

645. *The Low-temperature Polymerisation of isoButene.*
Part III. The End-group Problem.*

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Polyisobutenes were prepared in hexane solution by using titanium tetrachloride as catalyst and trichloroacetic acid as co-catalyst. The polymers were examined by infra-red spectroscopy. The predominant end-group was the methylene group. Trisubstituted double bonds and trichloroacetate end-groups were also found.

THE first observations on the infra-red spectrum of polyisobutene were made by Thompson and Torkington (*Trans. Faraday Soc.*, 1945, **41**, 246), who stated that the main features of the spectrum were independent of the degree of polymerisation for molecular weights between 10^3 and 10^5 . As the theory of cationic polymerisation developed, it became of interest to examine polyisobutenes of low molecular weight for the presence of end-groups which might shed some light on the reaction mechanisms involved. The first investigation of this nature (Dainton and Sutherland, *J. Polymer Sci.*, 1949, **4**, 37) showed that polyisobutene of low molecular weight, prepared with boron fluoride as catalyst and water as co-catalyst by the method of A. G. Evans and his collaborators (*Nature*, 1946, **158**, 94; *J. Polymer Sci.*, 1949, **4**, 359), had as end-groups mainly $R^1R^2C:CH_2$, with possibly small quantities of $R^1R^2C:CHR^3$ and $-OH$ groups.

The present work is concerned with the spectra of various samples of polyisobutene prepared with titanium tetrachloride as catalyst.

EXPERIMENTAL

Hexane, isobutene, and titanium tetrachloride were purified as described previously.* A number of different co-catalysts were used, and polymers were prepared by two different methods: (1) The adiabatic technique described previously (Plesch, *loc. cit.*). (2) An isothermal method at 0° , in which the reaction was followed by observing the change in the vapour pressure of the polymerising solution.

Method (1) with initial temperatures of -20° to -50° gave polymers of mean molecular weight $2-3 \times 10^4$, and method (2) gave molecular weights of about 500-1000. The spectra of two polymers of molecular weight 5×10^5 , prepared, respectively, with water and trichloroacetic acid as co-catalysts, were used for comparison.

In method (2) hexane and isobutene were distilled into the evacuated reaction vessel fitted with a phial breaker, and the titanium tetrachloride and co-catalysts were introduced by crushing weighed, sealed phials. The batch-size was about 100 c.c., the concentration of isobutene about 30% wt./wt., and the concentrations of catalyst and co-catalyst of the order of 100 and 10 millimole/l., respectively. In the earlier experiments, after the end of the reaction, about 5 c.c. of alcohol were added to the reaction mixtures, whereby the titanium tetrachloride was precipitated, as a heavy, greenish, transparent layer. The polymer solutions were separated from this and then either washed with dilute sodium hydrogen carbonate and water and then dried, or they were twice precipitated by alcohol and redissolved in hexane. These specimens were not prepared originally for infra-red analysis, and it transpired in the course of this work that the use of alcohol to precipitate the titanium tetrachloride gave rise to certain artefacts which will be discussed below. Specimen 305 is typical of the products obtained by this procedure. The polymers in the preparation of which water or sulphuric acid were used as co-catalysts were also separated from the reaction mixture by this method.

Subsequently, in order to avoid the artefacts, polyisobutenes prepared by method (2) at 0° with trichloroacetic acid as co-catalyst were precipitated by acetone, then redissolved in hexane and dried. Specimen 318 is typical of these products.

The spectra were measured with a Hilger D. 209 infra-red spectrometer, single-beam photographic recording being used. Between 600 and 1400 cm^{-1} , films about 0.1 mm. thick proved

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convenient, and at shorter wave-lengths films of 0.5 mm. thickness were used. The wave-numbers recorded are believed to be accurate to at least ± 2 cm.⁻¹.

Molecular weights were determined viscometrically as described previously (Plesch, *loc. cit.*) or cryoscopically in cyclohexane.

Methyl, ethyl, and *tert.*-butyl trichloroacetates were commercial products which were purified by standard methods. Their infra-red spectra were recorded for comparison.

Results.—The conclusions set out below were obtained by examining the spectra of some two dozen polyisobutenes prepared and treated in different ways. Most of the results were obtained from the spectra of polymers produced by method (2). The mean molecular weights of the polymers made by method (1) were too high for there to be sufficient end-groups to give conclusive spectra; but those bands which were found to differentiate the spectra of these polymers from those of the very high polymers, *i.e.*, the end-group bands, corresponded closely with the end-group bands found in the low polymers.

Unsaturated End-groups.—If the polymer contained terminal double bonds, these could be expected to give rise to bands characteristic of hydrocarbons such as 2:4:4-trimethylpent-1- and -2-ene, and therefore the infra-red absorption spectra of these two hydrocarbons were used for comparison.

It was found that the presence of R¹R²C:CH₂ groups was indicated in all polymers of molecular weight less than about 3×10^4 [whether prepared by method (1) or (2)] by the presence of well-marked bands at 895, 1642, and 1780 cm.⁻¹. If trichloroacetic acid had been used as co-catalyst the spectra showed a strong carbonyl band near 1775 cm.⁻¹, which could be distinguished from the double-bond band in this vicinity by the fact that its intensity was greater than that of the band at 1642 cm.⁻¹, whereas the double-bond band at 1780 cm.⁻¹ is much weaker than that at 1642 cm.⁻¹. The assignment of these bands is confirmed by the spectra of polymers treated with bromine water, which had shown these bands originally. This treatment causes the almost complete disappearance of the bands at 895 and 1780 cm.⁻¹, and a reduction in the intensity of the band near 1650 cm.⁻¹.

The partial persistence of a band near 1650 cm.⁻¹ after the bromination is ascribed to its being due partly to double bonds of the type R¹R²C:CHR₃, which are much more difficult to brominate. This assignment is confirmed by the presence of a band at 825 cm.⁻¹, which is characteristic of trisubstituted double bonds. Bands near those frequencies are found in the spectra of polymers made with water, sulphuric acid, and trichloroacetic acid as co-catalysts, but the intensity of the bands compared to that of the R¹R²C:CH₂ band at 895 cm.⁻¹, after allowance for the difference in extinction coefficient, indicates that the latter group is present in much higher concentration.

The spectra of polyisobutenes prepared by method (2) with water or sulphuric acid as co-catalyst were very similar. In addition to the usual methylene bands, the former showed bands at 803, 1019, and 1102 cm.⁻¹, and the latter showed strong bands at 800, 828, 1019, 1075, and 1102 cm.⁻¹. Evacuation of the latter specimen at 80° for several hours removed the bands at 828 and 1102 cm.⁻¹, the 1075 band became very prominent, and new bands appeared at 1117, 1267, and 1286 cm.⁻¹. The interpretation of these changes is not clear; the bands near 800 cm.⁻¹ are, as before, assigned to trisubstituted double bonds.

The Trichloroacetate End-group.—According to a recent suggestion (Plesch, *loc. cit.*), one of the ways in which the growth of polyisobutene chains, catalysed by titanium tetrachloride and trichloroacetic acid, may come to an end, is by formation of a terminal trichloroacetate group from the ion-pair at the growing end of the polymer chain. It was an obvious step to search for this group by infra-red spectroscopy, but this has proved unexpectedly difficult. The principal reason for this was the production of a number of artefacts; by use of acetone instead of alcohol these artefacts were eliminated.

The bands due to esters of trichloroacetic acid present in the polymer were identified as those which vanished when a solution of the polymer was refluxed with an aqueous solution of sodium hydroxide.

The table gives the absorption bands of methyl, ethyl, and *tert.*-butyl trichloroacetates in the region 670—1100 cm.⁻¹. It also shows the absorption bands in the spectra of specimens 305 and 318 which disappeared when these polymers were treated with alkali. In addition, the strong carbonyl band near 1760 cm.⁻¹, present in the spectra of both polymers, vanished on hydrolysis.

The table shows that No. 305 contained methyl and ethyl trichloroacetate, presumably derived from the precipitant. No. 318 contained neither of these, but its spectrum shows other bands which are now attributed to trichloroacetate end-groups, *i.e.*, poly(isobutyl trichloro-

acetate). This diagnosis was confirmed by hydrolysing some of polymer No. 318 with dilute sodium hydroxide: on acidification the aqueous layer there was a marked smell of trichloroacetic acid. The acid solution was thoroughly extracted with hexane and the infra-red spectrum of the hexane then showed the presence of trichloroacetic acid.

The Chlorine Content.—Micro-analysis of polyisobutenes of molecular weights of 500—10,000 showed not only that those prepared with trichloroacetic acid contained chlorine, but that even when water or sulphuric acid was used as co-catalyst chlorine was present. (In polymers

Main absorption bands of methyl, ethyl, and tert.-butyl trichloroacetates, and the absorption bands removed by treatment with alkali in the spectra of polyisobutenes 305 and 318, in the region 650—1100 cm.⁻¹.

Me	Et	Bu ^t	No. 305	No. 318	Me	Et	Bu ^t	No. 305	No. 318
683	683	683	683	(683)	—	—	—	—	844
—	—	—	727	727	—	—	870	—	—
—	750	—	750	—	—	885 *	—	—	—
(758)	—	—	—	—	916 *	—	—	—	—
—	—	785	—	—	—	—	968	—	—
—	—	—	—	812	1018	—	—	1018	—
—	828	826	826	—	—	1030	—	(1030)	—
835	—	—	831	—	—	—	(1037)	—	—

1. The parentheses indicate that the bands are weak.

2. The asterisks indicate bands which cannot be detected in the polymer spectra because of their proximity to polymer bands.

prepared with the latter co-catalyst a trace of sulphur was also found.) However, for polymers of the same molecular weight the chlorine content is much smaller than in the polymers prepared with trichloroacetic acid.

The presence in the polymer of chlorine, which must have come from the catalyst, indicates a new and hitherto unsuspected feature of these polymerisations. It may well be due to the reaction of titanium tetrachloride or hydrochloric acid with terminal double bonds in the polymer. It is noteworthy that when polyisobutene is kept in contact with titanium tetrachloride for some weeks a violet colour, characteristic of titanium dichloride develops.

The presence of chlorine in all the polyisobutenes prepared with titanium tetrachloride is in apparent contradiction to an earlier statement (Plesch, *loc. cit.*, Table III). The explanation lies in the higher molecular weights of the specimens used in the earlier work. Subsequent tests of these specimens (Nos. 119 and 121) by the Beilstein flame test showed that they too contained traces of chlorine.

In agreement with the analytical results, the spectra of all the polymers concerned show the C—Cl band at 683 cm.⁻¹, though often it is only vestigial.

Discussion.—The polyisobutene chain is now believed to be propagated by a carbonium ion associated with an anion consisting of a complex between catalyst and co-catalyst, less one proton. The termination can take place by several different mechanisms which have been discussed by a number of authors (Hamann, *Angew. Chem.*, 1951, 63, 231; for older literature see Plesch, *J. Appl. Chem.*, 1951, 269). One alternative is the loss of a proton from carbon atom 1, one of the methyl groups attached to the positive carbon atom at the growing end of the chain, leaving the polymer with a terminal R¹R²C:CH₂ group. Since this is undoubtedly the predominant end-group in all the polymers examined, this seems to be the most probable process. The R¹R²C:CHR³ groups could be formed in a similar way by loss of a proton from carbon atom 3, or they may be formed by isomerisation of the C:CH₂ groups under the influence of the catalytic complex.

It is frequently found that polymerisations under the conditions described above may cease before all the monomer has been consumed, and that they can be restarted by the addition of more trichloroacetic acid (Plesch, *loc. cit.*). If this is accepted as evidence that the acid as such is consumed during the reaction, the most likely explanation may be that the ion-pair at the growing end of the polymer chain rearranges to form poly(isobutyl trichloroacetate). The evidence presented here strongly supports this.

The nature of the end-groups formed when the trichloroacetate group is removed by hydrolysis, or when water or sulphuric acid is used as co-catalyst, is less clear. The pre-

dominant end-groups are undoubtedly double bonds, but there are certainly other end-groups as well. In view of the uncertain band assignments involved, the matter is not now discussed further.

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