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**Optically Active Polymers: The Asymmetric Synthesis
of Polynaphthofurans**

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Optically Active Polymers: The Asymmetric Synthesis of Polynaphthofurans

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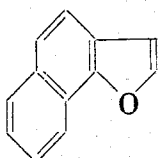
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Introduction

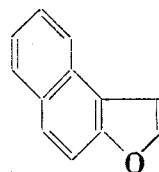
After the results achieved in the study of the asymmetric synthesis of polybenzofuran¹⁻³), we examined the asymmetric polymerization of other unsaturated cyclic ethers. The results obtained in the case of naphthofurans seem worthy to be reported, both owing to the stereospecificity and selectivity of their polymerization process, and to the peculiar properties of the relating polymers.

Like benzofuran, these monomers are not dissymmetric and it is only when the molecule reacts that a sequence of asymmetric carbon atoms forms along the main chain of the polymer¹). We have thus obtained different stereoregular polynaphthofurans, exhibiting both crystallinity and high specific rotatory powers.

The monomers studied are shown below:



naphtho(1':2'-2:3)furan
(α -naphthofuran)



naphtho(2':1'-2:3)furan
(β -naphthofuran)

Their polymerization occurs very easily in the presence of the catalysts acting by cationic mechanism. Among these, particularly suitable are the catalysts used for the stereospecific polymerization of benzofuran and alkenylethers.

The polymerization takes place by addition on the furan double bond, as revealed by the IR spectrum of the polymer, where double bonds derived from the furan ring opening are absent.

Properties of polynaphthofurans

In general, the polymers obtained from unsaturated cyclic ethers do not show any crystallinity, even when they are obtained by the most stereospecific catalyst systems. Until now, our attempts to polymerize benzofuran, dihydrofuran, substituted dihydrofurans, and dihydropyrane have always led to amorphous polymers, which remain amorphous even after annealing. Anyhow, the possibility to obtain optically active poly-benzofuran demonstrates that its structure at least partially must be considered isotactic.

Polynaphthofurans, though always amorphous after precipitation can crystallize by thermal treatment.

Figs. 1 and 2 show the X-ray diffraction spectra respectively of poly- α -naphthofuran and poly- β -naphthofuran, subjected to annealing at high temperatures.

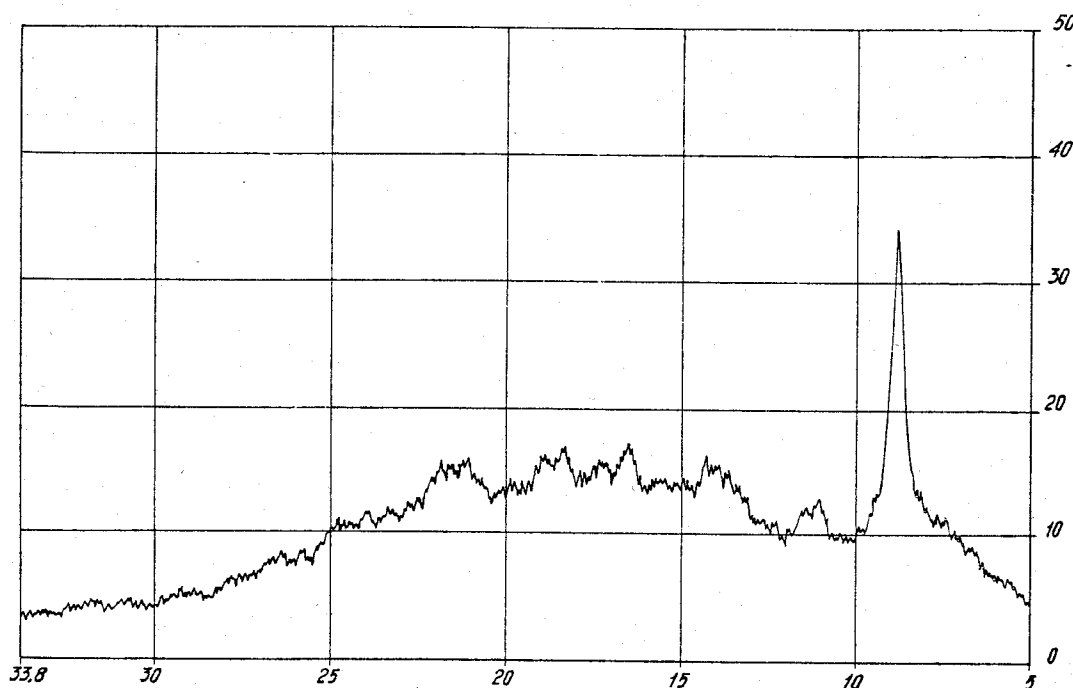


Fig. 1. X-ray spectra recorded with a GEIGER counter of poly- α -naphthofuran

Optically Active Polynaphthofurans

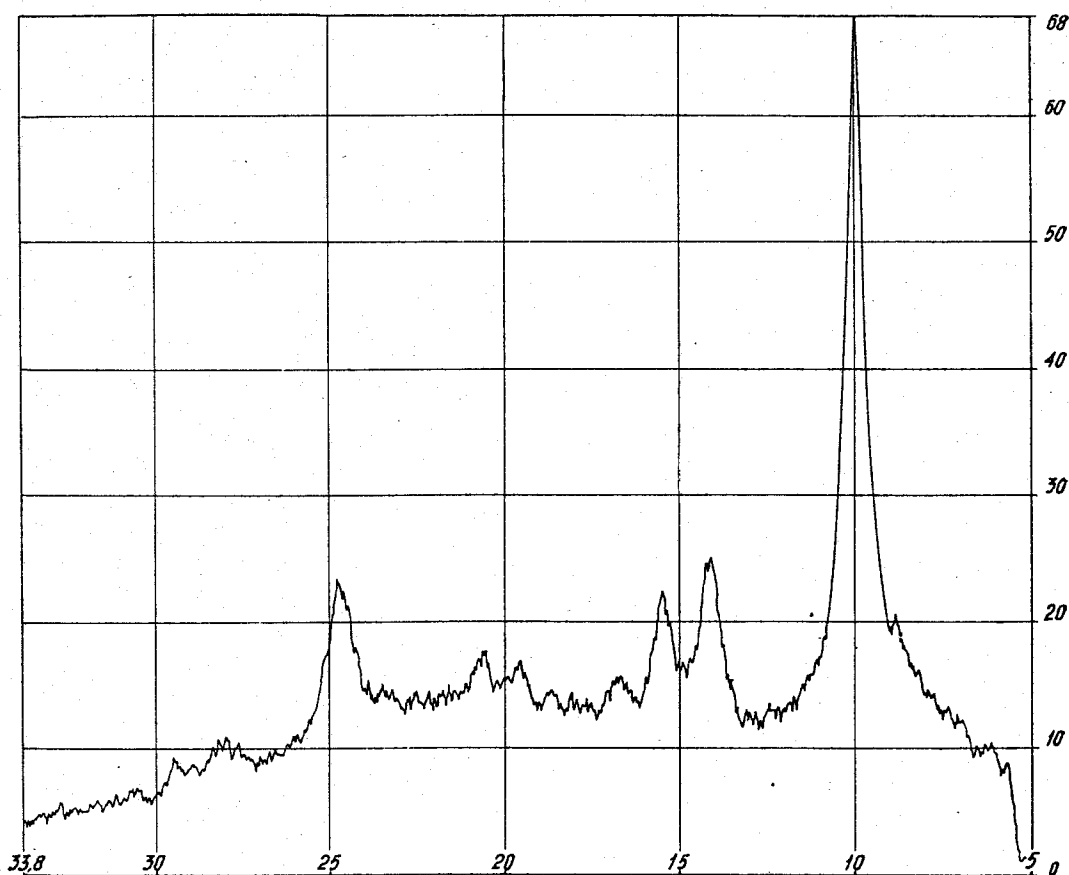


Fig. 2. X-ray spectra recorded with a GEIGER counter of poly- β -naphthofuran

The catalyst systems tested by us, which allowed us to obtain stereoregular polynaphthofurans, comprise aluminum diethyl monochloride, aluminum monoethyl dichloride and the complexes between aluminum chloride or titanium tetrachloride and β -phenylalanine. The polymerizations were carried out in toluene at temperatures not exceeding -70°C .

The thermal treatment leading to the crystallization, which requires temperatures above 250°C . always involves a certain depolymerization. With regard to the polymers obtained by the stereospecific catalyst systems, there is no melting even at temperatures near 400°C ., but only a decomposition, which is more and more rapid with increasing temperature, with formation of pure monomer. As shown by the comparison of the IR spectra, the polymer left as residue, however, is identical with the starting polymer, except for a decrease in molecular weight. With regard to the optically active polynaphthofurans, thermal treatment does not modify to a considerable extent the value of the optical activity. Table I reports the conditions of some polymerizations, the physical properties of the polymers, the temperatures and times used for crystallization. The polymer weight losses on heating vary from 5 % to 30 %.

Poly- β -naphthofurans are markedly insoluble and can be just partially dissolved in chloroform, contrary to poly- α -naphthofurans that are soluble in chlorinated and aromatic solvents. The crystalline polymers become amorphous when dissolved and reprecipitated. However, by subsequent annealing they become crystalline again.

X-ray determination of the structure could not be performed, as it is very difficult to obtain oriented fibres. The films obtained, even from mixtures with other amorphous polymers, are always extremely brittle and do not endure even the slightest stretching.

Optical Activity of Polynaphthofurans

In analogy to benzofuran, the best results in the asymmetric polymerization of α - and β -naphthofuran were obtained by a catalyst system consisting of the complex between aluminum chloride and optically active β -phenylalanine in toluene at low temperatures.

The use of complexes of aluminum chloride with *d*-alanine and *l*-histidine always led to polymers with no rotatory power, both for benzofuran and naphthofurans.

The analysis of the most active catalyst system shows that in solution there exist two complexes of aluminum chloride with β -phenylalanine, having approximately 3 and 2 molecules of halide per molecule of amino-acid respectively. Both of them can be obtained by mixing the components in anhydrous toluene at moderate temperatures, the former in the presence of a high excess of aluminum chloride, and the latter either with equimolecular amounts of the components or in the presence of an excess of β -phenylalanine. Under these conditions, the formation of the complex 1:1 does not occur.

The asymmetric induction due to the two catalytic complexes are in this case nearly equivalent.

As shown in Table 1, the highest rotatory powers have been observed for poly- α -naphthofurans with specific values of (+) or (−) 145°, obtained respectively with (+) or (−)- β -phenylalanine. This figure represents the highest value for the optical activity obtained in the asymmetric polymerization of non-dissymmetric monomers.

The presence of optically active end groups derived from β -phenylalanine can be excluded on the basis of the IR analysis of the polymer and of what already noticed for polybenzofuran^{1,2}.

Optically Active Polynaphthofurans

Table 1. Polymerization of naphthofurans in toluene at -75°C . (Phe = β -phenylalanine)

Monomer	mmole/l.	Catalyst complex	mmol./l.	Condit. for polym.		$[\eta]^*)$ 100 ml./g.	$[\alpha]_D^*)$	Condit. for annealing		$[\alpha]_D^*)$ cryst. polym.
				Time (hrs.)	Yield (%)			Temp. ($^{\circ}\text{C}.$)	Time (min.)	
β -Naphthofuran	200	$\text{AlCl}(\text{C}_2\text{H}_5)_2$	40	15	100	n.d.	—	300	180	—
β -Naphthofuran	30	$2\text{AlCl}_3-(-)\text{Phe}$	5	8	98	n.d.	-41	380	5	n.d.
β -Naphthofuran	150	$\text{TiCl}_4-(-)\text{Phe}$	20	1	100	1.02	-16	300	15	-13
α -Naphthofuran	60	$2\text{AlCl}_3-(-)\text{Phe}$	10	15	100	n.d.	-145	350	3	-110
α -Naphthofuran	50	$2\text{AlCl}_3-(+)\text{Phe}$	12	18	75	0.26	+123	285	60	+110

*) Determinations were done in chloroform at 30°C . for the intrinsic viscosity and at 20°C . for the rotatory power. With regard to poly- β -naphthofurans, only the soluble fractions were examined.

The low solubility of poly- β -naphthofuran did not allow us to evaluate its rotatory power, except for the soluble portions, which probably represent less sterically ordered fractions of the polymer. Therefore, the values are generally low.

The polymers exhibit a very high configurational stability, and even if they are subjected to thermal treatments at about 400°C ., only a partial racemization takes place. This result is quite surprising, especially by considering the high depolymerization rate at this temperature, which in a few minutes can originate a weight loss of about 20 %.

The similarity between the polymerization processes of naphthofurans and of benzofuran already studied by us²⁾ allows us to state that also in this case the asymmetric induction is given to the growing chain in every polymerization stage and is caused by the presence of an asymmetric counterion containing phenylalanine.

Experimental Part

Monomers

β -Naphthofuran was prepared by cyclization of β -naphthoxyacetaldehyde diethyl-acetal^{4,5)}. The product, after steam distillation, melted at $61,5^{\circ}\text{C}$. Its purity was proved by IR spectrum.

The preparation of α -naphthofuran by cyclization of the corresponding α -naphthoxy-acetal did not give appreciable yields; therefore we prepared it from the corresponding coumarine, following a method previously adopted by STOERMER for the production of β -naphthofuran^{4,5)}. The 7,8-benzocoumarine⁶⁾ was converted into its dibromoderivative, and the latter into naphtho(1',2':2,3)furan(5)-carboxylic acid; by decarboxylation α -naphthofuran was obtained.

The product, after distillation on LiAlH_4 , was over 99% pure, as revealed by gas-chromatographic analysis. Its picrate melted at 127–128°C.; this value is in contrast with that reported by STOERMER.

Preparation of the catalyst complex

Aluminum chloride was sublimed under nitrogen and the optically active β -phenylalanine was recrystallized from water and accurately dried in vacuum.

Commercial toluene was first purified according to conventional methods, then dried by chromatography on active alumina. After reflux on sodium-potassium alloy, it was directly distilled in the reaction vessel, where aluminum chloride and β -phenylalanine were subsequently added for the preparation of the catalyst complex. For instance, from AlCl_3 (6.0 mmole), β -phenylalanine (3.3 mmole) and toluene (200 ml.), under stirring for half an hour at 50°C. and for one hour at room temperature in pure nitrogen atmosphere we obtained a solution containing 15 mmole/l. of the complex of approximate composition: $\text{Phe} \cdot 2 \text{AlCl}_3$. This catalytic solution was employed in several polymerization runs.

Polymerization and treatment of the polymer

Polymerizations were carried out according to the methods described in a previous paper for benzofuran²⁾.

The polymer annealing was performed in oven at temperatures ranging from 250 to 350°C. and in pure nitrogen atmosphere.

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³⁾ M. FARINA, G. NATTA, and G. BRESSAN, *J. Polymer Sci. C* **4** (1963) 141.

⁴⁾ R. STOERMER, *Ber. dtsh. chem. Ges.* **30** (1897) 1701.

⁵⁾ R. STOERMER, *Liebigs Ann. Chem.* **312** (1900) 308.

⁶⁾ K. BARTSCH, *Ber. dtsh. chem. Ges.* **36** (1903) 1966.