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STUDIES ON THE CATIONIC POLYMERIZATION OF *o*-METHYLSTYRENE

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Abstract—The polymerization of *o*-methylstyrene by H_2SO_4, $AlBr_3$, or $BF_3.Et_2O$ gave polymers showing i.r. spectra identical to that of a polymer formed by thermal polymerization. It follows that the cationic polymerization of this monomer proceeds normally, i.e. without isomerization, as is the case for the cationic polymerizations of *p*-methyl-, *p*-isopropyl-, and *o*-isopropylstyrenes.

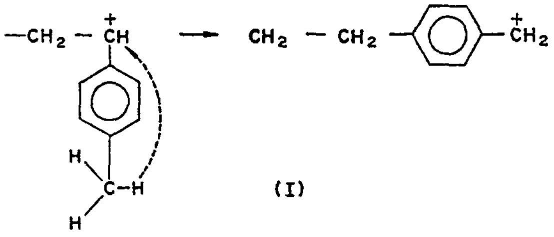
INTRODUCTION

IT IS well known that under suitable conditions some monomers give polymers with repeat units whose structure differs from that of the monomer. This kind of polymerization, known as isomerization–polymerization, can be defined by the general equation:

$$nA \rightarrow (-B-)_n$$

where A is the monomer and B is the rearranged repeat unit. This subject has been reviewed recently.$^{(1)}$

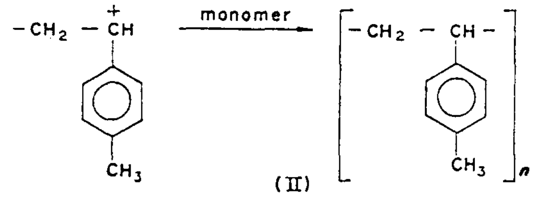
Some Russian authors have attempted the isomerization–polymerization of styrene$^{(2)}$ and styrene derivatives$^{(3,4)}$ to prepare polymers with the phenyl rings built into the main chain. On the basis of some questionable spectroscopic and thermogravimetric evidence, they claimed$^{(3,4)}$ in particular that the cationic polymerization of *p*-methylstyrene with $BF_3.Et_2O$ in toluene or ethyl chloride gives a polymer containing up to 35 per cent of rearranged repeat units, provided that the polymerization temperature is below −78° and the monomer and catalyst concentrations are sufficiently low (less than 0·4M and 0·02M respectively). Under these conditions, the polymer yields are usually below 1 per cent. The mechanism proposed for the alleged rearrangement was not explained clearly; the Russian authors depicted it thus:



(I)

but stated that the isomerization was not the result of migration of a hydride ion. They were forced to this conclusion because no isomerization had been found in the cationic polymerization of *p*-isopropyl styrene(1,4–6) for which the hydride shift would at least be energetically favourable.

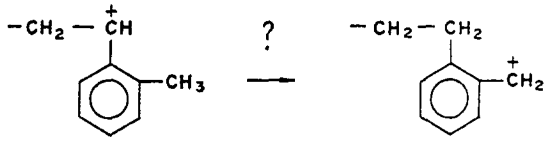
Although this claim seemed doubtful on theoretical grounds, we were interested enough to reinvestigate the cationic polymerization of *p*-methylstyrene, using various catalysts and polymerization conditions.(7) A considerable body of experimental results, together with theoretical considerations, convinced us that the alleged isomerization–polymerization of *p*-methylstyrene does not take place and that the polymers obtained are in fact formed exclusively by the conventional route:



(II)

Among the styrene derivatives, *o*-isopropylstyrene is certainly the most favourable for hydride migration but, contrary to claims by Aso and co-workers,(8) it has been shown definitely to polymerize cationically by the conventional 1,2 mechanism.(9)

Some years ago we sought evidence for isomerization–polymerization of *o*-methylstyrene, which would involve the following hydride shift:



(III)

Although this reaction is also energetically unfavourable, it seemed at the time slightly more plausible than reaction (I) in view of the shorter path required in this case for the hydride migration. However, the polymerization was found to be completely normal. The present paper is an account of this work.

EXPERIMENTAL

o-Methylstyrene was synthesized from commercial *o*-bromotoluene by the Grignard method. The crude monomer was twice fractionated under reduced pressure in the presence of a trace of picric acid. The purified monomer (b.p. 33°/1·5 torr, purity 99·3 per cent by GLC) was then introduced into flask A (Fig. 1) through tube B which was then sealed. It was thoroughly degassed through C and the constriction C was sealed off. Break-seal D was crushed and the monomer was distilled into flask F which contained about 10 g BaO previously baked at about 300° for 12 hr under high vacuum. Flask A was sealed off at constriction E. The monomer was stored over BaO at room temperature for three days with occasional magnetic stirring. It was then degassed again and the assembly was then sealed off at G. The monomer was distilled into tipping device I and the latter was sealed off at constriction H. The monomer phials were prepared by the usual method and their contents determined by the mid-point method.(10)

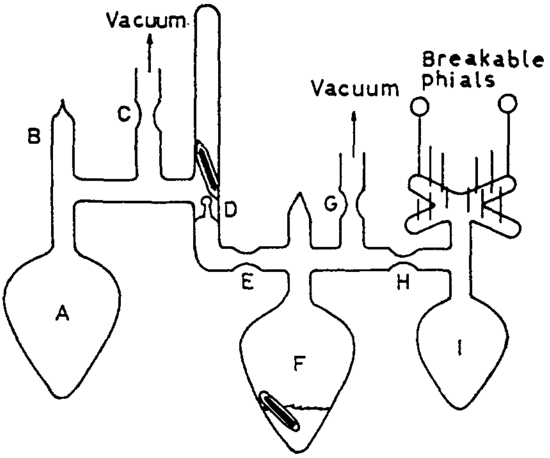


Fig. 1. Glass apparatus used for the preparation of monomer phials under high vacuum.

The i.r. spectrum of the monomer contained in one of the phials is shown in Fig. 2.

Methylene dichloride and ethyl chloride were purified, dried and dispensed as already described.(9) $AlBr_3$(9) and $BF_3.Et_2O$(7) phials were prepared as described.

Commercial H_2SO_4 (100 per cent) was introduced directly into a fragile phial with a microsyringe, without further purification. The phial, attached to the vacuum line, was evacuated with its contents frozen in liquid nitrogen and then sealed off. The amount of sulphuric acid was cross-checked by weighing the phial by the mid-point method.(10) However, the H_2SO_4 concentration shown in Table 1 is only the nominal concentration, since it is unlikely that the acid was completely dissolved at the start of the polymerization; thus the reaction may have occurred partly heterogeneously.

The cationic polymerizations of *o*-methylstyrene were carried out using the two-arm apparatus described.(9) The monomer and catalyst solutions were prepared in separate arms of the apparatus at room temperature and the device was then immersed in a cooling bath. After thermo-equilibration, the monomer and catalyst solutions were mixed rapidly and the polymerization device was left in the bath for the appropriate time with gentle occasional shaking. Polymerizations were stopped by melting a small hole at the top of the apparatus, through which a small amount of precooled ammonia–methanol mixture was introduced. The polymer was precipitated and dried conventionally.

The radical polymerization of *o*-methylstyrene was carried out by immersing a monomer phial in a bath at 70° for 48 hr. The product was dissolved in benzene and the polymer was obtained in the usual manner.

The molecular weights were determined by a High Speed Membrane Osmometer (Hewlett-Packard 501). The i.r. spectra were scanned with a Perkin–Elmer 521 instrument with polymer films prepared by evaporation of benzene or CS_2 solutions on KBr discs.

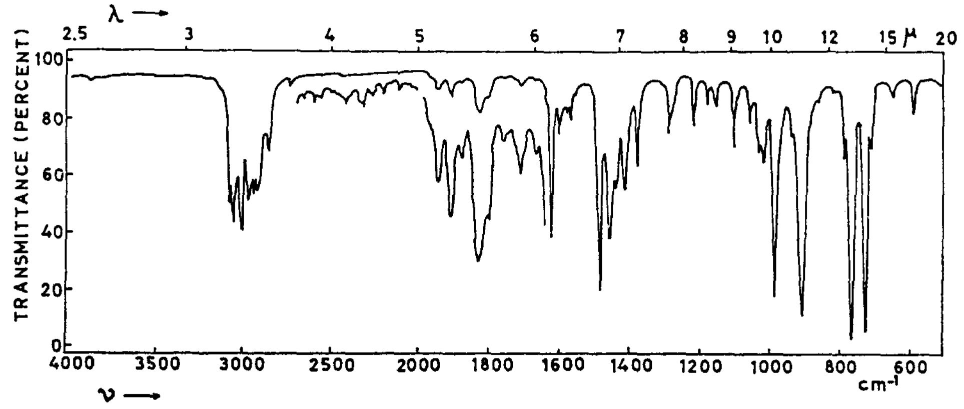


Fig. 2. Infrared spectrum of *o*-methylstyrene.

RESULTS

The polymerization conditions and the results are given in Table 1.

TABLE 1

Polymer No.	Initiator	Solvent	Initiator concn. (10^3 mole/l.)	Monomer concn. (mole/l.)	(°C)	Time (hr)	Yield (%)	$10^{-3} M_n$
1				Bulk	70	48	75	58
2	H_2SO_4	CH_2Cl_2	15·6	0·4	−10	2·5	48	18
3	$AlBr_3$	C_2H_5Cl	4·3	0·4	−126	0·5	4·5	27
4	$BF_3\cdot Et_2O$	CH_2Cl_2	27·4	0·6	−90	10	2·3	21

The i.r. spectra of all samples were found to be virtually identical and superposable. Figure 3 shows the spectra of two representative polymer samples: No. 1 obtained by thermal polymerization and No. 3 prepared with $AlBr_3$. Comparison of these spectra with that of the monomer in Fig. 2 shows that both the polymer spectra have aromatic substitution bands, similar to those of the monomer, in the 2000–1650 cm^{-1} and 800–700 cm^{-1} ranges. Also the 1378 cm^{-1} methyl band, which appears in the monomer spectrum, is retained with similar relative intensity in the spectra of the polymers. Most of the differences between the monomer and polymer spectra can be easily associated with the disappearance of the vinyl groups and the formation of $—CH_2—CH=$ sequences. The i.r. analysis, therefore, points to a conventional 1,2 enchainment of the repeat units of poly-*o*-methylstyrene.

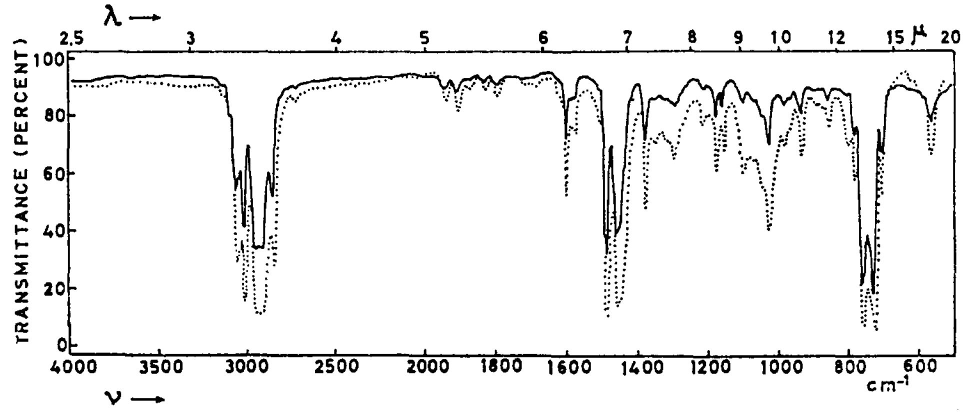


FIG. 3. Comparison of i.r. spectra of poly-*o*-methylstyrenes: —— Polymer 1 in Table 1 (Free radical, 70°). ---- Polymer 3 in Table 1 ($AlBr_3$, −126°).

However, even stronger evidence against hydride-shift polymerization is provided by the essential identity of the i.r. spectra of polymers prepared under very different polymerization conditions (Fig. 3). Since the sample prepared by thermal polymerization is certainly of a conventional, unrearranged structure, we can safely conclude that the product prepared with $AlBr_3$ at −126° also has a conventional structure. The spectra of polymers 2 and 4 were essentially the same as those in Fig. 3.

These facts clearly demonstrate that, under the conditions investigated, the cationic polymerization of *o*-methylstyrene does not give polymers of rearranged structure, i.e. that the hydride shift of Eqn. (III) does not occur with this monomer. On the contrary, *o*-methylstyrene resembles *p*-methylstyrene,(7) *p*-isopropylstyrene(1,5,6) and *o*-isopropylstyrene,(9) in that when polymerized with Lewis or protonic acids (as well as by radical polymerization), it gives a polymer of normal structure.

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Résumé—La polymérisation de l'*o*-méthylstyrène amorcée par H_2SO_4, $AlBr_3$ ou $BF_3 \cdot Et_2O$ a donné des polymères dont les spectres infra-rouges sont identiques à celui d'un polymère produit par polymérisation thermique. On en déduit que la polymérisation cationique se produit de façon normale, c'est-à-dire sans isomérisation. Ce résultat est en accord avec ce que nous avions également trouvé dans le cas des polymérisations cationiques des *p*-méthyl-, *p*-isopropyl et *o*-isopropylstyrène.

Sommario—La polimerizzazione dell'*o*-metilstirolo, iniziata da H_2SO_4, $AlBr_3$ o $BF_3 \cdot Et_2O$, ha fornito polimeri i cui spettri infrarossi son o praticamente identici a quelli di un polimero prodotto per polimerizzazione termica. Ciò dimostra che la polimerizzazione cationica di questo monomero decorre in modo convenzionale, cioè senza isomerizzazione. Questo risultato è in accordo con quanto da noi già dimostrato per la polimerizzazione del *p*-metil-, del *p*-isopropil- e dell'o-isopropilstirolo.

Zusammenfassung—Die Polymerisation von *o*-Methylstyrol durch H_2SO_4, $AlBr_3$ oder $BF_3 \cdot Et_2O$ ergab Polymer, welche identische i.r. Spektren zu denen, eines durch Wärmepolymerisation gebildeten Polymers zeigten. Es folgt, dass die kationische Polymerisation dieses Monomers normal von statten geht, d.h. ohne Isomerisation, wie im Falle der kationischen Polymerisationen von *p*-Methyl-, *p*-Isopropyl- und *o*-Isopropylstyrols.