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Stereospecificity in the Cationic Co-ordinated Polymerization of Methoxystyrenes

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SUMMARY:
   Investigations were performed in order to establish whether the "modified Friedel-Crafts catalysts", which are stereospecific in the cationic co-ordinated polymerizations of the vinyl and alkenyl ethers, are stereospecific also when the ether oxygen is not directly bound to the vinyl double bond. For this purpose the polymerization of ortho, meta and para methoxy styrenes were studied.
   Whereas the meta methoxy styrene does not polymerize due to the unfavorable influence of the substituent upon the π-electrons of the vinyl group, the ortho and para isomers furnish amorphous polymers. By hydrogenating the phenyl groups of the poly ortho methoxy styrene to crystalline poly ortho methoxy vinyl cyclohexane it has been proved that the polymerization of the ortho methoxy styrene is stereospecific and that the mechanism is cationic co-ordinated.

ZUSAMMENFASSUNG:
   Es wird untersucht, ob die bei der kationisch-koordinierten Polymerisation der Vinyl- und Alkenyläther stereospezifisch wirkenden „modifizierten Friedel-Crafts-Katalysatoren" auch dann noch Stereospezifität entfalten, wenn der Äther-Sauerstoff nicht unmittelbar an die Vinyl-Doppelbindung geknüpft ist. Zu diesem Zweck wird die Polymerisation des o-, m- und p-Methoxystyrols untersucht.
   Während das m-Methoxystyrol wegen des ungünstigen Einflusses des Substituenten auf die π-Elektronen der Vinylgruppe nicht polymerisiert, erhält man bei den o- und p-Isomeren amorphe Polymere. Durch Hydrierung der Phenylringe des Poly-o-methoxystyrols zu kristallinem Poly-o-methoxy-vinyl-cyclohexan wird der Beweis erbracht, daß die Polymerisation des o-Methoxy-styrols stereospezifisch verlaufen ist und daß der Mechanismus kationisch-koordinativ ist.

I. Introduction

The stereospecific polymerization of vinyl monomers has attained high consideration both from a scientific and a practical point of view, after the discovery, made in 1954, of isotactic polymers obtained by polymerization of α-olefins. It had been observed, since the beginning, that the stereospecific polymerization of both aliphatic and aromatic mono-olefinic

hydrocarbons to stereoregular polymers with an isotactic structure, requires heterogeneous catalysts. Subsequent investigations have demonstrated that heterogeneous catalysts are necessary only in the case of mono-olefinic hydrocarbon monomers that do not contain other groups (e.g. other olefin groups) able to donate π-electrons, or atoms (e.g. oxygen, nitrogen, etc.) possessing free electron pairs. The latter generally show a poisening action on the Ziegler-type catalysts and therefore they cannot be polymerized in the presence of heterogeneous catalysts, which polymerize α-olefins stereospecifically. As it is known, it was possible to polymerize those monomers with the aid of other types of catalysts, even homogeneous, acting through a cationic or an anionic mechanism, depending on the chemical nature of the substituents and on their influence on the increase or decrease of the electron density of the olefinic double bond.

Monomers of this type, which have been particularly studied are: vinyl alkyl ethers[1-6], alkenyl alkyl ethers[7], vinyl carbazole[8], vinyl diphenyl-amine[9]), acrylo nitrile[10], methyl methacrylate[11], acrylates[12-14], 2-vinyl pyridine[15] and sorbates[16].

Diolefins as well, in particular the conjugated ones that polymerize stereospecifically in the presence of some heterogeneous catalysts containing organometallic compounds and particular transition metal compounds, can polymerize stereospecifically with the aid of suitable homogeneous catalysts[17].

As it was already pointed out by several authors[18,19] and by ourselves[3,15,20], the stereospecific polymerization in the homogeneous phase (with the use of soluble catalysts) requires the presence of atoms or of groups able to donate electrons thus forming a dative bond with the catalytic complex, such as to impose a constant type of presentation of the polymerizable double bond with respect to the bond between the growing macromolecules and the catalytic complex. The importance of the constancy of the type of presentation and of the type of opening of the double bond was widely discussed in a recent paper by this Institute[21]. A particular interest is shown by the stereospecific polymerization obtained with the aid of homogeneous catalysts, with formation of isotactic polymers of vinyl monomers, as well as of monomers containing internal double bonds and ether oxygen atoms, adjacent to the polymerizable double bond. To this class of compounds belong vinyl alkyl ethers, which have been polymerized in this Institute, using soluble catalysts, as well as the alkenyl alkyl ethers, which differ from the former since they contain an internal double bond and therefore yield di-isotactic polymers[7].

In both these types of monomers, the oxygen atom is directly bound to the polymerizable double bond. Since its presence has a determinating action on the stereospecific polymerization of the above-mentioned monomers with catalysts acting through a cationic mechanism, in order to yield isotactic polymers, we thought it interesting to examine other monomers containing ether oxygen, but not directly bound to the double bond; therefore we studied the polymerization of alkoxy styrenes using catalysts, acting in the homogeneous phase, which are stereospecific in the polymerization of vinyl alkyl ethers.

II. *Results of the Polymerizations of Methoxy Styrenes*

Some catalysts, which proved suitable for the cationic co-ordinated polymerization of vinyl alkyl ethers to crystalline isotactic polymers ("modified FRIEDEL-CRAFTS" catalysts[3]) were used for the polymerization of the methoxy styrenes. The results of the polymerization runs with the three methoxy styrenes are given in Table 1. In particular, from it results:

1) meta methoxy styrene, in the conditions we used, does not yield polymers, not even in traces. This result, which agrees with facts already observed in the polymerizations of other series of aromatic vinyl compounds (*e.g.* in the series 2-3-4-vinyl pyridine[15]) can be explained by the particular electronic situation of the aromatic compounds with functional groups in meta position. In fact the co-ordination of the ether oxygen of the monomer to the catalyst induces a polarization of the vinyl double bond in the opposite sense to that induced when the substituent is in ortho or para position, thus preventing a cationic polymerization mechanism.

2) in the case of ortho and of para methoxy styrene, where the polarization of the vinyl double bond by the ether oxygen favours a cationic polymerization mechanism, some, but not all the "modified FRIEDEL-CRAFTS" catalysts, used by us under the conditions of the stereospecific polymerizations of vinyl alkyl ethers (low temperature, slow addition of the monomer to the catalyst diluted with much solvent), promote the polymerization of the said monomers.

3) The polymerization of ortho methoxy styrene is particularly favoured by the catalysts having strong cationic activity ($AlCl_2C_2H_5$), whereas para methoxy styrene can be polymerized also with the aid of catalysts showing a weaker cationic activity (*e.g.* $AlCl(C_2H_5)_2$).

4) The yield of poly ortho methoxy styrene is increased in the presence of an aromatic hydrocarbon solvent with respect to an aliphatic one, contrary to what observed in the case of analogous polymerizations of vinyl alkyl ethers.

Table 1. Polymerization of Methoxy Styrenes in the Presence of "Modified FRIEDEL-CRAFTS" Catalysts

(Temperature −78 °C.; time: 6 hrs.; molar ratio methoxy styrene: catalyst = 40:1)

Methoxy-styrene	Catalyst	Solvent	Conversion to polymer (%)	X-ray examination	$[\eta]$ *)
ortho	$AlCl_2C_2H_5$	toluene	92	amorphous stereoregular	0.16
ortho	$AlCl_2C_2H_5$	toluene + propylene	48	do.	0.11
ortho	$AlCl_2C_2H_5$	n-heptane	32	do.	0.09
ortho	$AlCl(C_2H_5)_2$	toluene	4	do.	n.d.
ortho	$TiCl_2acetate_2$	toluene	traces	—	—
ortho	$TiCl_2(O\text{-}n\text{-but})_2$	toluene	0	—	—
meta	$AlCl_2Cl_2H_5$	toluene	0	—	—
meta	$AlCl_2C_2H_5$	toluene + propylene	0	—	—
meta	$AlCl(C_2H_5)_2$	toluene + propylene	0	—	—
para	$AlCl_2C_2H_5$	toluene	27	amorphous	2.19
para	$AlCl(C_2H_5)_2$	toluene	82	amorphous	2.09
para	$TiCl_2acetate_2$	toluene	7	amorphous	0.52
para	$TiCl_2(O\text{-}n\text{-but})_2$	toluene	12	amorphous	0.16

*) Determined in toluene at 30 °C in the case of poly ortho methoxy styrene, in tetralin at 135 °C. in the case of poly para methoxy styrene.

III. *Hydrogenation of the Poly Methoxy Styrenes*

The polymers of ortho and of para methoxy styrene, obtained according to the above-described method, do not differ essentially, in their physical properties, from analogous atactic polymers (prepared by radical polymerizations), which were previously known[22, 23]. This could be attributed either to a lack of steric regularity along the macromolecular chain, or to difficulty in the crystallization, due to the steric hindrance of the methoxy phenyl side groups.

An analogous problem had already risen for some vinylaromatic polymers having substituents in the aromatic nucleus, polymerized with stereospecific catalysts[24]. In those cases it had often been possible to solve the problem by hydrogenating these vinylaromatic polymers.

Polymers of vinylaromatic monomers, substituted in the ring with halogen, such as poly para chloro styrene, thus yielded poly vinyl cyclohexane by hydrogenation and simultaneous dehalogenation, whereas in the case of nuclei substituted with alkyl groups, the corresponding alkyl-substituted poly vinyl cyclohexanes were obtained. Such hydrogenated polymers appeared to be crystalline, thus demonstrating the regular steric structure (isotactic) of the starting polymer, since it is impossible that an atactic chain can become isotactic by simple hydrogenation of the side group. Analogous hydrogenations of poly methoxy styrenes were unknown up to now.

Therefore, we subjected the polymers of ortho and para methoxy styrene to catalytic hydrogenation with Raney-nickel at fairly high temperature (180 °C). Thus it was possible to hydrogenate poly ortho methoxy styrene without any difficulty quantitatively to poly ortho methoxy vinyl cyclohexane. By X-ray examination this polymer revealed crystallinity, as can be observed from the diffraction spectrum, reported in Fig. 1, together with that of the corresponding amorphous poly ortho methoxy styrene. The crystallinity of poly ortho methoxy vinyl cyclohexane is due to the stereoregularity of the structure of its main chain. It demonstrates that also the poly ortho methoxy styrene, from which this polymer has been obtained by hydrogenation of the aromatic rings, possesses a main chain in which the tertiary carbon atoms have a stereoregular structure.
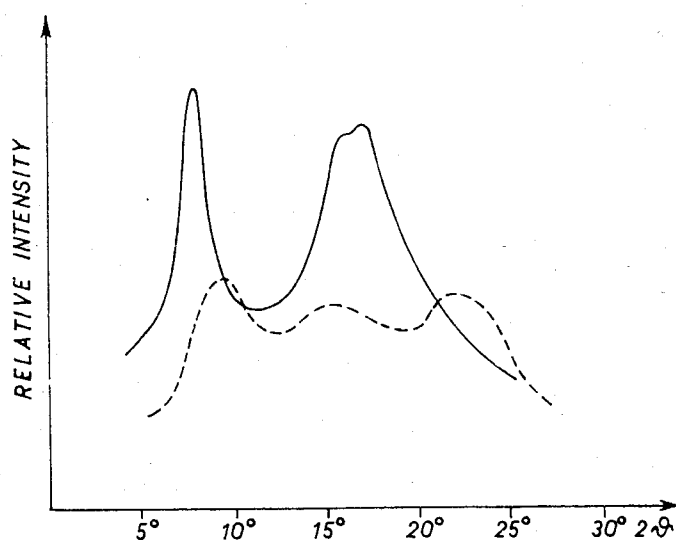

Fig. 1. Geiger-counter registred X-ray spectrum (Cu K_α-radiations) of amorphous poly o-methoxy styrene (dotted line) and of crystalline poly o-methoxy vinyl cyclohexane (full line)

The transformation into a crystallizable polymer caused remarkable variations of the physical properties. The melting temperature of poly ortho methoxy vinyl cyclohexane (190–195 °C), for instance, is about 70 °C higher than the softening temperature of the starting poly ortho methoxy styrene (110–130 °C). The intrinsic viscosity of the polymer was not varied by the hydrogenation. This means that such hydrogenation did not cause any degradation of the polymer.

The evidences that allow us to attribute to the said hydrogenated polymer the chemical structure of a poly ortho methoxy vinyl cyclohexane are mainly based on the examination of the I.R. spectra (Fig. 2).

In the spectrum of the poly ortho methoxy styrene we find strong absorption bands at 6.27, 6.32 and 6.72 μ, due to the presence of an aromatic nucleus, and also another strong band at 13.40 μ, due to 1,2-di-substituted phenyl groups (out-of-plain deformation). On the contrary, in the spectrum of the hydrogenated product (poly ortho methoxy vinyl cyclohexane) none of the above-mentioned four bands, characteristic of the phenyl group, are practically visible any more.

In addition, it is observed how the band present at 8.10 μ in the poly ortho methoxy styrene (characteristic position of alkyl phenyl ethers) is shifted in the hydrogenated product to 9.17 μ (position characteristic of dialkyl ethers).

This demonstrates not only that the hydrogenation of the aromatic rings took place practically completely, but also that the methoxylic group has not been removed during the hydrogenation.
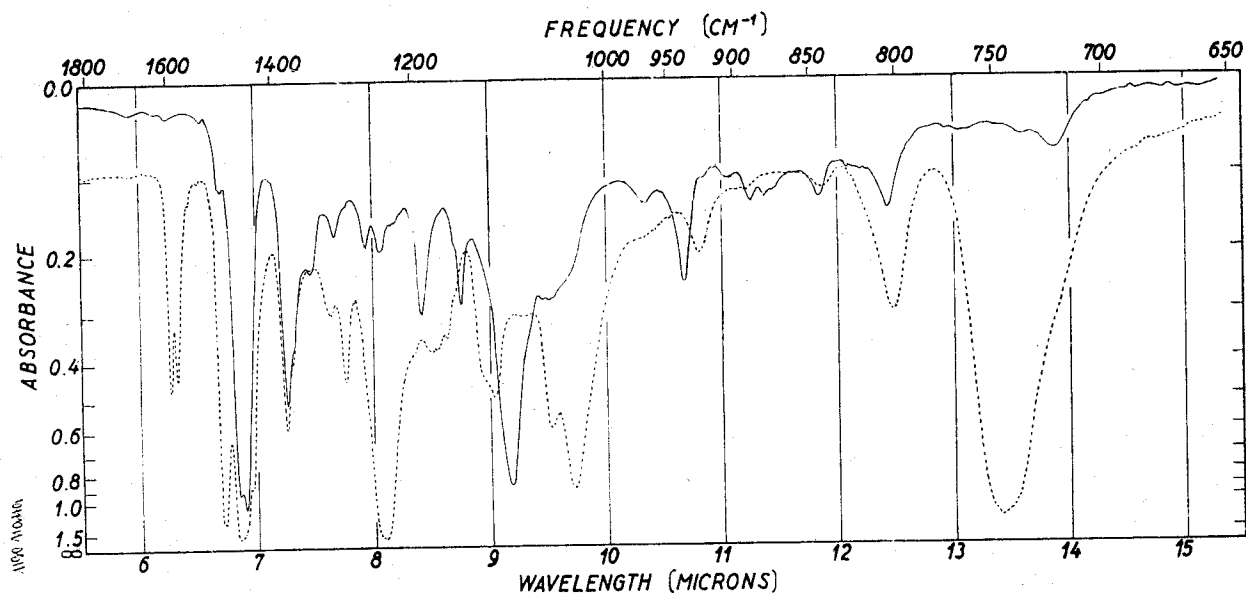

Fig. 2. Infra-red spectrum of poly o-methoxy styrene (dotted line) and of its hydrogenation product poly o-methoxy vinyl cyclohexane (full line)

The crystalline structure of poly ortho methoxy vinyl cyclohexane has not been determined up to now. In analogy with what observed for all poly vinyl alkylethers and poly alkenyl alkyl ethers known up to now, it is most likely that also this polymer has an isotactic structure.

Contrary to what stated above, poly para methoxy styrene could not be hydrogenated, not even in part, to the corresponding poly para methoxy vinyl cyclohexane. This in spite of the many attempts made using several types of hydrogenation catalysts (RANEY-Ni, PtO_2; supported Pd and Rh) within a wide range of temperatures (between 60 to 210 °C.) and by varying the solvent.

Even taking into account the far lower solubility of the para compound (in comparison with the ortho compound) in the organic solvents, and the softening temperature, which is much higher (230—240 °C.), it is difficult to give a plausible explanation of this lack of reactivity of poly para methoxy styrene.

IV. *Conclusions*

The above-described demonstration of the stereoregular structure of the main chain of poly ortho methoxy styrene, allows us to draw some conclusions about the polymerization mechanism of ortho methoxy styrene. In fact, we can state that the described cationic polymerization in the homogeneous phase must necessarily occur through a co-ordinated mechanism, in analogy with what was found for vinyl alkyl ethers and alkenyl alkyl ethers.

Thus, even in this case, the polymerization should be preceded by a co-ordination of the ether oxygen to the metal of the catalyst.

It is interesting to observe how the higher distance, with respect to that existing in the vinyl alkyl ethers, between the vinyl double bond and the ether oxygen does not prevent the orientation effect of the co-ordination complex on the addition step of the new monomer molecules to the growing chain. On the other hand, it must be considered that the group of atoms comprised between the ether oxygen and the tertiary carbon of the vinyl group has a planar and very rigid conformation and therefore it is subjected to a very limited extent to space displacements due to rotations.

In the case of meta methoxy styrene the lack of correspondence to the cationic catalytic systems of polymerization can be attributed to chemical reasons, in analogy with what occurs for other aromatic monomers with substituents in meta position.

The problem whether a greater distance between oxygen and vinyl group, like in the case of para methoxy styrene, makes the stereospecific cationic polymerization impossible, allowing only the sterically non-regulated one, could not be solved, at least for the present.

V. *Experimental*

Preparation of Poly Ortho Methoxy Styrene

100 ml of anhydrous toluene and 0.20 ml (1.86 millimoles) of freshly distilled monoethyl aluminum dichloride are put in nitrogen atmosphere into a 250 ml flask, equipped with stirrer, dropping funnel and a nitrogen inlet tube. The mixture is cooled to −78°C., and is kept well stirred; 10 g (75 millimoles) of previously distilled ortho methoxy styrene are added dropwise. After introduction of the whole monomer, the mixture is kept for 5 hours under stirring at −78°C. Then the reaction is stopped by pouring the reaction mixture in 500 ml of methanol containing 10 ml of concentrated hydrochloric acid. The obtained polymer is filtered, washed with methanol and dried under reduced pressure at 70°C. Thus 9.2 g (92% conversion) of poly ortho methoxy styrene are obtained as a white powder. Its intrinsic viscosity, determined in toluene at 30°C., is 0.16. The product softens at about 120°C. It is completely soluble in aromatic hydrocarbons, partially soluble in aliphatic ethers and in boiling aliphatic hydrocarbons (for example in boiling *n*-octane it can be extracted to about 30%). It is insoluble in aliphatic hydrocarbons at room temperature and in alcohols, such as methanol and ethanol, even at boiling.

Preparation of Poly Para Methoxy Styrene

Freshly distilled para methoxy styrene is polymerized under the same conditions as described above for the ortho methoxy styrene. It is advisable to use aluminum diethyl monochloride as catalyst. The polymer, which is obtained with a conversion of 82%, is a white powder, with an intrinsic viscosity of 2.1, determined in tetralin at 135°C. It softens at about 230°C. It is insoluble in various solvents, even at boiling, such as in aliphatic hydrocarbons (*n*-pentane, *n*-heptane), alcohols (methanol, ethanol), ethers (diethyl ether, di-isopropyl ether). It is soluble in some higher boiling solvents, such as toluene, dioxane, chloroform, at their boiling temperatures.

Preparation of a Crystalline Poly Ortho Methoxy Vinyl Cyclohexane

A solution of 4.5 g of poly ortho methoxy styrene (obtained as said above, having [η] = 0.15) in 120 ml of 1,2-diethoxyethane is introduced in a 600 ml autoclave. A suspension of about 2 g of Raney-nickel in 15 ml of anhydrous ethyl alcohol is added. After closing, hydrogen is pressed into the autoclave up to a pressure of 110 at.; it is then heated to 180°C. under rocking. After a reaction time of 65 hours, the autoclave is cooled, and the reaction products are discharged. (Another equal amount of Raney-nickel was added after half the reaction time with the purpose to make the hydrogenation more complete.) The suspended nickel is separated by repeated filtrations, and the polymer is precipitated, by pouring the solution in 800 ml of methanol. The polymer is filtered, washed with methanol and dried at reduced pressure at 150°C. Thus 4.3 g of poly ortho methoxy vinyl

cyclohexane are obtained. As revealed by I.R. analysis, the hydrogenation of the aromatic rings is practically complete (hydrogenation exceeds 97%).

The polymer is a white powder, with an intrinsic viscosity of 0.15, determined at 30°C. in toluene. It melts at about 190–195°C., and it is crystalline by X-ray examination. It is soluble in aromatic hydrocarbons and in some ethers (e.g. 1,2-diethoxyethane); insoluble in aliphatic hydrocarbons (n-heptane) and in alcohols (methanol).

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