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Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band XXXVII

Heft 1/2 · 1960

Seite 160—162

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(Eingegangen am 31. März 1960)

Amorphous non crystallizable polymers of vinyl pyridines, obtained by free radical polymerization are known¹⁾).

Using particular catalysts, acting through an anionic mechanism, we have now prepared high molecular weight crystallizable polymers of 2-vinyl pyridine.

Some of the most suitable catalysts consist of organometallic compounds or of amides of magnesium, such as diethyl magnesium, phenyl magnesium bromide or halides of magnesium diethyl amide.

As it results from Table 1, in the presence of these catalysts, high conversions of the monomer are obtained in few hours even at room temperature.

The crude polymers can be purified from the catalyst residues by dissolution in aqueous hydrochloric acid and successive precipitation with ammonia, in the presence of ammonium chloride. The product thus obtained is in general amorphous by X-rays. By treatment with acetone at its boiling temperature for about 1 hour, part of the polymer (not exceeding 10 %) remains dissolved, while the remaining part precipitates as a finely divided white powder, which proved to be crystalline at X-ray examination (see Fig. 1). By extruding the molten polymer and by successive stretching, fibers can be obtained, showing a different crystalline structure and an identity period of approximately 6.7 Å, which is very near to the value found for isotactic polystyrene²⁾).

The crystalline polymers of 2-vinyl pyridine are insoluble in boiling aliphatic hydrocarbons, in diethyl ether and in methyl ethyl ketone. They are soluble in methyl alcohol, chlorinated solvents and in boiling aromatic hydrocarbons.

¹⁾ See e.g.: E. B. FITZGERALD and R. M. FUOSS, *Ind. Engng. Chem.* **42** (1950) 1603; C. C. PRICE and C. E. GREENE, *J. Polymer Sci.* **6** (1951) 111; U. P. STRAUSS, S. I. ASSONY, E. G. JACKSON, and L. H. LAYTON, *J. Polymer Sci.* **9** (1952) 509; P. F. ONYON, *Trans. Faraday Soc.* **51** (1955) 400.

²⁾ G. NATTA, P. CORRADINI and I. W. BASSI, *Nuovo Cimento, Suppl.*, **15** (1960) 68.

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Table I. Stereospecific anionic polymerization of 2-vinyl pyridine in the presence of some metallorganic compounds or of amides of magnesium. Time of polymerization: 2 hrs.

Catalyst Type	Milli- moles	Mono- mer [g.]	Toluene [ml.]	Temp. [°C.]	Obtained Polymer		
					[g.]	Fraction insol- uble in boiling acetone	
						[%]	[η]
$(C_2H_5)_2Mg$	2.4	20	140	45	19.5	95	0.30
$(C_6H_5)_2Mg$	1.1	10	70	45	9.4	96	0.35
C_6H_5MgBr	3.0	10	100	15	9.5	98	1.07
C_6H_5MgBr	1.1	10	100	40	8.7	98	0.48
$(C_2H_5)_2NMgBr$	1.5	13	90	45	12.4	94	0.20
$(C_2H_5)_2NMgBr$	2.0	17	120	45	16.0	94	0.26
$(C_6H_5)N(CH_3)MgBr$	1.5	14	100	45	13.3	96	0.60

$[\eta]$ = Intrinsic viscosity (100 ml./g.) in dimethylformamide at 30°C.

Melting temperatures (determined by polarizing microscope) between 185 and 215 °C have been found, depending on the steric purity of the different samples. Contrary to the low thermal stability of most 2-vinyl pyridine amorphous polymers obtained with radical initiators, the new crystalline polymers melt without any decomposition.

Infrared analysis of the polymers obtained in the presence of aryl-magnesium compounds or of magnesium aryl amides proved that at least part of the aryl groups which were initially present in the catalyst, are present, as terminal groups of the macromolecules. This result agrees with an anionic mechanism of polymerization.

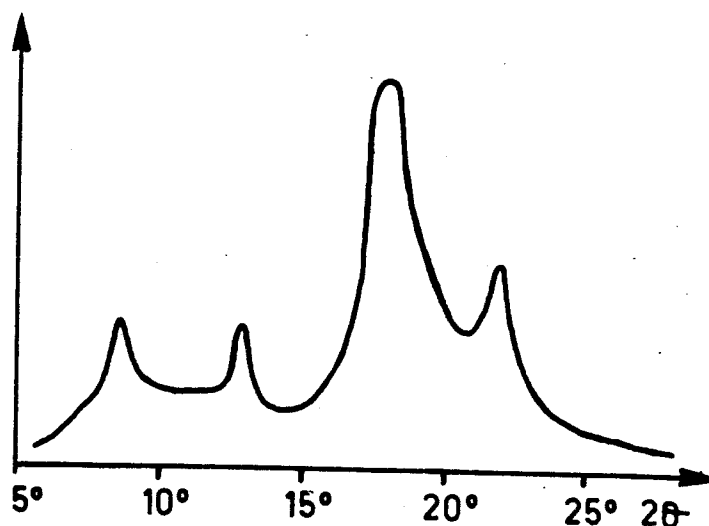


Fig. 1. Geiger registration of X-rays diffractions (Cu $K\alpha$) of crystalline poly-2-vinylpyridine

The catalysts indicated in Table I are soluble in pyridine and only slightly soluble in the pure solvents used for the polymerization (e.g. toluene), but they are completely dissolved when introducing the monomer. This agrees with the hypothesis of an association between the monomer molecules and the catalyst.

As we have already proposed for some stereospecific polymerizations, taking place in a homogeneous phase, stereospecificity in this 2-vinyl pyridine polymerization is attributable to the presence, besides the vinyl group, of another group in the monomer molecule, which may be coordinated with the catalyst³). This coordination should cause a constant presentation of each reacting monomer molecule with respect to the last monomeric unit of the growing chain. A constant presentation and a constant type of opening of the double bond (probably *cis* like in other stereoregulated polymerizations⁴)) cause the stereospecificity of the process.

In fact we have observed a lowering (or a lack) of stereospecificity in the 2-vinyl pyridine polymerization, when adding to the catalytic system some organic bases, like ethers (or pyridine) which may associate to the catalyst thus acting in a competitive way with respect to the coordination of the monomer molecules.

³) G. NATTA and G. MAZZANTI, *Tetrahedron* **8** (1960) 86; G. NATTA, G. DALL'ASTA, G. MAZZANTI, U. GIANNINI, and S. CESCA, *Angew. Chem.* **71** (1959) 205.

⁴) G. NATTA, M. FARINA and M. PERALDO, *Chimica e Industria* **42** (1960) 255.