for k_{-1} one can calculate the acidity constant K_{HA} for the reaction $\mathrm{CH_3SOCH_3} \rightleftarrows \mathrm{H^+} + \mathrm{CH_3SOCH_2^-}$, since $K_{\mathrm{HA}} = (k_1/k_{-1})(K_{\mathrm{w}}/[\mathrm{H_2O}])$, where K_{w} is the ion product of water.[1] This places the pK_{HA} of DMSO between 32 and 33, in close agreement with the revised value of 32.9 obtained by Steiner, *et al.*, from indicator measurements.[5,11]

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A New Kind of Asymmetric Synthesis. The Radiation Polymerization of *trans*-1,3-Pentadiene Included in Optically Active Perhydrotriphenylene

Sir:

We wish to describe a novel example of an asymmetric synthesis in which a prochiral diene monomer, included in the crystal lattice of a chiral host compound, forms an optically active polymer on γ-ray irradiation.

We have been studying for some years the stereochemical properties of *trans,anti,trans,anti,trans*-perhydrotriphenylene (PHTP, I)[1] and its inclusion compounds with several substances having linear structure and in particular with macromolecular substances.[2] By γ irradiation of PHTP inclusion compounds with different unsaturated monomers, it is possible to obtain the corresponding high molecular weight polymers. By this method we obtained the first synthesis of an isotactic polymer in the solid state, *trans*-1,4-polypentadiene, using *trans*-1,3-pentadiene as guest monomer.[3]

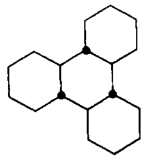
In spite of the high symmetry, PHTP does not possess any alternating axis (point group D_3) and has been recently resolved into optical antipodes.[4] Optically active PHTP forms inclusion compounds which are very similar to those of racemic PHTP: the size of the unit cell and, to a first approximation, the projection of the atoms on the *xy* plane are identical; the space group is $P6_3$, that of the racemic compound is $P6_3/m$. On principle, the channels that exist in the crystal lattice should be influenced by the lower symmetry, although an approximate examination of the channel walls shows that the differences should be rather small (<0.1 A). However, such an asymmetry is real, as we demonstrate by the asymmetric polymerization described here.

The structural properties required for the monomers to give optically active polymers were described in other papers;[5] they fully occur in *trans*-1,3 pentadiene, which had already been polymerized in an isotactic way in racemic PHTP.

A sealed vial containing 1.2 g of (−)(*R*)-PHTP (I) ($[\alpha]^{25}_{\mathrm{D}}$ −93°) and 0.4 g of *trans*-1,3 pentadiene (II) was irradiated by γ rays for 3 hr with a dose rate of 1×10^{18} ev/g min by a ^{60}Co source. After irradiation, the vial content consists of an inclusion compound of the polymer in PHTP, as revealed by the high melting point (≃190°). An analogous increase of melting point during the polymerization had already been observed for racemic PHTP.[3] After boiling acetone extraction, we obtained 64 mg of solid polymer having an infrared spectrum identical with that of isotactic *trans*-1,4-polypentadiene (III) obtained by coordination polymerization.[6] The nmr spectrum reveals a very high chemical and steric purity.

The polymer shows an unambiguous optical activity of sign opposite to that of PHTP: $[\alpha]^{25}_{\mathrm{D}}$ +2.5 ±0.3° ($\mathrm{CHCl_3}$) (Perkin-Elmer 141 polarimeter). At shorter wavelengths the rotatory power increases considerably: $[\alpha]^{25}_{436}$ +6.4°, $[\alpha]^{25}_{365}$ +9.8°.

As a checking run, pentadiene was polymerized in the presence of (+)(*S*)-PHTP with low optical purity ($[\alpha]^{25}_{\mathrm{D}}$ +35°). The polymer obtained shows a negative rotation, slightly higher than the sensitivity limit of the polarimeter.



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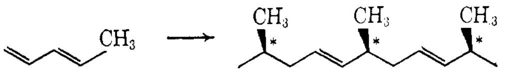

II III

Our experiments show that optical activity may be induced in simple chemical systems under rather primitive and scarcely selective conditions, like the use of ionizing radiations and the absence of complex reagents or catalysts. We are presently investigating whether the polymerization starts from asymmetric radicals or ions obtained by irradiation of PHTP, or it exclusively involves the guest molecules. In the latter hypothesis this reaction sharply differs from the other asymmetric syntheses known so far;[7] actually only weak van der Waals forces are responsible for the geometric arrangement that favors one of the sequences (*e.g.*, DDD...) with respect to the other.

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