504. *Some Nuclear-methylated Styrenes and Related Compounds. Part III. Absorption Spectra.*

By K. C. Bryant, G. T. Kennedy, and (Miss) E. M. Tanner.

The infra-red and ultra-violet spectra of *m*- and *p*-methylstyrene, 2 : 4 : 5-trimethylstyrene, 2 : 4 : 6-trimethylstyrene, and their polymers, and of 1 : 4 : 5-trimethyl-2-ethylbenzene and 1 : 3 : 5-trimethyl-2-ethylbenzene have been measured. The ultra-violet spectrum of 2 : 4 : 6-trimethylstyrene indicates that the rotation of the vinyl group is restricted by the *o*-methyl groups. The application of differences in absorption to the analysis of appropriate mixtures is discussed.

It was expected that the methylated styrenes obtained by any process using the aromatic hydrocarbons in petroleum as a starting material might consist of a mixture of isomers. The normal methods of estimating styrene and its homologues do not differentiate between the various isomers (which may yield polymers of widely differing properties). To investigate the suitability of the spectroscopic method the infra-red and ultra-violet spectra of some of these compounds have been measured.

The presence of small amounts of monomer or other polar impurities in a polymerised styrene may seriously affect its electrical properties. Differences between the spectra of styrene and its polymer have already been used for estimating the amount of monomer present in the latter (McGovern, Grimm, and Teach, *Analyt. Chem.*, 1948, **20**, 313). In order to extend this method to the substituted styrenes, it was necessary to measure the infra-red and ultra-violet spectra of their pure precipitated polymers.

EXPERIMENTAL.

The preparation and properties of the styrenes and trimethylethylbenzenes are described in Part I of this series, and of the polymers in Part II (preceding papers).

The infra-red spectra were measured in the regions 5—15μ., using a Hilger D.209 double-beam recording spectrometer, with a rock-salt prism. The monomers were also examined by Dr. H. W. Thompson on a similar spectrometer, with a fluorite prism. The liquids were measured in a cell approx. 0·1 mm. thick, with rock-salt windows. The polymers were examined as thin films, made by evaporation from carbon tetrachloride solution.

The ultra-violet absorption of the monomers was determined in *iso*octane, by use of a Hilger E. 498 Medium quartz spectrograph and a Spekker spectrophotometer, with a spark struck between tungsten-steel electrodes as a source of radiation. The monomers were washed free from inhibitor with dilute sodium hydroxide solution, washed with water, dried ($CaCl_2$), and redistilled immediately before use. The polymers were examined in carbon tetrachloride solution, using a hydrogen discharge tube as source, since only those from 2 : 4 : 5- and 2 : 4 : 6-trimethylstyrene were soluble in *iso*octane.

RESULTS AND DISCUSSION.

Infra-red Spectra.—1. *Monomers.* The infra-red absorption spectra of styrene, *m*- and *p*-methylstyrene, and 2 : 4 : 5- and 2 : 4 : 6-trimethylstyrene are shown in Fig. 1. The sample of *p*-methylstyrene gave weak bands at 773, 795, 1485, and 1670 cm.$^{-1}$ not reported by Barnes *et al.* (*J. Appl. Physics*, 1945, **16**, 77); these were presumably due to impurities and are omitted from the figure. The first four of the compounds give bands at 905 and 990 cm.$^{-1}$ which may be attributed to deformations of the C–H bonds attached to the C$=$C link (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246). However, there are small but definite shifts to 920 and 995 cm.$^{-1}$ in the case of 2 : 4 : 6-trimethylstyrene, which may be due to the restricted rotation of the vinyl group in this compound but not in the others. It has also been pointed out by Dr. H. W. Thompson that only in the case of the two trimethylstyrenes does the band at *ca.* 1630 cm.$^{-1}$ (C$=$C valency frequency) split up into two components of approximately equal intensity; this feature appears to be absent from α- and β-methylstyrene (A.P.I. " Catalogue of

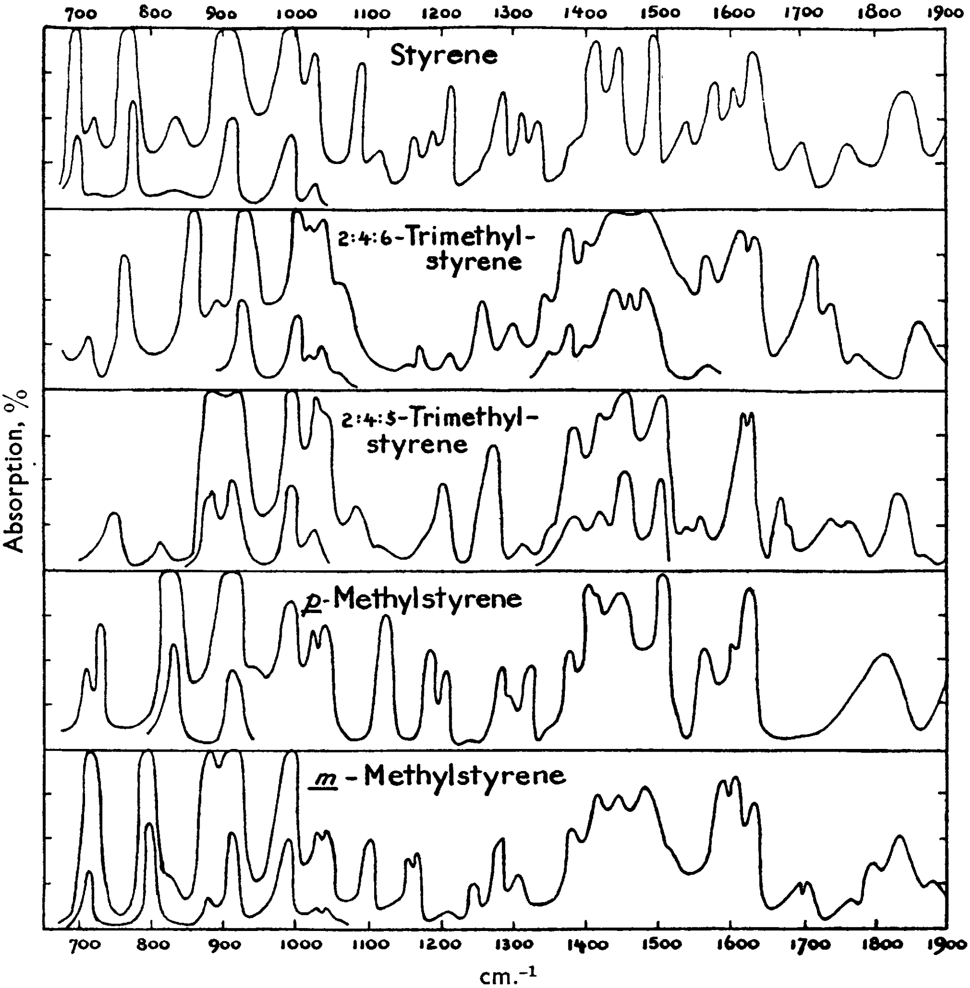
Spectra"). In general, these compounds conform to the correlation rules put forward by Barnes *et al.* ("Infra-Red Spectroscopy," Reinhold) and Thompson (*J.*, 1948, 328) connecting frequencies with specific atomic groupings and with the orientation of nuclear substituents.

It is very probable that a successful method for the analysis of mixtures of *m*- and *p*-methylstyrene on the one hand, and of the two trimethylstyrenes on the other, could be developed using their bands in the 700—900-cm.$^{-1}$ region.

2. *Polymers.* The spectra of the pure precipitated polymers are shown in Fig. 2. The spectrum found for polystyrene is similar to those given by Thompson and Torkington (*loc. cit.*) and the A.P.I. (*op. cit.*). It may be noted that the polymers show the bands characteristic of the orientation of the substituents round the benzene nucleus. Thus poly-*m*- and -*p*-methylstyrene have bands at 785 and 820 cm.$^{-1}$, characteristic of *m*- and *p*-dialkylbenzene, respectively; poly-2 : 4 : 5-trimethylstyrene shows a strong band at 875 cm.$^{-1}$ (cf. durene 865 cm.$^{-1}$, and 1 : 4 : 5-trimethyl-2-ethylbenzene 870 cm.$^{-1}$) and poly-2 : 4 : 6-trimethylstyrene shows a strong band at 855 cm.$^{-1}$ (cf. *iso*durene 845 cm.$^{-1}$, and 1 : 3 : 5-trimethyl-2-ethylbenzene 850 cm.$^{-1}$). However, it should be noted that the band usually found at *ca.* 1600 cm.$^{-1}$ in benzene derivatives and assumed to arise from a vibration of the benzene nucleus (Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803) is weak or absent in poly-2 : 4 : 5-trimethylstyrene. This is also the case with durene (though symmetry considerations may forbid it here) and 1 : 4 : 5-

FIG. 1.

Infra-red absorption spectra of styrene homologues.



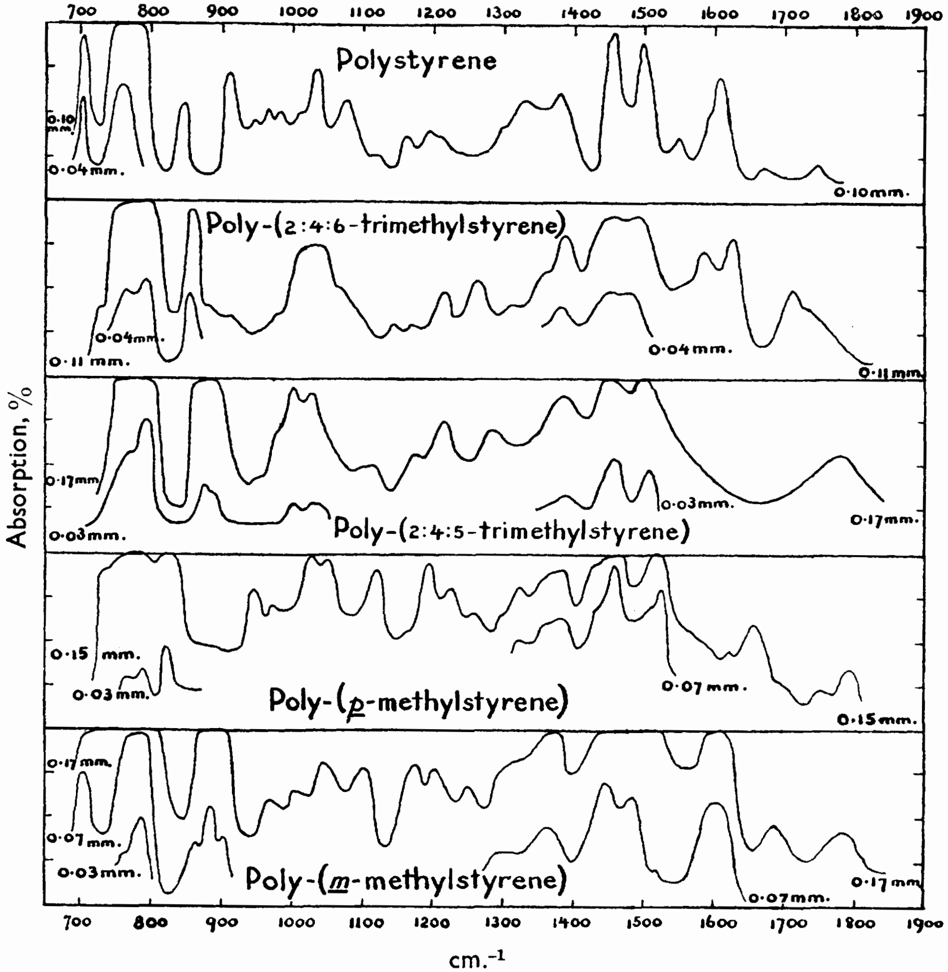
trimethyl-2-ethylbenzene, whose spectrum is shown in Fig. 3, together with that of 1 : 3 : 5-trimethyl-2-ethylbenzene.

Ultra-violet Spectra.—1. *Monomers.* The ultra-violet absorption spectra are shown in Fig. 4, with that of styrene for comparison.

The spectra of *m*- and *p*-methylstyrenes in *iso*octane are similar both in the position and in the intensity of absorption. The spectrum of *p*-methylstyrene in alcohol has been measured by Elliott and Cook (*Ind. Eng. Chem. Anal.*, 1944, **16**, 20); in both solvents the absorption is similar to that of styrene, in which, however, corresponding bands lie at shorter wave-lengths and show weaker absorption. The wave-length of the same band seems to vary only slightly from one solvent to the other, and it is reasonable to assume that this is also the case with 2-methylstyrene whose spectrum in alcohol has been reported (Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1938, **5**, 848). It thus appears that the ultra-violet spectra of the three nuclear methylstyrenes are much more similar than those of the methylethylbenzenes (A.P.I., *loc. cit.*), and their use for the identification and determination of individual isomers in a mixture is not practicable.

FIG. 2.

Infra-red absorption spectra of polystyrene homologues.



There is a considerable difference between the spectra of the two trimethylstyrenes examined (see Fig. 4); 2 : 4 : 6-trimethylstyrene shows very much weaker absorption than does styrene in the region 2700—3000 A. Similarly reduced absorption has also been observed for mesitylene derivatives containing, for example, an acetyl group (O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906), a nitro-group (Brown and Reagan, *J. Amer. Chem. Soc.*, 1947, **69**, 1032), or a dimethylamino-group (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838). This has

FIG. 3.

Infra-red absorption spectra of 1 : 3 : 5(*top*)- *and* 1 : 4 : 5(*bottom*)-*trimethyl-2-ethylbenzenes.*

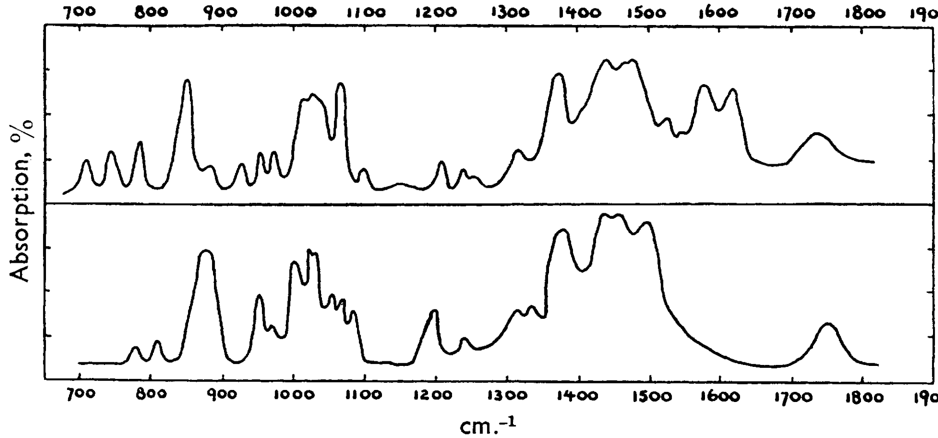
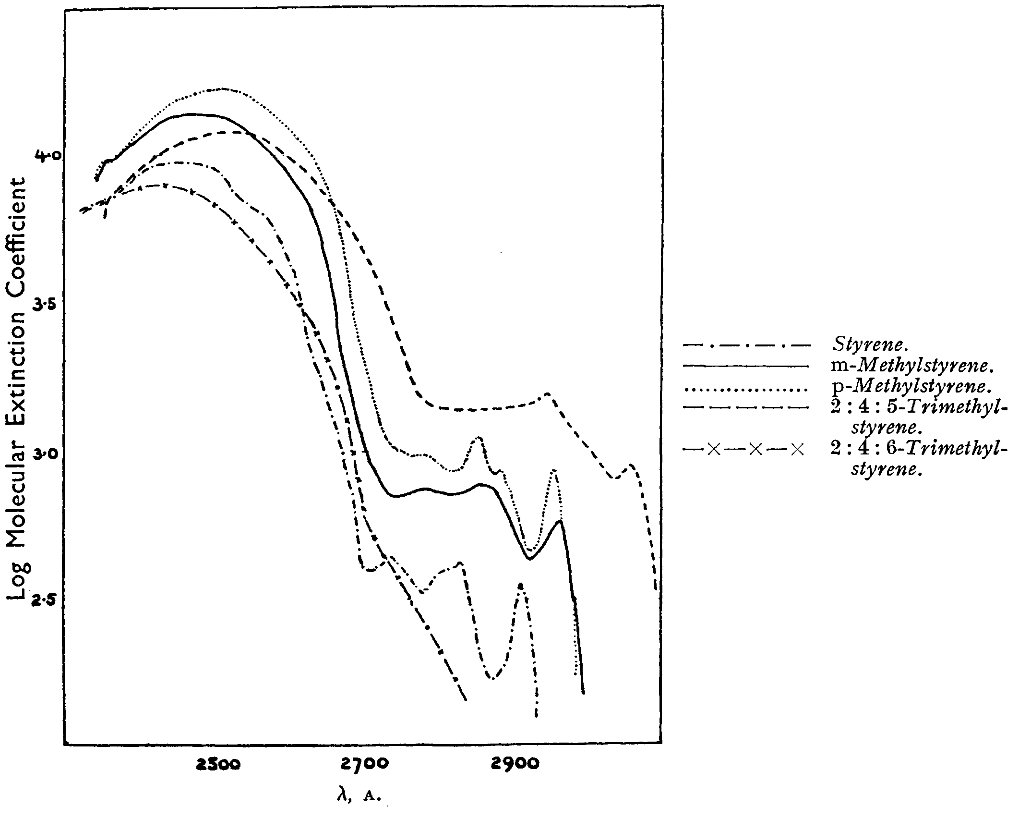


FIG. 4.



been attributed to the restriction, by the adjacent methyl groups, of the rotation of the larger group about the single bond joining it to the nucleus, leading to a higher energy barrier to the assumption of the co-planar configuration necessary for resonance with the benzene nucleus.

The same effect is presumably operative with 2 : 4 : 6-trimethylstyrene. It may be noted that α-methylstyrene (A.P.I., *op. cit.*) and *p* : α-dimethylstyrene (Elliott and Cook, *loc. cit.*) also show reduced absorption relative to styrene. In both cases a scale model indicates that steric factors similar to that in 2 : 4 : 6-trimethylstyrene may operate (see Part I).

The differences between the spectra of 2 : 4 : 5- and 2 : 4 : 6-trimethylstyrene can be used for determining the former in mixtures of the two, but the absence of suitable selective absorption in the latter precludes the use of its ultra-violet absorption spectrum for analysis.

2. *Polymers.* The spectra of the polymers examined qualitatively in carbon tetrachloride exhibit an effect analogous to that observed in the infra-red region, namely, the possession of absorption bands characteristic of the corresponding nuclear-methylated ethylbenzene. Thus, the spectrum of poly-2 : 4 : 5-trimethylstyrene is similar to that of 1 : 4 : 5-trimethyl-2-ethylbenzene but displaced to slightly longer wave-lengths.

The differences between the ultra-violet spectra of the monomers and polymers can thus be used for the detection of very small amounts of a monomer in its polymer, except in the case of 2 : 4 : 6-trimethylstyrene.

The authors thank Dr. H. W. Thompson, F.R.S., for his co-operation, and Dr. F. Morton for his interest and advice.

TRINIDAD LEASEHOLDS LIMITED,
CENTRAL LABORATORY, KING'S LANGLEY, HERTS.

[*Received, January 27th,* 1949.]