

Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band 83

1965

Seite 161—166

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Alternating 2-Vinylpyridine / α -Stilbazole Copolymers

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(Eingegangen am 26. Juni 1964)

SUMMARY:

From pyridine monomers and stilbazole, copolymers of the regular alternating type have been prepared. In particular, a crystalline alternating copolymer has been obtained by copolymerizing 2-vinylpyridine with α -stilbazole, in the presence of some catalysts (e.g., phenylmagnesium bromide) already proved as stereospecific in the 2-vinylpyridine homopolymerization.

Crystallinity of this copolymer was attributed to a chemical regularity caused by the alternate repetition of the two monomeric units, and to a steric regularity of the asymmetric carbon atoms. Such a crystalline copolymer was found the only stereoregular synthetic polymer, known up to now, whose repeating unit contains in the main chain 3 tertiary carbon atoms which may assume enantiomorphic configurations.

ZUSAMMENFASSUNG:

Von Pyridinmonomeren und Stilbazol wurden regelmäßig alternierende Copolymere hergestellt. Insbesondere wurde ein alternierendes Copolymeres aus 2-Vinylpyridin und α -Stilbazol in Gegenwart einiger Katalysatoren (wie Phenyl-Mg-bromid) gewonnen, die sich schon bei der Homopolymerisation des 2-Vinylpyridins als stereospezifisch erwiesen hatten.

Die Kristallinität dieser Copolymeren wird einer chemischen Regelmäßigkeit, die einer alternierenden Folge von zwei Monomereinheiten entspricht, und einer sterischen Regelmäßigkeit von asymmetrischen Kohlenstoffatomen zugeschrieben.

Dies ist das erste bisher bekannte, synthetische sterisch regelmäßige Copolymeres, dessen Grundeinheit in der Hauptkette 3 asymmetrische Kohlenstoffatome enthält, die enantiomorphe Konfigurationen annehmen können.

Stereoregular alternating copolymers have been obtained in these laboratories both from hydrocarbon¹⁾ and oxygen containing monomers²⁾. The structure of the copolymers was found consistent with a ditactic type of stereoregularity. The present paper is concerned with the preparation of alternating copolymers of nitrogen containing monomers.

Anionic stereospecific polymerization of 2-vinylpyridine³⁾ and *trans*-2-propenylpyridine⁴⁾ by means of organometallic and metalamide magnesium compounds as catalysts has been already described.

It has been found now that α -stilbazole, though unable to homopolymerize in the presence of anionic catalysts, can produce copolymers with 2-vinylpyridine, containing high amounts of α -stilbazole. In particular, by using phenylmagnesium bromide as a catalyst and such experimental conditions as to hinder the direct enchainment of the 2-vinylpyridine monomeric units (e.g., by keeping very low concentrations of this monomer during the copolymerization process), the molar content of α -stilbazole in the copolymer obtained ranges between 48 to 50 %, as result of the nitrogen content analysis and of the IR spectra examination. After annealing (heating at 330 °C. under reduced pressure), the copolymer shows a high crystallinity by X-ray examination. Its diffraction diagram (Fig. 1) is quite different from those of the two crystalline modifications (A and B, Fig. 2) which can be obtained from the stereoregular poly-2-vinylpyridine³⁾.

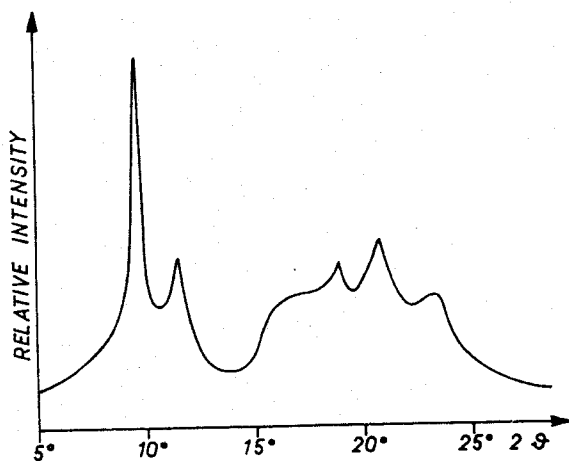


Fig. 1

Fig. 1. X-ray diffraction diagram (CuK α , GEIGER counter) of the crystalline 1:1,2-vinylpyridine: α -stilbazole copolymer

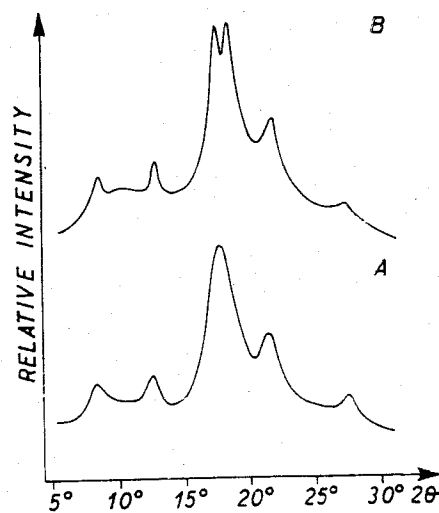


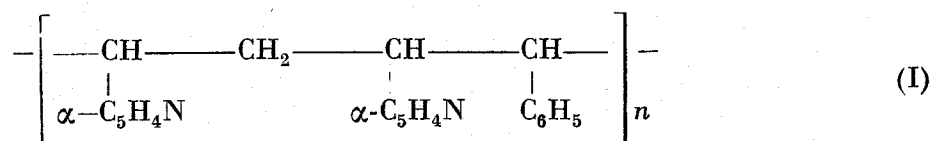
Fig. 2

Fig. 2. X-ray diffraction diagram (CuK α , GEIGER counter) of the two crystalline poly-2-vinylpyridine modifications (A and B)

The crystalline copolymer melts at a very high temperature (about 350°C.) and is insoluble in boiling isopropanol, wherein the crystalline or amorphous 2-vinylpyridine homopolymers and its amorphous, non crystallizable copolymers with α -stilbazole are soluble (*v.i.*). No change in the composition (50 mole-%) of the crude copolymer was observed after annealing and extracting by boiling isopropanol.

Taking into account the inability of α -stilbazole to yield homopolymer (or even dimers) in the presence of anionic catalysts and the 1:1 molar

composition of the crystalline copolymer, it can be inferred that any α -stilbazole monomeric unit has to be essentially preceded and followed by only one 2-vinylpyridine unit. Therefore, the structure of the crystallizable 1:1 vinylpyridine: α -stilbazole copolymer has to be essentially consistent with a regularly alternate repetition (even regular from a steric point of view) of the 2 monomeric units*):

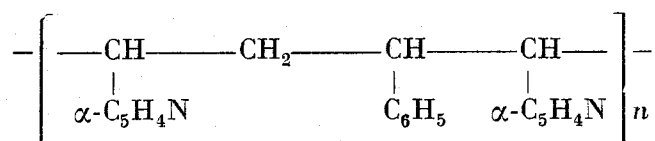


Because of the low molecular weight of this copolymer, no X-ray diffraction spectra from stretched fibers can be obtained, so that no identity period or lattice structure of the crystalline alternating copolymer was determined. However, taking into account that a) the same catalysts which produce the crystalline copolymer can also produce stereoregular polymers when used for homopolymerizing 2-vinylpyridine, b) the crystalline copolymer was found the only stereoregular synthetic polymer known up to now whose repeating unit (I) contains in the main chain 3 tertiary carbon atoms which may assume enantiomorphic configurations, it can be inferred that the crystallinity of the above mentioned copolymer may be due to stereoregularity of the tritactic type.

Moreover, it can be pointed out that 2 of the 3 above mentioned carbon atoms are asymmetric with respect to the chemical structure of the nearer substituents where as the asymmetry of the third carbon atom is only due to the different lengths of the chains connected to it and to the steric configurations of the two former asymmetric carbon atoms. With a suitable asymmetric catalyst, selective formation of peculiar steric configurations for one or both of the above mentioned asymmetric carbon atoms might be expected; the copolymers obtained might therefore show optical activity.

Magnesium metalloamide compounds or lithium and sodium organometallic or metalloamide compounds as catalysts can also be used for copolymerizing 2-vinylpyridine and α -stilbazole. However, though having

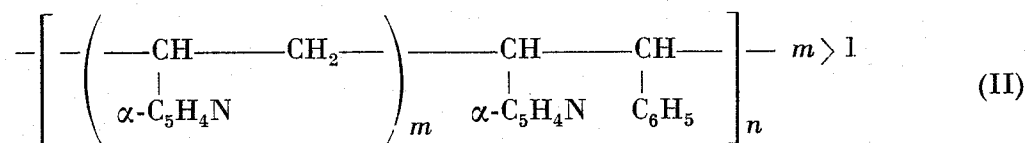
*) Because of the anionic copolymerization mechanism and of the strong electron-attracting character of the pyridine ring, the enchainment:



can be excluded.

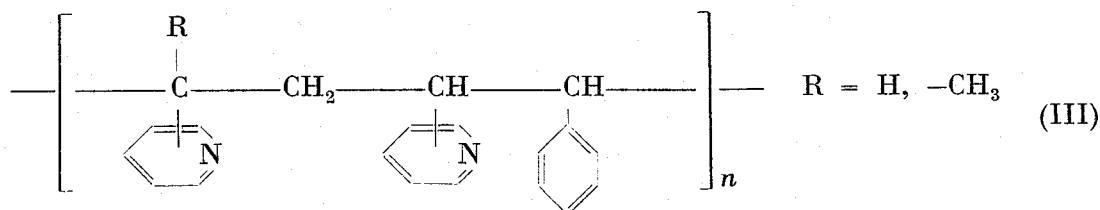
a 1:1 molar composition the copolymers obtained are amorphous, not crystallizable, and quite soluble in boiling isopropanol. Due to the different nature of the catalyst used the macromolecules of these copolymers do not have steric order, although they are essentially consistent with a regular enchainment of the repeating unit (I) along the main chain. Therefore, no crystallization of these copolymers can take place.

On the other hand when the 2-vinylpyridine / α -stilbazole copolymerization is carried out by using any of the above mentioned catalysts and such experimental conditions to allow also the direct enchainment of the 2-vinylpyridine monomeric units (*e.g.*, by keeping high concentrations of this monomer during the copolymerization process), the molar content of α -stilbazole in the copolymers was found much lower than 50%. Although the properties of these copolymers (*e.g.*, lack of crystallinity, solvent-solubility, glass-transition temperature, *etc.*) are similar to those of the amorphous alternating copolymer, their structure should have to be described as follows:



i.e., containing various length sequences of 2-vinylpyridine units.

Amorphous, essentially alternating copolymers have been obtained also by copolymerization of 2-vinylpyridine with γ -stilbazole and of 4-isopropenylpyridine with α -stilbazole in the presence of phenylmagnesium bromide as a catalyst. In these cases, a lack of sufficient stereoregularity along the macromolecular chains having the following structure:



may be attributed both to the peculiar position of the pyridine nitrogen with respect to the polymerizable double bond (*e.g.*, the γ -position, which does not allow the formation of stereoregular homopolymers¹⁾) and to some steric hindrance (such as that of the methyl group).

Experimental

1. Reagents

Phenylmagnesium bromide, 2-vinyl- and 4-vinylpyridine have been prepared and purified according to ¹⁾; α -stilbazole (m.p. = 91 °C.) and γ -stilbazole (m.p. = 133.5 °C.) have been prepared by reacting α - and γ -picoline with benzaldehyde in the presence of anhydrous $ZnCl_2$, according to BAURATH⁵⁾ and FRIEDLÄNDER⁶⁾ respectively.

4-Isopropenylpyridine (b.p.₁₄ = 78–78.5 °C., n_D^{18} = 1.5453) has been obtained by 3 hrs. dehydration of 4-pyridyl dimethylcarbinole at 120 °C. with a 2:1 $CH_3COOH:H_2SO_4$ (vol.) mixture. The carbinole (m.p. = 135 °C.) was prepared by reacting 1 mole of methylisonicotinate with 3 moles of methylmagnesium iodide, according to the procedure described by BACHMAN and MICUCCI⁷⁾ for the preparation of 3-pyridyldimethylcarbinole.

2. Preparation of a Crystalline Alternating 1:1 2-vinylpyridine : α -stilbazole Copolymer

C_6H_5MgBr (1.1 g.), α -stilbazole (15 g.) and anhydrous toluene (150 ml.) are introduced in a 500 ml. capacity three-necked flask, under nitrogen, equipped with mechanical stirrer, dropping funnel and oil-bath at 50 °C. After 15 min. stirring, a 2-vinylpyridine (4 g.) solution in toluene (100 ml.) is regularly added within 6 hrs. Methanol (20 ml.) is then added and the content of the flask is poured in a separatory funnel with water (700 ml.) and *conc.* HCl (50 ml.). After shaking, the toluene layer is removed and *conc.* water-ammonia (200 ml) is added to the aqueous layer.

The white precipitate thus obtained is extracted with chloroform (700 ml.). Most of the chloroform is evaporated and the polymer precipitated by adding hot *n*-heptane (500 ml.). After filtering and drying, 9.5 g. of polymer are obtained; after extracting by boiling *n*-heptane (in order to remove the α -stilbazole monomer) 9 g.

The polymer, previously heated at 330 °C. for 2–4 hrs. at 0.1 mm. Hg pressure, shows a high crystallinity by X-ray examination (CuK α , GEIGER counter, see Fig. 1). In particular, the following BRAGG distances (and related intensities) are observed: 9.42 (strong), 7.73 (medium weak), 4.75 (very weak), 4.30 (medium), 3.77 (medium), 2.93 (weak), and 2.59 (very weak). Analysis of the polymer gives N = 9.55%. The calculated value for the nitrogen content of the pure alternating 2-vinylpyridine/ α -stilbazole copolymer is N = 9.78%. The IR spectrum of the polymer shows a content of 49 mole-% of α -stilbazole. After annealing, only 2% of the crude copolymer is soluble in boiling isopropanol so that the absence of 2-vinylpyridine homopolymers, both crystalline and amorphous, can be inferred.

The crystalline copolymer has a melting temperature of about 350 °C. Number average molecular weight is about 2000. The crystalline copolymer is soluble in methanol, acetic acid and inorganic acids; it is partially soluble in dimethylformamide, aromatic hydrocarbons, chloroform and methylene chloride.

By analogous technique, other copolymerization runs with different monomers such as γ -stilbazole or 4-isopropenylpyridine were carried out.

3. Preparation of an Amorphous Alternating 1:1 2-Vinylpyridine : α -stilbazole Copolymer

The copolymerization run described above was repeated except that 0.24 g. of *n*-butyl lithium was employed as catalyst and only 3 hrs. for the addition of the 2-vinylpyridine solution.

Although the IR spectrum of the polymer obtained (5.8 g) shows a α -stilbazole content of 49.5 mole-%, the X-ray ($\text{CuK}\alpha$) diffraction spectrum does not show any crystallinity.

The glass-transition temperature is about 150°C. and the number average molecular weight 3000.

The copolymer is completely soluble in isopropanol, methanol, acids, dimethylformamide, aromatic hydrocarbons, chloroform, and methylene chloride.

4. Preparation of an Amorphous, non Alternating 2-Vinylpyridine: α -Stilbazole Copolymer

In a copolymerization run the addition of the 2-vinyl pyridine solution was accomplished in 0.5 hrs. The polymer obtained (7.5 g.) does not show any crystallinity from X-ray diffraction. The glass-transition temperature is about 160°C. and the number average molecular weight is 3500.

From the IR spectrum a content of 39 mole-% of α -stilbazole can be calculated; hence the obtained copolymer should be consistent with the structure (II), with $m \simeq 1.6$.

5. Analytical Methods

The composition of the copolymers from the IR spectra was determined by comparing the intensity of the 14.25 μ band (phenyl groups) with the corresponding IR band of samples prepared by mixing definite amounts of polystyrene and polyvinyl- or polypropenylpyridines.

The number average molecular weight was determined cryoscopically in nitrobenzene solutions of the amorphous copolymers.

The melting temperature was determined by a polarized light microscope (heating rate: ca. 1°C./min.). A dilatometric method (heating rate: ca. 0.3°C./min.) was used for estimating approximate values of the glass-transition temperature.

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