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Kurzmitteilung

**Anionic Catalytic Systems for Asymmetric Synthesis
of Polymers**

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Kurzmitteilung

Anionic Catalytic Systems for Asymmetric Synthesis of Polymers¹⁾

By G. NATTA, M. FARINA, and M. DONATI

(Eingegangen am 18. März 1961)

Alkyl esters of sorbic (I) and β -styryl acrylic acids (II), which do not contain asymmetric carbon atoms, have been polymerized to optically active polymers by metal-organic catalysts containing asymmetric alkyl groups. In Table 1, we report some unpublished results obtained in polymerizations initiated by (*R*) 2-methyl-butyllithium*).

Table 1. Asymmetric polymerizations in the presence of (*R*) 2-methyl-butyllithium (from (*S*)(-)-2-methylbutanol) (in toluene at -40°C .)

Monomer	$\alpha_D^*)$	$[\alpha]_D$	$[M]_D^{**})$
Methyl sorbate	-0.70	-7.95	-10.0
Butyl sorbate	+0.36	+3.3	+5.5
Butyl β -styryl acrylate	+0.31	+2.0	+4.6

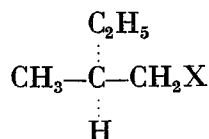
*) in CHCl_3 at 2-4%, $l = 4$ dm.

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

1) Previous papers on the asymmetric synthesis of polymers: a) G. NATTA, M. FARINA, M. DONATI, and M. PERALDO, *Chim. e Ind. [Milano]* **42** (1960) 1363; G. NATTA, M. FARINA, M. PERALDO, and G. BRESSAN, *Chim. e Ind. [Milano]* **43** (1961) 161; G. NATTA, M. FARINA, M. PERALDO, and G. BRESSAN, *Makromolekulare Chem.* **43** (1961) 68.

*) For the absolute configuration of optically active compounds, we use in this Communication the unequivocal nomenclature proposed by R. S. CAHN, C. K. INGOLD, and V. PRELOG, *Experientia [Basel]* **12** (1956) 81, and commonly used by Beilsteins *Handbuch der Organischen Chemie*, IV Ed., Springer Verlag (1958 and seqq.).

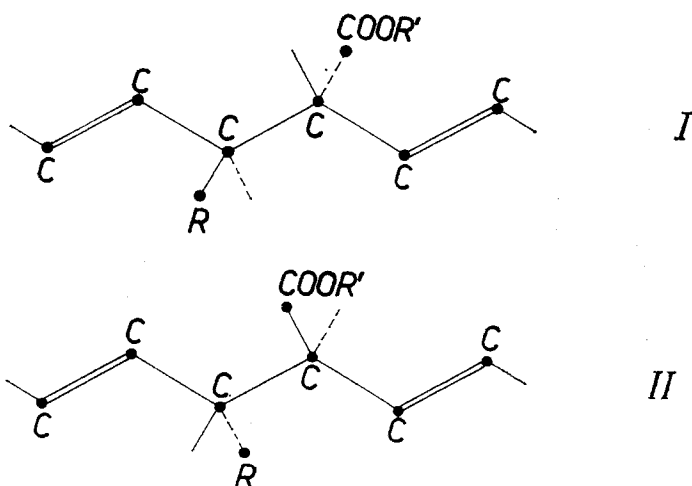
(*R*) 2 methyl-butyl lithium and (*S*) 2 methyl-butanol, like (*S*) 2 methyl-butyl chloride have the following absolute configuration:



(X = Li, OH, Cl)

As previously reported²⁾, the polymers of sorbic and β -styryl acrylic esters are crystalline and have linear head-to-tail 1,4 enchainment with a *trans*-di-isotactic structure; the two lateral substituents of each base unit are in the *erythro* steric position. Asymmetries in the tetrahedral chain atoms are due to the different chemical constitution of the vicinal substituents. Determinations of the intrinsic viscosity carried out in CHCl_3 at 30°C ., gave values ranging from 1 to $3 \cdot 100$ ml./g.

As shown by experiments carried out using ^{14}C labelled butyllithium as initiator, the polymer contains one alkyl group derived from the catalysts per 150–250 monomeric units. The optical activity observed cannot be attributed to the asymmetric alkyl group derived from the catalyst, present as end-group or otherwise bound to the polymeric chain. In fact, the possible contribution of such groups should be from 20 to 100 times lower than the values obtained. The optical activity must, therefore, be attributed to the prevalence in the polymer of one of the two enantiomorphous structures I and II³⁾.



From X-ray examination, it has been established that the main chain of these macromolecules has, in the crystalline state, the same conformation as, and an identity period (4.83 \AA) very near a *trans*-1,4-polybutadiene⁴⁾. Therefore for these asymmetric polymers, one can

²⁾ G. NATTA, M. FARINA, P. CORRADINI, M. PERALDO, M. DONATI, and P. GANIS, *Chim. e Ind. [Milano]* **42** (1960) 1361.

³⁾ According to the nomenclature proposed for the high polymers (M. L. HUGGINS, *J. Polymer Sci.* **8** (1952) 257; *Makromolekulare Chem.* **9** (1953) 195) and to that used for asymmetric compounds (R. S. CAHN, C. K. INGOLD, and V. PRELOG, *Experientia [Basel]* **12** (1956) 81) a polymethyl sorbate corresponding to structure I, will be called: poly (1 (*R*), 4 (*S*), 1-carbomethoxy, 4-methyl, but-2-enamer).

⁴⁾ G. NATTA, P. CORRADINI, L. PORRI, and D. MORERO, *Chim. e Ind. [Milano]* **40** (1958) 362.

not foresee a large conformational contribution to the optical activity due to a preferred screw sense, as observed in the helix-shaped poly- α -olefins, obtained from optically active monomers⁵⁾.

The inactive monomers (I) and (II) have also been polymerized with the aid of optically inactive metal-organic compounds complexed with optically active LEWIS bases, such as (–) menthyl ethyl ether. As revealed by X-ray and IR investigations, the macromolecules thus obtained show a chain structure which is identical to those observed in polymers obtained from non-complexed alkyllithium. The values of $[\eta]$ range from 0,5 to 2·100 ml./g.

Although the bond between the LEWIS base and butyllithium is of the donor type and can be easily dissociated⁶⁾, we find, however, that the asymmetric ether plays an essential role in the polymerization mechanism, and more precisely, it determines the steric configuration of the asymmetric centers in the chain, at least in the initiation step, as proved by the remarkable optical activity observed (Table 2).

Table 2. Asymmetric polymerizations in the presence of butyllithium and (–) menthyl ethyl ether (in toluene at –40 °C.)

Monomer	R ^{*)}	α_D ^{**)}	$[\alpha]_D$	$[M]_D$ ^{***)}
Methyl sorbate	1:1	+0.17	+6.1	+7.7
Methyl sorbate	2:1	+0.27	+6.4	+8.0
Butyl sorbate	1:1	+0.46	+5.3	+8.9
Butyl sorbate	2:1	+0.37	+8.4	+14.1
Butyl β -styryl acrylate	1:1	+0.42	+3.7	+8.5

*) R = menthyl ethyl ether/butyllithium molar ratio.

***) in CHCl_3 at 0.7–3%, $l = 4$ dm.

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

In this case, the presence in the polymer of asymmetric groups coming from the complexing agent should be reasonably excluded. In fact, we have found that secondary reactions between the metal-organic compound and the ether are negligible under the temperature conditions and with the concentrations which we have employed. The remarkable optical activity is therefore due *only* to the asymmetric carbon atoms obtained from the inactive monomer.

⁵⁾ P. PINO and G. P. LORENZI, J. Amer. chem. Soc. **82** (1960) 4745.

⁶⁾ F. J. WELCH, J. Amer. chem. Soc. **82** (1960) 6000, indirectly determined a constant of dissociation of some complexes between butyllithium and LEWIS bases.

G. NATTA, M. FARINA, and M. DONATI

In view of the information which can be derived regarding the mechanisms of both stereospecific and asymmetric polymerizations, the two different methods for the preparation of optically active polymers are being the subject of further study.

Acknowledgments

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