

717. *The Kinetics of Catalytic Polymerisations. Part VIII.* The Constitution of Polystyrene formed by Di- and Tri-chloroacetic Acid Catalysis.*

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The constitution of polystyrene formed by di- and tri-chloroacetic acid catalysis in different environments has been studied chemically and by infrared spectroscopy. Each polymer molecule contains a terminal chloroacetate group, which is lost above 70° and on alkaline hydrolysis. Polymers of low molecular weight lose this group more readily. No exchange of hydrogen between water and the acid catalysts occurs, and no fragments from the solvents nitromethane, ethylene dichloride, and butyl bromide are incorporated in the polymer. The polymer contains a very small amount of unsaturation. The relation between the molecular weight of the polymer M and its intrinsic viscosity $[\eta]$ in benzene solution is $[\eta] = 5.2 \times 10^{-5}M$.

IN studies of the mechanism of polymerisations, knowledge of the exact constitution of the polymer generally permits certain definite conclusions to be drawn. It is at least as important as kinetic measurements, since these can sometimes be interpreted in terms of more than one reaction mechanism. It is possible for the same monomer, polymerised in different ways, to yield polymers of slightly different constitution. A knowledge of the molecular weight and the molecular-weight distribution, of certain simple chemical reactions of the polymer, and of the results of chemical and spectral analysis enables the constitution of the polymer to be completely described. Polystyrene prepared by catalysis with di- and tri-chloroacetic acid in various media has now been thus examined.

RESULTS AND DISCUSSION

Microchemical Analysis.—Polystyrene samples prepared by catalysis with trichloroacetic acid were analysed microchemically, and the results are shown in Table 1. Samples 1—5 are unfractionated polymers of normal molecular weight produced by polymerisation

TABLE 1. *Microchemical analysis.*

No.	C (%)	H (%)	Cl (%)	Mol. wt.		No.	C (%)	H (%)	Cl (%)	Mol. wt.	
				Obs.	Calc.					Obs.	Calc.
1	87.9	7.1	7.4	1100	1089	9	73.4	7.6	18.4	520	480
2	83.3	6.9	7.0	1300	1350	10	81.6	8.3	8.4	910	910
3	83.1	6.9	6.6	1310	1360	11	80.3	7.1	9.7	370	(950)
4	90.1	8.7	2.1	1550	1600	12	79.2	7.0	9.5	385	(950)
5	86.4	7.3	3.3	1850	1850	13	88.9	7.4	3.7	425	(2000)
6	59.5	5.2	24.6	260	280	14	81.4	8.7	9.5	475	(920)
7	59.2	5.5	24.3	270	275	15	86.4	7.4	3.3	520	(2500)
8	70.4	6.8	17.5	340	340						

in absence of solvent. Comparison of their molecular weights measured cryoscopically with the molecular weights calculated from the chlorine : carbon ratio by assuming that on average one catalyst molecule is incorporated in each polymer chain shows that this assumption is correct.

More than one catalyst molecule might be incorporated per polymer molecule if some catalyst molecules lost chlorine atoms, but in view of the agreement of measured and calculated molecular weights and of the improbability of such loss under the experimental conditions, this possibility can be rejected. Samples 6—10 are polymers of low molecular weight obtained by fractionation by vacuum distillation below 30°. The agreement between their measured and calculated molecular weights confirms that one catalyst molecule is incorporated in each polymer chain. Since this is true for both unfractionated and fractionated polymers, the number of catalyst molecules incorporated per polymer molecule is not a function of molecular weight, but is unity for polymer molecules of all sizes.

Samples 11—15 are fractions of low molecular weight obtained by vacuum distillation above 70°. Here the calculated molecular weights are all too high, which shows that the incorporated catalyst is readily lost on distillation at these temperatures.

In Part VII it was shown that catalyst is consumed during polymerisation, and values of the mole ratio (acid consumed) : (monomer consumed) were given. This ratio for trichloroacetic acid is never greater than 1 : 3.14, so clearly only a part of this consumed acid can be accounted for by incorporation.

Analysis for Unsaturation.—Addition of bromine proved unsuitable, the uptake of bromine by the polymers continuing slowly for fairly long periods, and it is probable that some substitution in the phenyl rings or along the polymer chain took place. Microhydrogenation of the polymers at a palladium-charcoal catalyst, specific for ethylenic double bonds, was therefore employed. No unsaturation was found in any sample extracted by the normal procedure, but fractions of low molecular weight prepared by distillation above 70° were unsaturated. Table 2 describes the effect of repeated distil-

TABLE 2. *Effect of repeated distillation at 70° on the degree of unsaturation.*

Wt. of polymer (g.)	0.0319	0.0276	0.0298	0.0255	0.0317
No. of distilns.	0	1	2	3	4
Hydrogen uptake (moles × 10 ⁵)	0	0.9298	1.945	2.738	3.537
Double bonds per molecule	0	0.16	0.31	0.51	0.53

lation at 70° on a mixture of polymers of initially an average molecular weight of 475. Together with the results in Table 1, which indicate a reduction of the chlorine content under the same conditions, these results show that at 70°, polymers of low molecular weight lose their incorporated catalyst, and a double bond is formed in its place. Polymers of higher molecular weight are stable at these temperatures, but the catalyst can be removed by alkaline hydrolysis, which suggests that the acid is incorporated as trichloroacetate end-groups. This is confirmed by a positive ester-linkages test for the polymers.

The Intrinsic Viscosity-Molecular Weight Relation.—The number-average molecular weights (M) of the polymer samples were determined cryoscopically in benzene, and the corresponding intrinsic viscosities ($[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$) were measured¹ at 25° for benzene solutions. The plot of intrinsic viscosity against molecular weight is linear and passes through the origin; its equation is

$$[\eta] = 5.2 \times 10^{-5}M \quad \dots \dots \dots (1)$$

This relation differs from those of Staudinger² and Jordan and Mathieson,³ who found $[\eta] = 1.81 \times 10^{-5}M + 0.0115$ for polystyrene of low molecular weight prepared by aluminium chloride catalysis. Kemp and Peters⁴ however found that eqn. (1) held for unfractionated polymers. The trichloroacetate end-group, which is relatively large, could lead to increased viscosities.

¹ Fitzgerald and Fuoss, *Ind. Eng. Chem.*, 1950, **42**, 1603.

² Staudinger, "Die Hochmolekularen Organischen Verbindungen," Springer, Berlin, 1932.

³ Jordan and Mathieson, *J.*, 1952, 611.

⁴ Kemp and Peters, *Ind. Eng. Chem.*, 1942, **34**, 1097.

TABLE 3. *Infrared spectra of benzyl esters (cm.⁻¹).*

Benzyl dichloroacetate	695 *	744	816 *	911	969	1000 *	1032	1165 *	1215
Benzyl trichloroacetate	680 *	759	828 *	893	969	1002		1159 *	1229 *
Benzyl dichloroacetate	1247 *	1280 *	1299	1375	1450	1499	1595	1760 *	
Benzyl trichloroacetate				1375	1450	1490	1595	1760 *	

Infrared Spectroscopy.—The infrared spectra were measured of a series of polystyrenes prepared under different conditions, and of benzyl dichloroacetate and benzyl trichloroacetate for comparison (Table 3). The polystyrene samples were examined as films 0.05 mm. thick prepared by evaporation of benzene solutions. The spectra of the polystyrenes are given in Table 4. Samples 1 and 2 are polystyrenes prepared by polymerisation without solvent by use of trichloroacetic acid and dichloroacetic acid as catalysts, respectively; samples 4 and 5 are fractions of low molecular weight (<800) of these polymers, respectively. Sample 9 was prepared by trichloroacetic acid catalysis without solvent, and then hydrolysed to remove trichloroacetate groups. Sample 11 was prepared by dichloroacetic acid catalysis without solvent in the presence of deuterium oxide (no H₂O). Sample 13 was prepared as sample 2, but is of higher molecular weight. Samples 16, 17, and 18 were prepared by dichloroacetic acid catalysis in ethylene dichloride, nitromethane, and *n*-butyl bromide solution respectively. Comparison of 1 and 2, and of 4 and 5 shows the influence of the two different catalysts; of 1 and 4 and of 2, 5, and 13 the influence of polymer molecular weight; of 1 and 9 the presence of catalyst fragments; of 1 and 11 the influence of water; and of 13, 16, 17, and 18 the rôle of the solvent.

TABLE 4. *Infrared spectra of polystyrene prepared by chloroacetic acid catalysis (cm.⁻¹).*

Sample nos.									
1	2	4	5	9	11	13	16	17	18
680m	680m	680m		680s	680s	680s	680s	680s	680s
700s	700s	700s	700s	742s	700s	700s	700s	700s	700s
762s	762s	750m	760m	760s	760s	760s	760m	760s	760s
830s	828w	760s	816m	800w	818m	830s	800w	820m	810s
885m	850w	845w	870w	844w	844m	860m	823w	843w	860m
917w	910w	910w	910w	870w	909m	880m	880w	875w	890m
965m	965w	940w	955m	909w	967m	925m	930m	900w	925m
983m	983w	960w	983m	938w	1015m	945m	985m	925w	945m
1005m	1020m	1005m	995m	967w	1035m	965m	1035m	947m	960m
1015m	1045m	1045m	1010m	980w	1070m	978m	1064w	995w	980m
1045s	1070w	1145w	1037m	1030m	1170m	998m	1160m	1030m	1005m
1180s	1180m	1175w	1057m	1070m	1233m	1035m	1225m	1070w	1035m
1215s	1215m	1235w	1077m	1110w	1376m	1060w	1235s	1090w	1060m
1255s	1240w	1255w	1155s	1150w	1441s	1110m	1278s	1140w	1110w
1290s	1280m	1290w	1200m	1176w	1474s	1135m	1290w	1180w	1135w
1350m	1455s	1350w	1230m	1250w	1555w	1195m	1310w	1240s	1195s
1390w	1470m	1445s	1268s	1303w	1770m	1235s	1360w	1278m	1225m
1470s	1485s	1460m	1325m	1323w	1800m	1278m	1470s	1310w	1278m
1515m	1555w	1475s	1435m	1376m	1880w	1310w	1500m	1360m	1310w
1600w	1585m	1525w	1475m	1450s	1930w	1360m	1560w	1470s	1360m
1635w	1770m	1565m	1590w	1470m	1980w	1470s	1600m	1500m	1470s
1740w	1800w	1585w	1620w	1485s	2520s	1500m	1760s	1560w	1500m
1760s	1880w	1760m	1680w	1615m	2940s	1560w		1600m	1560w
1930w	1930w	1880w	1760s	1670w		1600m		1760s	1600s
2520m	2520s	1930w	1860w	1760w		1760s			1760s
2940m	2940m	1980w	1930w	1880w					
3190w		2710m	2530m	1930w					
		2940s	2940m	1980w					
		3190m	3190m	2710m					
			3330w	2940s					
				3190m					
				3350w					

Examination for Catalyst Fragments and Unsaturation.—In Table 3 bands characteristic of the chloroacetate groups are marked by asterisks. Substitution of chlorine for hydrogen causes small shifts in the bands. Comparison of any of the polystyrene spectra in Table 4

(except no. 9) with the spectrum of polystyrene prepared by a free-radical mechanism shows clearly the presence of di- or tri-chloroacetate groups. For example, no. 5, which contained 24.6% of Cl, shows no new bands in the regions 1610—1550, 1420—1300, or 2500—2700 cm^{-1} characteristic of the $\text{O}=\text{C}-\text{O}^-$ and OH groups, from which it is clear that no free acid is present, since dichloroacetic acid itself shows strong bands in these regions. The strong absorption at 1760 cm^{-1} in all the polymers shows the presence of combined ester groups, and this is supported by the C—O absorptions at 1268, 1230, and 1200 (no. 5) and 1290, 1255, and 1215 cm^{-1} (no. 1). Moreover, the intensity of the absorption at 1760 cm^{-1} is proportional to the chlorine content of the polymer, no. 2 (of high molecular weight and low chlorine content) showing a much weaker absorption here than no. 5. The spectroscopic evidence supports the conclusion, already drawn from chemical analyses and molecular-weight measurements, that the catalyst becomes combined in the polymer as a di- or tri-chloroacetate group, there being one such group per polymer molecule. The band at 680 cm^{-1} (all samples except no. 5), however, cannot be assigned to C—Cl bending vibrations since it is present in polystyrene prepared by a free-radical mechanism and in polystyrene hydrolysed to remove chloroacetate groups (no. 9); it could be due to C—CH deformation vibrations of residual benzene. The strong band near 760 cm^{-1} present in all polystyrene samples prevents observation of the C—Cl band in this region.

The band at 816 cm^{-1} (no. 5) can be correlated with a similar band in the spectrum of benzyl dichloroacetate and may be due to C—O stretching vibrations which are sensitive to the mass of the polymer chain. The bands at 828 (no. 2) and 830 cm^{-1} (nos. 1 and 13) can be similarly assigned. Comparison of the spectrum of the hydrolysed polymer (no. 9) with that of no. 1 shows that the strong absorption at 1760 cm^{-1} has almost disappeared and the bands at 1290 and 1255 cm^{-1} are missing. The band at 830 also has been lost, permitting the observation of the 844 cm^{-1} band due to C=CH deformation vibrations in the benzene ring, which can be seen also in polystyrene prepared by a radical mechanism and no. 4. The bands at 1180 and 967 cm^{-1} are also much reduced in intensity in the hydrolysed polymer which suggests that they also are associated with the chloroacetate group. Clearly this group has been removed by hydrolysis. New weak bands at 3350, 1303, and 1110 in the hydrolysed polymer may arise from the replacement of the chloroacetate group by a hydroxyl group. It is not possible to determine whether hydrolysis leads to the formation of terminal unsaturation since the bands at 980 and 967 cm^{-1} (no. 9) due to unsaturation are also present in the unhydrolysed polymers (965 and 983 cm^{-1} in no. 1). This unsaturation in the polymer may arise through loss of a small proportion of terminal chloroacetate groups, or by the existence of a minor termination mechanism not involving catalyst recombination, or it may appear along the polymer chain in some way. Since chemical analysis revealed no unsaturation, it is clear that it is very limited.

The Rôle of Water.—Since water was shown to be a cocatalyst for polymerisation in absence of solvent (Part VII) it is possible that the proton which is donated to the monomer by the catalyst-cocatalyst complex is derived from water. A polymer, prepared in the absence of water but in the presence of deuterium oxide (no. 11), showed no band in the region of 2180 cm^{-1} , which can be assigned to the C—D stretching frequency. This suggests that the proton is donated exclusively by the acid, and the function of water in initiation is obscure. Evidently no exchange of hydrogen between water and the acid occurs at the initiating step of the reaction.

The Influence of Solvents.—Increased dielectric constant of the medium greatly enhances the rate of polymerisation, and no dependence of rate on water could be discovered for ethylene dichloride solutions (Part VII). Mechanisms involving ions derived from the solvent have been invoked to account for the absence of obvious cocatalysis in the polymerisation of styrene catalysed by titanium tetrachloride.⁵ Infrared spectroscopy might

⁵ Plesch, "Cationic Polymerisation," Heffer, Cambridge, 1953.

reveal the occurrence in the polymer of groups derived from the solvent. The positions of the absorption bands in nos. 13 and 18 are virtually identical, and so no bands are present in no. 18 which could be associated with terminal $\text{CH}_3\cdot[\text{CH}_2]_4\cdot$ groups. Such groups would absorb ⁶ at 720—740, 760—780, 1070, and 1480 cm^{-1} , and strong bands already occur in these regions which would mask any bands due to *n*-butyl groups and so their detection is not possible.

Comparison of nos. 13 and 17 shows that no. 17 has a new band at 843 and the bands at 965 and 978 cm^{-1} are absent. No nitrogen was found in the polymer prepared in nitromethane (no. 17) and it shows no bands which could be correlated with the nitromethyl group (1510—1560 and 1300—1350 cm^{-1}) which would arise if $\text{O}_2\text{N}\cdot\text{CH}_2\cdot$ ions became incorporated. Again it can be concluded that ions from the solvent are not incorporated in the polymer, and the observed differences in the spectra of nos. 13 and 17 can be attributed to the different molecular weights of the polymers, since comparison of nos. 1 and 4, and nos. 2, 5, and 13 shows clearly that molecular-weight differences cause many minor differences in the spectra.

Sample no. 16, prepared in ethylene dichloride, shows new bands at 800 and 1290 cm^{-1} when compared with no. 13, whilst the band at 860 is missing and bands at 945, 965, 978, and 998 are replaced by one at 985, and bands at 1110, 1135, and 1195 by one at 1160 cm^{-1} . Incorporation of chloroethyl residues would lead to bands at 680, 720—740, 1070, and 1480 cm^{-1} but since absorptions are already present at 680, 700, 1064, and 1470 cm^{-1} they would tend to be obscured. There is therefore no evidence for the incorporation of solvent ions, and the discrepancies may again be due to molecular-weight differences.

EXPERIMENTAL

For general details see Parts VI and VII (preceding papers). Viscosities were measured at 25° with Ostwald dilution viscometers with flow times greater than 100 sec. for benzene. The infrared spectra were measured with Hilger single-beam D209 and Grubb-Parsons double-beam instruments. The polymers were hydrolysed by refluxing them for several hr. with potassium hydroxide in octyl alcohol.

We are indebted to C. R. Davies, of the Shell Petroleum Co., and M. St. C. Flett, of Imperial Chemical Industries Limited, in whose laboratories the infrared spectra were measured; to P. H. Plesch for valuable discussions on the interpretation of the spectra; and to Mrs. S. M. Bark for the microchemical analyses.

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[Received, December 10th, 1956.]

⁶ Plesch, *J.*, 1953, 1653.