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Polymers from Cyclic Monomers**

by

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**Asymmetric Synthesis of Optically Active Di-isotactic
Polymers from Cyclic Monomers**

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SUMMARY:

A new asymmetric synthesis of polymers is described; it was obtained from monomers which do not contain asymmetric carbon atoms.

The polymerization, in the presence of asymmetric cationic catalysts, of an unsaturated cyclic compound, benzofuran, by opening of the double bond of the furan ring, led to polymers having high optical activity.

The rotation dispersion curve, which shows a maximum at 303 m μ ($[M] = -800$) is here shown. Each monomeric unit of these polymers contains two carbon atoms in the chain, which are asymmetric, even if considered in their immediate surrounding.

Optically active polybenzofurans do not remarkably contain asymmetric end-groups deriving from the catalyst. The asymmetric synthesis may therefore be related to the orienting effect of the negative asymmetric counter-ion.

ZUSAMMENFASSUNG:

Es wird eine neue asymmetrische Synthese von Polymeren beschrieben, die aus Monomeren ohne asymmetrische C-Atome erhalten werden.

Als ungesättigte cyclische Verbindung konnte Benzofuran durch Öffnung und Polymerisation der Doppelbindung des Furanringes in Gegenwart von asymmetrischen kationischen Katalysatoren in Polymere überführt werden, die eine hohe optische Aktivität besitzen. Die Rotationsdispersionskurve zeigt ein Maximum bei 303 m μ ($[M] = -800$). In diesen Polymeren enthält jede Monomereinheit zwei C-Atome in der Kette, die — auch in unmittelbarer Umgebung betrachtet — asymmetrisch sind.

Die optisch aktiven Polybenzofurane enthalten praktisch keine aus dem Katalysator stammenden asymmetrischen Endgruppen. Die asymmetrische Synthese kann daher auf die orientierende Wirkung des negativ asymmetrischen Gegenions zurückgeführt werden.

Optically active polymers had been prepared in the past, only starting from optically active monomers. Synthetic polymers obtained by this way are, for instance, the optically active polypropylene oxides obtained by PRICE¹⁾ by anionic polymerization of (–) propylene oxide prepared by

¹⁾ C. C. PRICE and M. OSGAN, J. Amer. chem. Soc. 78 (1956) 4787.

biological methods. More recently, PINO obtained optically active isotactic vinyl polymers²⁾ starting from one of the enantiomeric forms of asymmetric monomers (3-methyl-pentene-1; 4-methyl-hexene-1; 5-methyl-heptene-1; 2-methyl-butyl vinyl ether) and observed a remarkable increase of the optical activity in comparison with that of the low-molecular-weight asymmetric compounds having a similar structure. The increase in the optical activity was due to a preferred skew sense of the main chain, induced by the presence of the asymmetric side substituent. Similar results have been obtained by BAILEY³⁾. The preferred direction of spiralization of the main chain of isotactic polymers remains, however, only as long as an asymmetric side group is present; the optical activity disappears when this side group is removed⁴⁾.

Attempts to obtain optically active isotactic polymers having no asymmetric substituents could never lead to positive results⁵⁾. The asymmetry of each tertiary carbon atom of the main chain of an isotactic polymer only depends, in fact, on the different lengths and/or configurations of the chain segments bound to them and on the difference of the end-groups, and is not detectable by optical methods. The different chemical nature of the end-groups can be neglected in high polymers and the configurational differences have no practical effect on the optical activity owing to internal compensation.

Recently, the preparation of optically active copolymers by radicalic copolymerization of optically active monomers like methacrylates and vinyl ethers⁶⁾ with maleic anhydride, has been described. The asymmetric side substituent induces, in this case, a preferred configuration to a limited number of asymmetric carbon atoms in the chain.

On the contrary, no catalytic asymmetric syntheses of high polymers starting from monomers free from sites of optical asymmetry were carried out in the past.

The first asymmetric synthesis of polymers, starting from monomers, which do not show any optical activity (alkyl sorbates), was, as far as

²⁾ P. PINO, G. P. LORENZI, and L. LARDICCI, *Chim. e Ind. [Milano]* **42** (1960) 711; P. PINO and G. P. LORENZI, *J. Amer. chem. Soc.* **82** (1960) 4745; P. PINO, G. P. LORENZI, and S. PREVITERA, *Rend. Acc. Naz. Lincei*, in press.

³⁾ W. J. BAILEY and E. T. YATES, *J. org. Chemistry* **25** (1960) 1800.

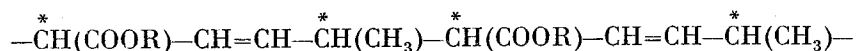
⁴⁾ C. S. MARVEL and C. G. OVERBERGER, *J. Amer. chem. Soc.* **68** (1946) 2106; C. G. OVERBERGER and L. C. PALMER, *J. Amer. chem. Soc.* **78** (1956) 666.

⁵⁾ S. MURAHASHI, S. NOZAKURA, S. TAKEUCHI, *Bull. chem. Soc. Japan* **33** (1960) 658.

⁶⁾ N. BEREDJICK and C. SCHUERCH, *J. Amer. chem. Soc.* **80** (1958) 1933; G. I. SCHMITT and C. SCHUERCH, *J. Polymer Sci.* **45** (1960) 313.

we know performed by us last year⁷⁾. In this case tertiary carbon atoms which are actually asymmetric, even if considered only in their immediate surrounding are present in the main chain.

These results were reached after observing that by polymerization of esters of *trans-trans* sorbic acid: $\text{CH}_3\text{-CH=CH-CH=CH-COOR}$, polymers could be obtained having a regular *trans*-1,4 enchainment, and two asymmetric carbon atoms for each monomeric unit in the chain⁸⁾ as follows:



The structure of these asymmetric atoms is repeated along the chain with a regularity of the *erythro*-di-isotactic type. The obtained polymers have been called "triotactic" (because each monomeric unit shows three sites of stereoisomerism: two optical ones and one geometrical) and more precisely "*erythro*-di-*iso-trans*-tactic"; two optically active antipodes can therefore exist. The asymmetric synthesis was made possible by the use of metallorganic catalysts containing asymmetric organic groups and acting through an anionic mechanism: the thus obtained polymers showed in fact a remarkable optical activity.

The presence in the polymer of asymmetric end-groups deriving from the catalyst could lead one to believe that the optical activity of the obtained polymer could derive from the induction of an asymmetric organic group from the catalyst, chemically attaching itself to the first monomeric unit of the chain, and from the ensuing induction of each monomeric unit on the subsequent one.

Data on the conditions under which monomers of the above type were polymerized, on the catalysts used, which allowed us to obtain values of the optical activity even higher than those given in the prior communication⁷⁾ as well as the crystal structure of such polymers will be published in detail later.

In the meantime, we think it of interest to report here in more detail the results obtained by us in the polymerization of other monomers having cyclic structure which, in the presence of catalysts usually acting by a cationic mechanism, have led to the formation of optically active polymers practically free from end-groups deriving from the catalyst⁹⁾.

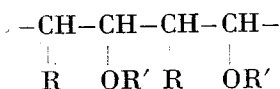
⁷⁾ G. NATTA, M. FARINA, M. DONATI, and M. PERALDO, *Chim. e Ind. [Milano]* **42** (1960) 1363.

⁸⁾ G. NATTA, M. FARINA, P. CORRADINI, M. PERALDO, M. DONATI, and P. GANIS. *Chim. e Ind. [Milano]* **42** (1960) 1361.

⁹⁾ G. NATTA, M. FARINA, M. PERALDO, and G. BRESSAN, *Chim. e Ind. [Milano]* **43** (1961) 161.

The monomers used are of the heterocyclic type and contain an oxygen atom placed in α -position with respect to the double bond. They polymerize with the aid of the same type of catalysts used for the polymerization of alkenyl ethers¹⁰⁾, by processes considered of the cationic type.

In the case of the stereospecific polymerization of non-cyclic alkenyl ethers: CHR=CHOR', one could not expect the formation of optically active polymers, since a highly polymeric chain of the type:

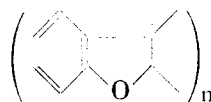


(both *erythro* and *threo*) cannot be distinguished in optical antipodes¹¹⁾. On the contrary, when employing cyclic alkenyl ethers, the same mechanism leads to the formation of enantiomeric chains, containing carbon atoms which are actually asymmetric, as it is possible to observe considering the immediate surrounding of each atom. In fact the two C-C bonds, which link a carbon atom of the main chain to the two neighbouring chain atoms, are not equivalent, since one belongs to a cycle and the other does not.

While one could foresee the possibility that stereoregular isotactic polymers obtained from monomers of cyclic structure would be optically active¹²⁾, this possibility was not demonstrated up to now either by direct synthesis or by resolution of racemic mixtures.

Among the monomers of this type, we have mainly studied benzofuran, which is very suitable for a study of the optical activity also in proximity of the UV absorption bands with the aid of the presently available spectro-polarimeters.

In the polymerization of benzofuran with the aid of (optically inactive) catalysts of the type suitable for the polymerization of alkenyl ethers, for instance aluminum monoethyl dichloride, and under conditions under which cationic polymerizations often take place stereospecifically, e.g. at low temperatures (-80 to -100°C .) we obtained an inactive polymer for which we established the following type of enchainment:



¹⁰⁾ G. NATTA, M. FARINA, M. PERALDO, P. CORRADINI, G. BRESSAN, and P. GANIS, Rend. Acc. Naz. Lincei (8), **23** (1960) 442.

¹¹⁾ G. NATTA, M. FARINA, and M. PERALDO, Makromolekulare Chem. **38** (1960) 13.

¹²⁾ C. L. ARCUS, J. chem. Soc. [London] **1955**, 2801.

In the IR spectrum of the polymer (Fig. 1), in fact, one cannot observe the presence of ethylene double bonds, conjugated or not with the aromatic ring, which could derive from the opening of the furan ring; on

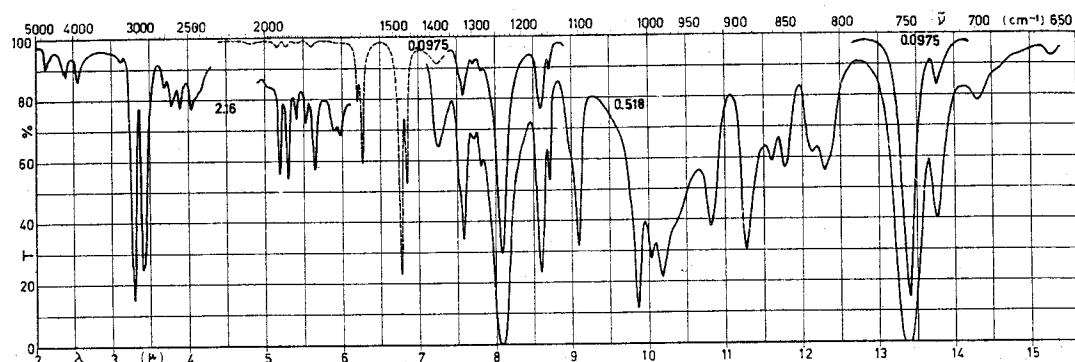


Fig. 1. IR spectrum of a sample of polybenzofuran in solution: full line, in CS_2 27.5 g./l.; dashed line, in CHCl_3 26.8 g./l. (thickness in mm)

the other hand one can observe the presence of saturated CH groups at 3.44μ and of aromatic rings only of the *ortho* disubstituted type, detectable, at 13.39μ , by the characteristic absorption pattern at between 5 and 6μ , and also at 6.25μ .

On the contrary, using catalysts of the mentioned type and obtained by reaction of a metallorganic compound with optically active com-

Table I. Asymmetric polymerization runs of benzofuran in the presence of aluminum monoethyl dichloride

Asymmetric co-catalyst	Polymerization temperature (°C.)	$[\eta]^*$ (100 cm ² /g.)	$[\alpha]_D^{**}$	$[M]_D^{***}$
(-) β -Phenyl alanine	-75	0.6	-33.1	-39.1
(-) β -Phenyl alanine	-75	0.75	-24.1	-28.5
(+) β -Phenyl alanine	-75	0.7	+13.1	+15.5
(+) 10-Camphorsulphonic acid	-75	1.4	-3.8	-4.5
(+) Tetramethylammonium 10-camphorsulphonate	-75	0.5	-2.4	-2.8
(-) Brucine	-100	0.2	+2.8	+3.3

*) determined in toluene at 30 °C.

***) in a benzene solution.

*** referred to the weight of the monomeric unit.

pounds, we obtained polymers showing, even after repeated purification by dissolution and reprecipitation, high optical activity in solution. The optical activity persists with time.

Many asymmetric compounds are able to induce, by reaction or association with the catalyst, the asymmetric polymerization; among these are the amino acids (β -phenyl alanine), sulphonic acids (camphorsulphonic acid), tetrasubstituted ammonium salts (camphorsulphonate of tetramethylammonium, methyl butyl benzyl phenyl ammonium iodide), alkaloids (brucine) etc.

In Table I, data on some asymmetric polymerization runs are reported. Fig. 2 shows the rotatory dispersion curve of a negative polybenzofuran, determined with the aid of a RUDOLPH spectro-polarimeter in dioxane solution, compared with its UV spectrum.

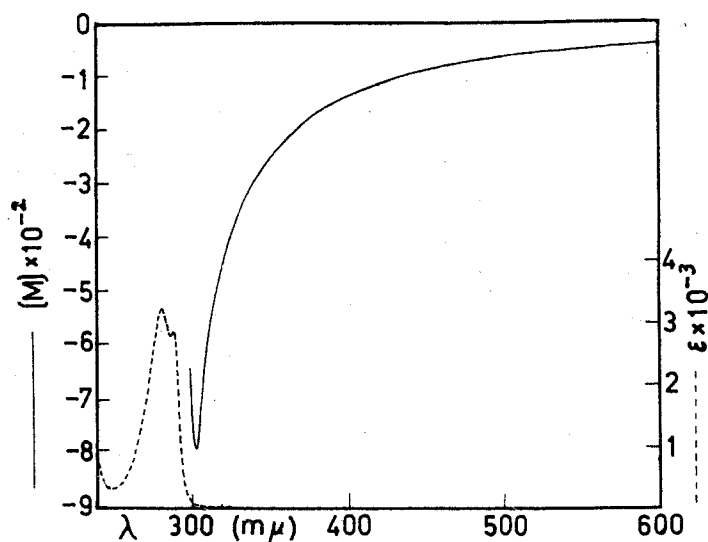


Fig. 2. Rotatory dispersion curve (full line) compared with UV spectrum (in dioxane) of a negative polybenzofuran obtained in the presence of (–) β -phenyl alanine

The optical activity is remarkably higher in the UV, with a rotation maximum ($[M] = -800^\circ$) at 303 $m\mu$, which is clearly attributable to the disubstituted benzenic chromophoric group bound to the asymmetric atoms. Owing to the very high absorption shown by the polymer ($\epsilon > 3.000$), it was impossible to register the dispersion spectrum below 296 $m\mu$. The curve is the one of the first polymer of Table I, obtained in the presence of (–) β -phenyl alanine; a positive symmetric curve, but weaker by 12 times, has been observed for the polymer obtained in the presence of (–) brucine.

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cular-weight substances, in which, generally, in the case of catalytic reactions, considerable optical yields are not observed. From this standpoint, asymmetric polymerization can be compared with enzymatic processes, the only ones which, up to now, have led to high yields in one of the optical antipodes.

We wish to thank Prof. PRATESI, Prof. LAMANNA, and Dr. GHISLANDI of the Pavia University, for permission of using the RUDOLPH spectropolarimeter, and for helpful assistance.

It is interesting to observe that negative polymers have been obtained in the presence of catalysts from both (-) β -phenyl alanine and (+) camphorsulphonic acid, whereas a positive polymer has been obtained in the presence of catalysts from (-) brucine. In the case of camphorsulphonic acid, it has been observed moreover that the catalytic solution shows, before the addition of monomer, a negative optical activity ($[\alpha]_D = -65$ referred to the weight of camphorsulphonic acid).

The polymers here described do not show crystallinity by X-ray examination when observed in the state in which they are obtained after polymerization and coagulation; however it can be assumed that they have a regular head-to-tail enchainment and, at least partially, an isotactic structure. The observed optical activity in fact cannot be connected with syndiotactic head-to-tail structures, since these are internally compensated. The difficulty in crystallizing may be ascribed to the particular structure of the monomeric units which form strongly sterically hindered chains, similarly to what happens in the case of certain polymers, such as those obtained by means of similar catalysts from *cis* alkenyl ethers, and also of polymers of para-substituted styrenes¹³⁾ which were recognized as isotactic.

From radiochemical and spectroscopical analyses one is led to conclude that organic asymmetric groups deriving from the catalyst are absent or present only in a small number of chains also in the obtained benzofuran polymers.

This seems to be confirmed by the IR spectra of polymers obtained with the aid of catalysts deriving from phenyl alanine. It has, in fact, been observed that these polymers have the same IR spectrum as the benzofurans obtained with the aid of catalysts free from phenyls. This holds in particular for the region around 14.35μ , where a strong band of the phenyls falls, which almost coincides with a weak band of the product. Considering the sensitivity and accuracy of the method, particularly in the case that ratio spectra of solutions are taken, it is possible to state that, at most, a phenyl group deriving from the catalyst, may be present per 4,000 monomeric units. Even when employing ³⁵S labelled camphorsulphonic acid, no radioactivity has been observed in the polymer.

These facts lead to the interesting conclusion that the asymmetric synthesis is made possible by the orienting effect of the negative counterion, facing the growing end of the polymeric chain.

The here described asymmetric synthesis of polymers is much more specific than the asymmetric processes known in the field of low-mole-

¹³⁾ G. NATTA and D. SIANESI, Rend. Acc. Naz. Lincei (8) **26** (1959) 418.