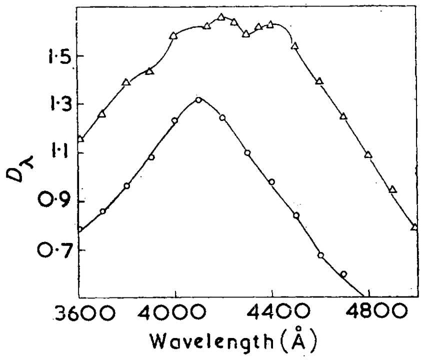

FIG. 1. *The spectra of polymerizing systems:*
○ *styrene*–AlCl$_3$–1,2-*dichloroethane.*
△ *styrene*–AlCl$_3$–*carbon tetrachloride.*

Discussion.—It is suggested that the peak at 4100 Å in 1,2-dichloroethane is due to the growing polymer ion $\mathrm{Me{\cdot}CHPh{\cdot}[CH_2{\cdot}CHPh]_n{\cdot}CH_2{\cdot}\overset{+}{C}HPh}$. This cannot be derived initially from a reaction between PhMeHC$^+$ and styrene since it is present in stationary concentration from the start of the reaction, when the concentration of 1-phenylethyl carbonium ions is negligible. Hence the initial reaction to form this ion must be either a combination of a 1-phenylethyl chloride–SnCl$_4$ complex with styrene, which subsequently forms the growing ion pair, or a termolecular reaction of styrene, 1-phenylethyl chloride, and SnCl$_4$. No free PhMeHC$^+$ ions are formed in the system, as shown by comparison with the spectrum of the same system which contains no styrene. After 18 hr. the concentration of 1-phenylethyl ions is very great indeed, but the system containing styrene shows only a slight fall-off in optical density due to the gradual cessation of polymerization.

In the total absence of 1-phenylethyl chloride, a very weak peak occurred at 4100 Å which, by comparison with solution 1 (Fig. 2), is to be attributed to the presence of the polymer ion. This will be formed since water is undoubtedly present and hence polymerization will be proceeding. The suggestion by Devlin and Pepper[3] that this is due to a complex between the olefin and stannic chloride is now untenable; their observation that the colour is destroyed by solvents which form strong complexes is most readily explained by the destruction of the ion by such solvents.

This interpretation of the results is in substantial agreement with the results of Colclough and Dainton[4] on the polymerization of styrene by stannic chloride in 1,2-dichloroethane

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[3] Devlin and Pepper, " Cationic Polymerization and Related Complexes," ed. P. H. Plesch, Heffer, Cambridge, 1953, p. 24.

[4] Colclough and Dainton, *Trans. Faraday Soc.*, 1958, **54**, 901.

with t-butyl chloride as cocatalyst. These authors suggested that the initial step in the reaction is either a reaction of the monomer with a catalyst–cocatalyst complex or a termolecular reaction. Since the 1-phenylethyl and t-butyl cations have nearly equal stabilities, the two systems are directly comparable. From the results presented here it is not possible to distinguish between the two possibilities suggested by Dainton and Colclough, but it is clear that no ions are involved in the initial step.

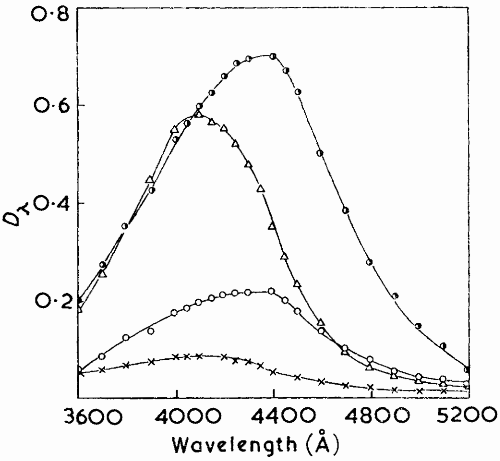

FIG. 2. *The spectra, in* 1,2-*dichloroethane, of the systems*: × *styrene* ($4\cdot22 \times 10^{-2}$M) *and* $SnCl_4$ ($1\cdot74 \times 10^{-1}$M) *after* 0·5 *and* 1·5 *hr.*, △ *styrene* ($4\cdot22 \times 10^{-2}$M), $SnCl_4$ ($1\cdot74 \times 10^{-1}$M), *and* 1-*phenylethyl chloride* ($8\cdot14 \times 10^{-3}$M) *after* 0·5 *and* 1·5 *hr.*; 1-*phenylethyl chloride* ($8\cdot14 \times 10^{-3}$M) *and* $SnCl_4$ ($1\cdot74 \times 10^{-1}$M), ○ *after* 0·5 *hr.*, ◑ *after* 1·5 *hr.*

In the carbon tetrachloride solution the 4450 Å peak must be attributed to the 1-phenylethyl carbonium ion in accordance with Part I,[1] while the 4200 Å peak is clearly due to the growing polymer ion. The Table, which summarizes the spectroscopic data on the two ions, shows clearly that solvent effects are the same in each case. It is interesting that the spectra show that both the 1-phenylethyl ion and the polymer ion exist together in carbon tetrachloride solution in agreement with some kinetic data [5] which suggest that preliminary ionization is rate-determining. Furthermore, the results on solutions in 1,2-dichloroethane indicate that there does exist a stationary concentration of growing chains, at least in this case, thus confirming an assumption universally made in investigations of polymerization kinetics.

Wavelength of maximum absorption for 1-*phenylethyl cation and growing polymer ion.*

Solvent	$PhMeHC^+$	Polymer ion
Sulphuric acid	4300	$<$4160 *
1,2-Dichloroethane	4400	4100
CCl_4	4450	4200

* The absorption maximum for 1,3-diphenylbut-1-ene or the styrene dimer in concentrated sulphuric acid [Inoue and Mima, *Chem. High Polymers* (*Japan*), 1957, **14**, 402].

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[5] Jordan and Treloar, unpublished results.