340. *The Polymerisation of Styrene by Titanic Chloride. Part II.* The End-groups.*

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Infra-red spectrographic analysis shows that polystyrenes prepared in various solvents, by titanic chloride as catalyst, have the following features. With toluene as solvent and trichloroacetic acid as co-catalyst, a large fraction of the polymer molecules contain tolyl end-groups. The co-catalyst is not incorporated in the polymer. With titanic chloride only, and ethyl, *iso*propyl, or *tert.*-butyl bromide, or ethylene dichloride as solvents, the polymer is found to contain initial and end-groups derived from the solvent. This is taken to indicate that these solvents can act as co-catalysts. The proportion of terminal double bonds, if they are present at all, is certainly small.

The object of this work was to discover the nature of the end-groups of the polystyrenes formed in different solvents and thus to obtain information about initiation, termination, and transfer mechanisms. The investigation was carried out by means of infra-red spectroscopy and degradation experiments.

EXPERIMENTAL

Materials.—Some of the polystyrenes used were the products of the reactions reported in Part I.* In addition, several specimens were prepared by the techniques described in Part I, and with similar concentrations of styrene and titanic chloride, ethyl, *iso*propyl, or *tert.*-butyl bromide being used as solvent. These materials were purified and dried by standard methods. After the polymerisations, the mixtures were shaken with dilute aqueous sodium carbonate to hydrolyse the titanic chloride, and titanic oxide was filtered off. The infra-red spectra were obtained from polymer films cast from these solutions by evaporation. In order to identify possible bands due to residual solvent, some specimens were separated from their original solvent by steam-distillation and dissolved in benzene, and the films cast from this solution.

Infra-red Spectroscopy.—The spectra of polymers produced in Pr^iBr and Bu^tBr solution were obtained by Mr. M. St. C. Flett, of Imperial Chemical Industries Limited, Dyestuffs Division, on a Hilger D.209 instrument using single-beam photographic recording. Thin films of the solid materials were used. The spectra of the other polymers were obtained by Dr. G. D. Meakins on the Perkin-Elmer double-beam instrument at Manchester University. The wave numbers recorded are believed to be correct to ± 2 cm.$^{-1}$. The spectra were analysed by a detailed comparison with each other, and with the published spectra of high-molecular-weight polystyrenes. In the Table are recorded all the bands which do not appear in all the spectra, and which are therefore ascribed to characteristic features of the particular polymer, such as end groups.

RESULTS AND CONCLUSIONS

The main features of all the spectra agree closely with that of polystyrene published by Bryant, Kennedy, and Tanner (*J.*, 1949, 2389). They all have a well-defined band at 1380 cm.$^{-1}$ suggesting the methyl group. The Table shows that there are characteristic differences between the spectra of the different specimens which must be ascribed to different end-groups. It follows that these must be derived from the solvent, and it has indeed been possible to interpret the differences in this way by means of the now well-known band assignments.

1. *Solvent, toluene*; *co-catalyst, trichloroacetic acid.* Strong bands at 820, 1020, 1515, and 1890 cm.$^{-1}$ indicate *para*-disubstitution. The weaker bands between 1000 and 1200 cm.$^{-1}$ support this. There is no evidence for *ortho*- or *meta*-disubstitution. The strong band at 730 cm.$^{-1}$ may be due to the presence of a (possibly substituted) phenyl group attached to $\cdot CH_2\cdot$ (McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318). The

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* Part I, preceding paper.

band lies just outside the limits given by these authors (737—747 cm.$^{-1}$) for $C_6H_5{\cdot}CH_2{\cdot}$. A strong band at 2970 cm.$^{-1}$ indicates the presence of CH_3 groups. The absence of any distinctive features in the 770 cm.$^{-1}$ region shows the absence of $CH_3{\cdot}CH_2{\cdot}$ groups. Oxidative degradation of these polystyrenes gave a small yield of terephthalic acid (subl. about 300°) [dimethyl ester (first m. p. 136—139°, on re-melting 140—141°)].

(The symbols +, ++, +++ mean that the bands are weak, moderate, and strong respectively. The strength is assessed qualitatively, partly in relation to the intensity of absorption in the immediate vicinity of the band; 0 means that the band is absent; — means that the relevant region was not recorded.)

	Solvent				
Wave no., cm.$^{-1}$	PhMe	EtBr	$C_2H_4Cl_2$	Pr^{i}Br	Bu^{t}Br
678	0	+++	+++	—	—
728	+++	0	0	—	—
798	+	0	0	0	0
820	+++	0	0	0	0
850	0	0	0	0	++
927	0	0	0	0	+
1020	+++	0	0	0	0
1045	++	0	0	0	0
1060	++	0	0	0	0
1070	0	+++	} +++	+++	+++
1080	++	0		0	1078+++
~1100	0	0	0	+	0
1115	++	+	0	0	0
1122	++	0	+	0	0
~1130	0	0	0	+	0
1235	0	0	0	0	+++
1250	0	0	+	0	0
1260	0	+	0	+	++
1365	0	+	+	0	+++
1380	+++	+++	+++	1370—1380++	0
1480	0	+++	+++	++	—
1515	+++	0	0	—	—
1540	0	+	+	—	—
1890	+	0	0	—	—
2970	+++	+	+	—	—

These results indicate the presence of *p*-dialkylphenyl groups in the polymers. Since these are only found in polystyrenes produced in toluene solution, it is concluded that they are due to *p*-tolyl groups. These may be present as end-groups, due to the reaction

$$-CH_2{\cdot}\overset{+}{C}H{\cdot}C_6H_5 + C_6H_5{\cdot}CH_3 \longrightarrow -CH_2{\cdot}CH(C_6H_5){\cdot}\overset{+}{C}_6H_5{\cdot}CH_3$$

followed by the proton-transfer reaction

$$R{\cdot}\overset{+}{C}_6H_5{\cdot}CH_3 + CH_2{:}CH{\cdot}C_6H_5 \longrightarrow R{\cdot}C_6H_4{\cdot}CH_3 + CH_3{\cdot}\overset{+}{C}H{\cdot}C_6H_5$$

Or they may be present as initial groups due to the reactions

$$-CH_2{\cdot}\overset{+}{C}H{\cdot}C_6H_5 + C_6H_5{\cdot}CH_3 \longrightarrow -CH_2CH_2{\cdot}C_6H_5 + \overset{+}{C}_6H_4{\cdot}CH_3$$

$$\overset{+}{C}_6H_4{\cdot}CH_3 + CH_2{:}CH{\cdot}C_6H_5 \longrightarrow CH_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}C_6H_5$$

It is not possible to decide definitely between these alternatives. The band at 730 cm.$^{-1}$ and the presence of terephthalic acid in the oxidation products make the second one appear rather more plausible. The spectra provide no evidence for the presence of trichloroacetate end-groups derived from the co-catalyst as was found for poly*iso*butenes (Flett and Plesch, *J.*, 1952, 3355). This agrees with the kinetic results, which gave no indication that the co-catalyst was consumed during the polymerisation.

2. *Solvent, ethyl bromide.* The spectra of the polystyrenes prepared in this solvent show only few distinctive bands. The strong band at 678 cm.$^{-1}$ has been assigned tentatively to a C–Cl or possibly a C–Br bond. The presence of halogen was confirmed analytically. The band at 755 cm.$^{-1}$, present in all polystyrenes and due to the $C_6H_5{\cdot}CHRR'$ group, is markedly broadened towards 740 cm.$^{-1}$ in these spectra. This,

and the bands at 1070 and 1480 cm.$^{-1}$, indicate the presence of at least two CH_2 groups with a terminal CH_3. These features have therefore been assigned to the $CH_3\cdot CH_2\cdot CH_2$ group. This is consistent with the theory that the alkyl halide acts as co-catalyst according to the reaction

$$\mathrm{Et + TiCl_4Br^- + CH_2{:}CH\cdot C_6H_5 \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot \overset{+}{C}H\cdot C_6H_5 + TiCl_4Br^-}$$

and that the chain is terminated by the reaction

$$\mathrm{-CH_2\cdot \overset{+}{C}H\cdot C_6H_5 + TiCl_4Br^- \longrightarrow -CH_2\cdot CH(C_6H_5)Cl + TiCl_3Br}$$

The solvent may also be involved in an analogous chain-transfer reaction giving rise to the same end groups. This will be discussed in Part III (following paper).

3. *Solvent, ethylene dichloride.* The bands at 678, 1070—1080, and 1480 cm.$^{-1}$ are given the same assignment as in the polystyrenes prepared in ethyl bromide. This is consistent with an initiation and termination mechanism analogous to that illustrated above for ethyl bromide, ethylene dichloride acting as co-catalyst. The fact that in the spectra of these polymers there is a prominent methyl band at 1380 cm.$^{-1}$ and a slight shoulder near 2970 cm.$^{-1}$ shows that some chains must have been started by a proton transfer reaction.

4. *Solvent,* tert.*-butyl bromide.* The bands at 927, 1235, 1260, and 1365 cm.$^{-1}$ indicate unambiguously the presence of *tert.*-butyl groups. This can be accounted for by a mechanism analogous to that suggested for ethyl bromide.

5. *Solvent,* iso*propyl bromide.* The presence of *iso*propyl groups in the polymer is made very probable by the bands at 1020 and near 1100, 1130, and 1480 cm.$^{-1}$, and the fact that the methyl band is very broad (1370—1380 cm.$^{-1}$). This suggests that this compound, too, can act as co-catalyst in the polymerisation of styrene by titanic chloride.

6. *General features.* It is noteworthy that none of the spectra of polystyrenes prepared in alkyl halide solvents shows any sign of disubstituted benzene rings. It has been shown that in poly*iso*butene there is a high degree of terminal unsaturation (Dainton and Sutherland, *J. Polymer Sci.*, 1949, **4**, 37; Flett and Plesch, *Proc. Roy. Dublin Soc.*, 1950, **25**, 150; *loc. cit.*) arising from the loss of a proton from a carbon atom next to the carbonium ion at the growing end of the polymer. If the same process occurred in the cationic polymerisation of styrene, the corresponding terminal groups would be $\cdot CH{:}CH\cdot C_6H_5$. In aliphatic compounds this type of double bond has a characteristic absorption band at 965 cm.$^{-1}$; in *trans*-stilbene there are bands at 964 and 986 cm.$^{-1}$ (Brackman and Plesch, *J.*, 1952, 2188). In all the polystyrenes examined here, there are three weak bands at 940, 965, and 980 cm.$^{-1}$. The relative intensities of the first and the third of these are the same in all spectra, whereas the intensity of the middle band varies considerably in relation to those of its neighbours. This band at 965 cm.$^{-1}$ might therefore be associated with terminal unsaturation. However, it also appears in the spectra of high-molecular-weight polystyrenes prepared by free-radical catalysis (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246; Bryant, Kennedy , and Tanner, *loc. cit.*). It is possible that even the material of high molecular weight used by these authors contained sufficient unsaturated low polymer, and that this band is indeed due to the suggested group. Moreover, this group should give rise to two bands between 1600 and 1700 cm.$^{-1}$. Although all our spectra and the published spectra show a weak, broad band near 1650 cm.$^{-1}$, it is doubtful whether this can be ascribed to a C=C bond. Thus, we conclude that even if there are terminal double bonds in these polymers, their number must be small. A detailed discussion of this feature will be given in Part III (following paper).

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[*Received, January 25th,* 1952.]