503. *Some Nuclear-methylated Styrenes and Related Compounds. Part II.*

By G. T. Kennedy and F. Morton.

The effects on the overall polymerisation rate, on the volume contraction accompanying polymerisation, and on the nature of the resulting polymer, of the introduction of nuclear methyl groups into styrene have been examined by a study of four styrene homologues. The presence of two *o*-methyl groups (as in 2 : 4 : 6-trimethylstyrene) has a profound influence on the ease of polymerisation, thus providing further evidence for the reduction in resonance energy in such compounds consequent upon steric hindrance to rotation of the vinyl group.

The polymers of *o*-, *m*-, and *p*-methylstyrene, and of certain dimethylstyrenes, have been made previously (Shorygin and Shorygina, *J. Gen. Chem. Russia*, 1935, **5**, 555; Marvel *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 736, 1088), but there have been no measurements of polymerisation rates or adequate characterisation and comparison of the polymers. Shorygin, however, showed that poly-*o*-methylstyrene has improved thermal stability and mechanical strength compared with polystyrene and its *m*- and *p*-methyl homologues. Valuable information on several dimethylstyrenes and their polymers has been given in two recent patent specifications (Dominion Tar and Chemical Co. Ltd., B.P. 598,069, 598,558).

As explained in Part I of this series, the first objective of the present investigation was to find a nuclear-methylated styrene which should be readily available from naturally-occurring crude oils and yield a polymer of characteristics similar to those of polystyrene but be capable of withstanding higher temperatures without softening. Poly-2 : 4 : 5-trimethylstyrene fulfils these requirements, at least partly; in the light of previous work (*loc. cit.*) it is probable that its increased thermal stability is largely the result of the presence of one *o*-methyl group.

The small effect of *m*- and *p*-methyl groups, and the effect of two *o*-methyl groups in altering the typical behaviour of styrene, afford a more complete understanding of the influence of substitution on the styrene molecule.

EXPERIMENTAL.

The hydrocarbon monomers used were those described in Part I.

Rates of Polymerisation.—Small glass tubes containing weighed amounts (*ca.* 0·9 g.) of each monomer were evacuated to a pressure of a few mm., sealed, and immersed in an oil-bath thermostatically controlled to ±0·1°. After a known time, a tube was rapidly cooled in ice, dried, and broken, and the contents were dissolved out by immersion in 20 ml. of benzene in a stoppered bottle. The resulting solution was transferred to a small dropping funnel, the bottle being washed out with six successive 5-ml. portions of benzene. The polymer was precipitated, as a white powdery solid, by dropping this solution slowly into 300 ml. of methanol in a three-necked flask, with vigorous mechanical stirring so as to yield the precipitate in a finely divided state. The product was filtered on a weighed sintered-glass Gooch crucible, washed with 50 ml. of methanol, and dried, first by suction at the pump and then over anhydrous calcium chloride in a vacuum desiccator, to constant weight. This procedure was carried out on several samples (heated for different times) of each monomer at temperatures between 80° and 120°.

Some measurements were also made on styrene and on *p*-methylstyrene by the volume-contraction method. For vinyl acetate, Starkweather and Taylor (*J. Amer. Chem. Soc.*, 1930, **52**, 4708) have shown that the volume contraction is linearly proportional to the degree of polymerisation. This was shown to be true also for the above two compounds by using polymerisation tubes *ca.* 25 cm. in length and 3 mm. in internal diameter, which were two-thirds filled with monomer before being sealed in a vacuum. The length of the monomer column could be measured at any time during the course of the polymerisation by reference to a scale consisting of a piece of broken thermometer stem fixed to the tube. Difficulty was often experienced, with this method, in obtaining the final value of the percentage contraction at 100% polymerisation because of the formation of bubbles in the column, probably caused by incomplete removal of air before sealing. However, by a combination of this method and one measurement by the gravimetric method, this final contraction can be calculated if linearity between volume contraction and degree of polymerisation is assumed. The validity of this assumption was shown by similarity of the polymerisation curves obtained by the two methods.

Polymer Samples: Refractive Index, Density, and Viscosity Determinations.—Small cylindrical bars (1 cm. in diameter and 2—3 cm. in length) of each polymer were made by thermal polymerisation *in vacuo* at 100° in thin glass tubes which could be readily broken away from the finished bar. The times of polymerisation were such as to ensure at least 99% conversion, in the light of the rate measurements found as above. The density of such bars was measured at room temperature by weighing in air and in alcohol, and their refractive indices and dispersions were determined (by use of suitably cut and polished pieces) on an Abbé refractometer, with a concentrated solution of potassium mercuri-iodide (K_2HgI_4) as contact liquid.

The densities at elevated temperatures were obtained by a simple dilatometric method, using a glass bulb, containing the weighed solid polymer bar, sealed to a capillary tube (*ca.* 50 cm. in length) of known bore. Each dilatometer was filled with a known volume of mercury by a vacuum technique, and the bulb immersed in an oil-bath. At any temperature the volume of the polymer sample could be calculated from the position (measured against an attached cm. scale) of the mercury meniscus in the capillary, since the bore of the capillary, the volumes of the sample and the mercury at room temperature, and the coefficient of expansion of mercury (0·000182) were known; no correction was made for the expansion of the glass (Pyrex) as this would have been of the same order as the experimental error. Dilatometer readings were taken for each sample at intervals of 1°, the heating rate being *ca.* 0·5° per minute, which was found to be near the maximum possible to obtain the necessary thermal equilibrium. When the maximum temperature used had been reached, readings were taken while the samples cooled at a similar rate.

The densities of monomeric *p*-methylstyrene and 2 : 4 : 5-trimethylstyrene at 100° were measured in a 10-ml. density bottle.

Viscosities of benzene solutions of the polymers (precipitated from solution by methanol as described above) were measured in an Ostwald viscometer, under conditions similar to those specified by Mark ("Physical Methods of Organic Chemistry," Vol. I, Interscience, 1946, p. 135).

RESULTS AND DISCUSSION.

Polymerisation Rates.—Curves showing percentage polymerisation plotted against reaction time were obtained for each monomer at several temperatures; the overall polymerisation reaction was in each case approximately unimolecular with respect to monomer concentration, as has been shown previously for styrene. Typical curves are shown in Fig. 1. Approximate activation energies were calculated from plots of the logarithm of the initial polymerisation rate against the reciprocal of the absolute temperature (Table I).

The data of Table I were all obtained by the precipitation–weighing method; the contraction method, used for styrene and *p*-methylstyrene, gave values which were not sufficiently consistent for the calculation of energies of activation.

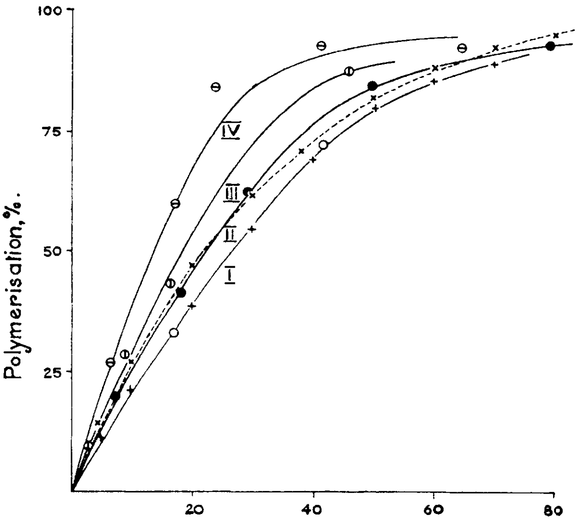
TABLE I.

Hydrocarbon.	Temp.	Initial polymerisation rate.*	Activation energy for overall polymerisation ± 1000 kcals.
p-Methylstyrene	80°	0·80	17,000 kcals.
	90	1·49	
	100	2·70	
	110	5·48	
m-Methylstyrene	80	0·67	
	90	1·54	19,000
	100	3·28	
	110	5·48	
2 : 4 : 5-Trimethylstyrene	80	1·44	
	90	2·63	18,000
	100	5·55	

* Percentage polymerising per hour, convertible into absolute units (moles $l.^{-1}$ $sec.^{-1}$), if desired, by use of densities and coefficients of expansion given in a later section.

At 100° the absolute rates of polymerisation of the above three methylated styrenes are greater than that of styrene (Fig. 1); similar, but larger, effects are known to be produced by nuclear chlorine atoms (Ushakov and Matuzov, *J. Appl. Chem. Russia*, 1944, **17**, 435).

FIG. 1.



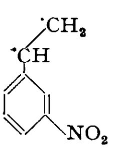
I. *Styrene* (+ *Contraction method*). II. p-*Methylstyrene* (× *Contraction method*).
III. m-*Methylstyrene*. IV. 2 : 4 : 5-*Trimethylstyrene*.

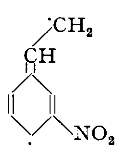
The overall activation energy of polymerisation appears to be somewhat reduced by nuclear methylation [17—19 kcals. as compared with about 21 kcals. for styrene (see discussion by Bamford and Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192**, 323)]; calculations from the data of Ushakov and Matuzov (*loc. cit.*) indicate that a similar reduction to *ca.* 18,000 kcals. is produced by *o*-, *m*-, or *p*-chlorination.

The data are inadequate for a detailed analysis of the effects of nuclear substitution on the individual reactions (initiation, propagation, etc.) involved in polymerisation, but it is likely that the major effect of such substitution will be by way of a change in the resonance stability and the reactivity of the free radicals.

In marked contrast to styrene and the three homologues already discussed, 2 : 4 : 6-trimethylstyrene was virtually unchanged by heating it at 100° for 19 days; the product showed no change in refractive index and gave only a trace of precipitate on addition to excess of methanol. At 190°, however, polymerisation to a brittle polymer, showing a marked violet fluorescence, was apparently complete after some 40 hours. The remarkable resistance of this compound to polymerisation was noticed, without comment, by Klages (*Ber.*, 1902, **35**, 2245) who stated that it could be distilled without change at atmospheric pressure, unlike other hydrocarbons of this type. This may be explained in terms of the steric effect of the two *o*-methyl groups, producing a barrier to the free rotation of the vinyl group, and hence to the assumption of the coplanar configuration necessary for resonance of the latter group with the benzene nucleus. Thus the resonance stabilisation of radicals of the type $\dot{C}H_2-\dot{C}HX$ will be much lower than in the simple cases where resonance is not inhibited; such resonance stabilisation is of great importance for polymerisation by a free-radical mechanism (see, *e.g.*, Bawn, "The Chemistry of High Polymers," 1948). At higher temperatures a greater proportion of the molecules can surmount the energy barrier to rotation of the vinyl group, and the rate of polymerisation becomes measurable.

The failure of *m*-nitrostyrene to polymerise under similar conditions (Marvel *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 736; Wiley and Smith, *J. Polymer Sci.*, 1948, **3**, 444) may be explained along similar lines. Radicals of the type (I) will be little stabilised by resonance with, for example (II), on account of the much greater stability of resonance forms such as (III):


(I.)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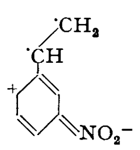
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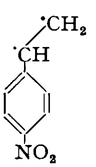
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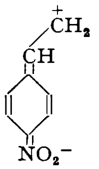
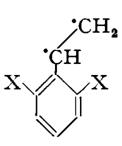
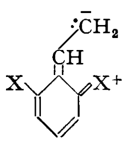

(V).


(VI.)


(VII.)

In *p*-nitrostyrene, however, the situation is reversed. The diradical (IV) is stabilised by a large contribution from (V); thus this compound polymerises extremely readily.

Since chlorine and methyl groups are similar in size, 2 : 6-dichlorostyrene is comparable with 2 : 4 : 6-trimethylstyrene, but the contribution of structures such as (VII) to the stability of the diradical (VI) will be higher if X = Cl than if X = Me. In fact, the stability of such structures (X = Cl) might be so great as to overcome the energy barrier to the assumption of the necessary coplanar configuration. If this is true, then the fact that 2 : 6-dichlorostyrene polymerises easily (Marvel *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 861), whilst 2 : 4 : 6-trimethylstyrene (and presumably 2 : 6-dimethylstyrene) does not do so, is readily explained.

Polymerisation of 2 : 4 : 6-trimethylstyrene to a product of low molecular weight was readily effected at room temperature by the presence of a trace of a Friedel–Crafts catalyst such as stannic chloride. Catalysts of this type also initiate the polymerisation of α-methylstyrene and *m*-nitrostyrene, neither of which is easily polymerised by a free-radical mechanism (Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, **37**, 1073; Wiley and Smith, *loc. cit.*).

The failure of α-methylstyrene to polymerise under ordinary conditions is probably caused by steric effects similar to those operating in 2 : 4 : 6-trimethylstyrene (see also Part I). Enhancing the steric effects by the introduction of sufficiently large *o*-substituents (Bachman and Finholt, *J. Amer. Chem. Soc.*, 1948, **70**, 622) destroys, in turn, its ability to copolymerise, *e.g.*, with butadiene.

Refractive Indices and Densities.—Introduction of nuclear methyl groups into polystyrene decreases the refractive index and the density, but has no effect on the specific dispersion (Table II); in the latter respect this series of polymers is analogous to saturated hydrocarbons, whose specific dispersions are independent of molecular weight. The decrease of density with increase of substitution might be expected to follow the reduced ability of the polymer chains to pack together; this would also explain the decrease in refractive index. Calculated and observed unit refractivities are in satisfactory agreement (cf. Wiley, *Ind. Eng. Chem.*, 1946, **38**, 959) except for poly-2 : 4 : 5-trimethylstyrene, which shows an exaltation of 1·0 unit.

All the polymers, when properly prepared, were transparent, colourless, and hard solids; they could be readily cut (with a hack-saw), filed, and polished without the development of cracks. Their surfaces, however, could readily be marred by scratches, a property typical of polystyrene itself.

From the densities of the monomers at 20° (Part I of this series) and at 100° (Table III), and of the polymers at the same temperatures (Table II and next section), the effect of temperature on the volume contraction accompanying polymerisation was calculated (Table IV). Nuclear methyl groups have a marked effect in reducing this contraction, which, for a given monomer, is increased at higher temperatures. These effects, and also the decrease in coefficient of expansion of the monomers with an increasing number of methyl groups (Table III), must, like the polymer densities, be explicable in molecular terms, being connected with the relative ease of packing of the various monomer and polymer molecules.

The contraction accompanying the polymerisation of 2 : 4 : 6-trimethylstyrene at 190° was 19—20%.

TABLE II.

Polymer.	n_D^{20}.	d_4^{20}.	Unit refractivity: Obs.	Unit refractivity: Calc.	$10^4(n_F - n_C)/d$ at 20°.
Polystyrene *	1·5920	1·050	33·51	33·35	177
Poly-*m*-methylstyrene	1·5831	1·030	38·27	37·96	177
Poly-*p*-methylstyrene	1·5766	1·022	38·26	37·96	176
Poly-2 : 4 : 5-trimethylstyrene	1·5711	0·996	48·17	47·18	177

* Commercial " Distrene " has n_D^{20} 1·5912.

TABLE III.

Hydrocarbon.	d_4^{100}.	Mean coefficient of volume expansion.[a]
Styrene	0·831 [b]	11·3 × 10^{-4}
p-Methylstyrene	0·831	9·75 × 10^{-4}
2 : 4 : 5-Trimethylstyrene	0·853	8·22 × 10^{-4}

[a] Calculated from the equation $d_4^{20} = d_4^{100}(1 + 80\alpha)$.
[b] Patnode and Scheiber, *J. Amer. Chem. Soc.*, 1939, **61**, 3449.

TABLE IV.

Hydrocarbon.	Contraction on polymerisation (% on initial volume) at 20° (calc.).	at 100° (calc.).	(obs.).*
Styrene	13·7	19·4	19·8
m-Methylstyrene	12·6	—	—
p-Methylstyrene	12·5	16·8	13·4
2 : 4 : 5-Trimethylstyrene	8·3	12·5	—

* From contraction experiments described in an earlier section.

Second-order Transition Points.—Poly-2 : 4 : 5-trimethylstyrene has an appreciably higher second-order transition point (T_g) than any of the other polystyrenes investigated (Table V, Fig. 2). This temperature, which Kauzmann (*Chem. Reviews*, 1948, **43**, 219) calls the glassy transformation point, is usually closely related to the more empirical softening and heat-distortion temperatures of polymers (Wiley, *Ind. Eng. Chem.*, 1942, **34**, 1052). It is depressed by the presence of *p*-, and unaffected by *m*-, methyl groups in polystyrene; its appreciably higher value for poly-2 : 4 : 5-trimethylstyrene is almost certainly caused by the presence of an *o*-methyl group rather than by the bulk effect of the three groups, in view of the work of Shorygin and Shorygina (*loc. cit.*) and, more particularly, of the Dominion Tar and Chemical Co. (*loc. cit.*), who found that the polymers of 2 : 3-, 2 : 4-, and 2 : 5-dimethylstyrene each had a heat-distortion temperature of 102—106°, whereas that of poly-3 : 4-dimethylstyrene was 81—83°.

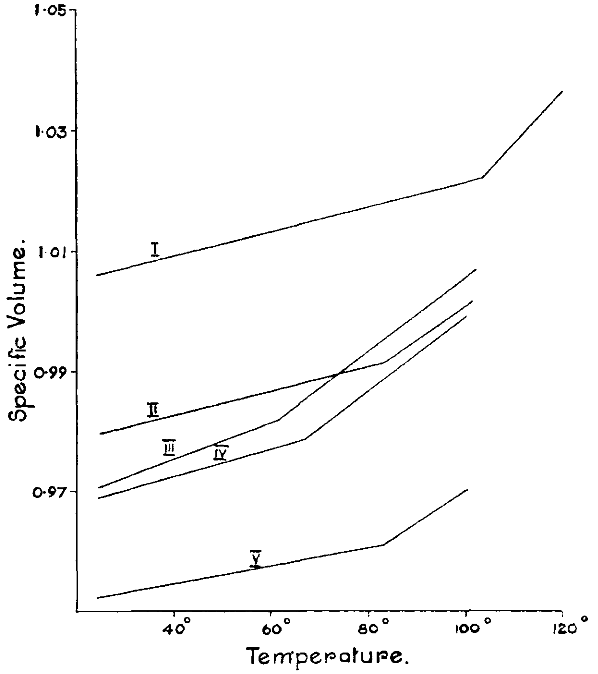
The coefficients of expansion (α) in Table V were calculated on the basis of the equation $V_t = V_0(1 + \alpha t)$, where V_t is the specific volume at temperature t (°c.) and V_0 is the (extrapolated) specific volume at 0°. Poly-2 : 4 : 5-trimethylstyrene has an appreciably higher expansion coefficient above its transition point than have the other polymers; previously recorded values of T_g, α_1, and α_2, for polystyrene vary from 76° to 82°, 2·1 × 10^{-4} to 2·7 × 10^{-4}, and 4·3 × 10^{-4} to 5·9 × 10^{-4}, respectively (Wiley, *loc. cit.*; Boyer and Spencer, *J. Appl. Physics*, 1944, **15**, 398; 1946, **17**, 398; Alfrey *et al.*, *ibid.*, 1943, **14**, 700; Clash and Rynkiewicz, *Ind. Eng. Chem.*, 1944, **36**, 279).

Time effects on specific volume at a constant temperature, similar to those described by Boyer and Spencer (*loc. cit.*) were observed during all these determinations, but were not examined quantitatively.

No measurements were made on the brittle polymer of low molecular weight which was obtained from 2 : 4 : 6-trimethylstyrene. The fluorescence of this polymer (see above) suggests that some condensation to conjugated polynuclear hydrocarbons takes place together with polymerisation.

The interpolymer of *m*- and *p*-methylstyrene in the ratio of 3 : 1, was prepared since *m*- and *p*-ethyltoluene normally occur together in natural petroleum in this ratio. A polymer of this composition might, therefore, be readily obtained by way of the dehydrogenation of ethyltoluenes extracted from petroleum.

FIG. 2.



I. *Poly-2 : 4 : 5-trimethylstyrene.* II. *Poly-*p*-methylstyrene.* III. *Poly-*m*-methylstyrene.* IV. *Polymethylstyrene* (m/p = 3/1). V. *Polystyrene.*

TABLE V.

Polymer.	Transition temp., T_g.	Coefficients of volume expansion × 10^4. Below T_g. a_1.	Above T_g. a_2.
Polystyrene	83°	1·96	5·75
Poly-*p*-methylstyrene	83	2·09	6·31
Poly-*m*-methylstyrene	61	3·15	6·31
Polymethylstyrene (*m* : *p* ratio, 3 : 1)	67	2·34	6·58
Poly-2 : 4 : 5-trimethylstyrene	104	2·07	9·24

Viscosity Measurements.—A comparison of the molecular weights of the polymers obtained by thermal polymerisation at 100° was made by calculation from the relative viscosities of 1% (by wt.) solutions in benzene at 30°, using the equation, $M = K \log_{10} (\eta_r/C)$, where M is the molecular weight, η_r is the relative viscosity, C is the concentration in base moles/l., and K is a constant, taken as 0·45 × 10^4 for all the polymers (Kemp and Peters, *Ind. Eng. Chem.*, 1942, **34**, 1097).

TABLE VI.

Polymer.*	Relative viscosity in solution.*	" Molecular weight."
Polystyrene	3·48	28,800
Poly-*m*-methylstyrene	5·22	43,200
Poly-*p*-methylstyrene	2·07	19,000
Polymethylstyrene (*m* : *p* ratio, 3 : 1)	4·05	36,600
Poly-2 : 4 : 5-trimethylstyrene	2·24	26,200
Poly-2 : 4 : 6-trimethylstyrene †	1·09	2,800

* See text for details. † 190° polymer, not purified by precipitation.

Molecular weights obtained in this way have little absolute significance, but are useful as a comparison between the different homologues (Table VI). *m*-Methylstyrene clearly yields a polymer having a much greater degree of polymerisation than has any of the others. The low molecular weight of the sample of poly-2 : 4 : 6-trimethylstyrene accords with its brittle nature and is due to the high temperature of polymerisation.

Two commercial samples of polystyrene, " Polystyrene 120 " and " Distrene 80," had molecular weights, as determined by this method, of 20,300 and 15,000, respectively.

The authors are indebted to Miss M. Scholtz for experimental assistance.

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