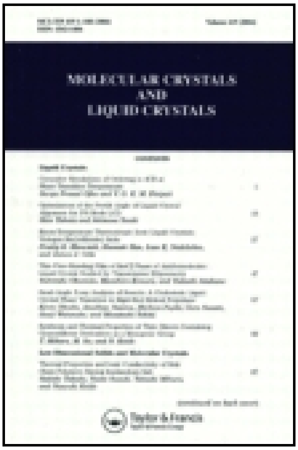

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Synthesis of Chiral Polymers by Reactions in Chiral Crystal Structures[1]

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Synthesis of Chiral Polymers by Reactions in Chiral Crystal Structures[1]

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In recent years there has been a growing interest in asymmetric synthesis via topochemically-controlled reactions in chiral crystals.[2] In such reactions the sole chiral influence derives from the asymmetric environment of the molecules in the crystal.

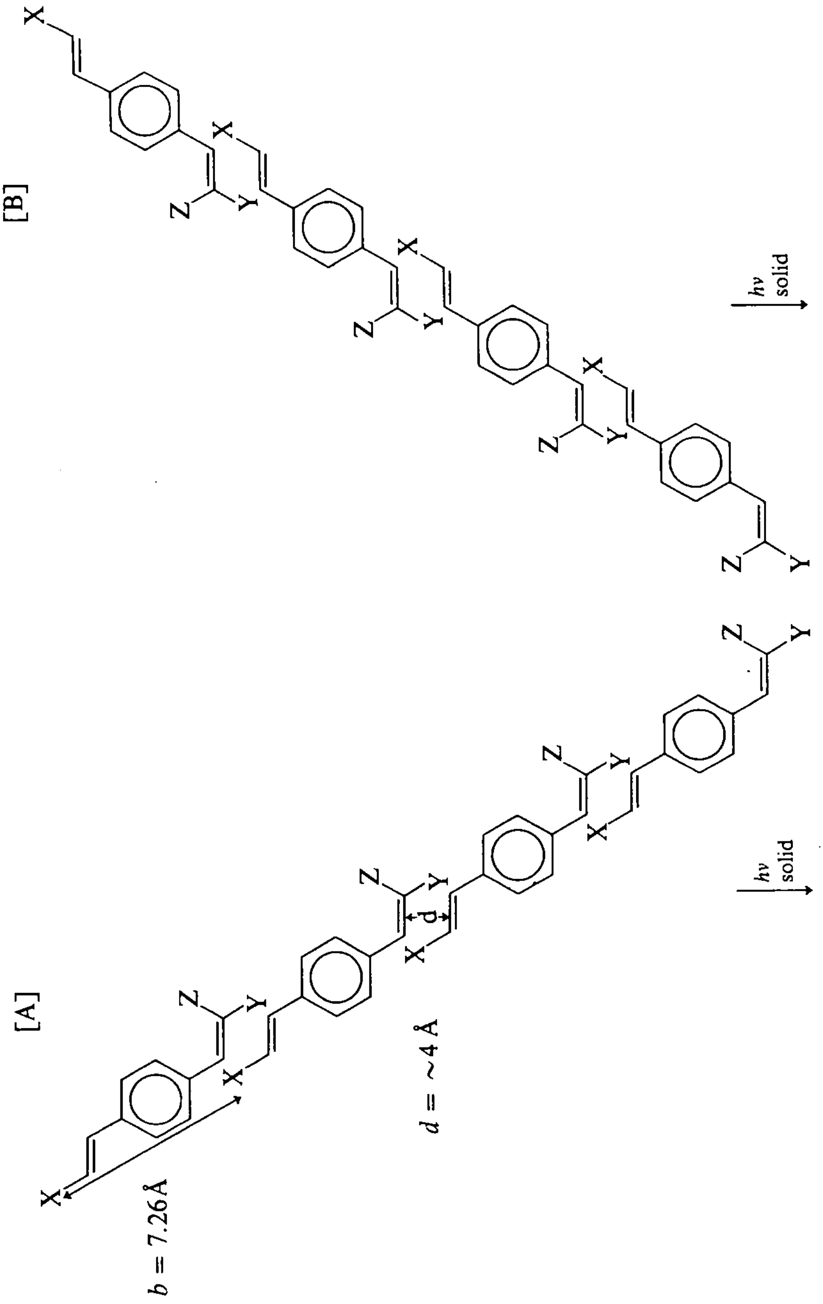
We want here to report the first successful asymmetric synthesis of chiral dimers and polymers in a one-component system, by (2 + 2) photocyclisation reaction, and the first asymmetric synthesis by reaction in a crystal of racemic composition.

We have prepared a number of unsymmetrically substituted divinyl-monomers, similar to the symmetric ones studied by Hasegawa's group, which are known to undergo lattice controlled photo-polycondensation.[3] A chiral handle was introduced in the monomer, in order to favour crystallisation in asymmetric structures.

Many of these monomers, on irradiation in the solid, give polymeric products, the relative yields of dimer, low M.W. polymer and high M.W. polymer depending on the wavelength of the exciting light. Thus far we have investigated one of these systems, (**1**), in some detail. In Figure 1 we show schematically the assumed monomer stacking and the nature of the overall reaction in two enantiomeric crystals (A) and (B).

Optically pure monomer (**1**) crystallises in a chiral space group P1 $a = 13.66$, $b = 7.26$, $c = 5.38$ Å; $\alpha = 104°$, $\beta = 95.5°$, $\gamma = 92°$, $Z = 1$; following irradiation and isolation of the products, both dimer and low M.W. polymers gave unambiguous optical rotations, of sign opposite to that of the monomer. Furthermore, replacement of the chiral sec.-butyl group of the dimer by methyls enhances the optical activity. (See Figure 2).

Racemic (**1**) crystallised too in the same chiral space group P1, $a = 13.49$, $b = 6.89$, $c = 5.28$ Å, $\alpha = 104°$, $\beta = 93°$, $\gamma = 92°$, $Z = 1$. From the cell


[A]
[B]
X
Y
Z
b = 7.26 Å
d
d = ~4 Å
hv
solid

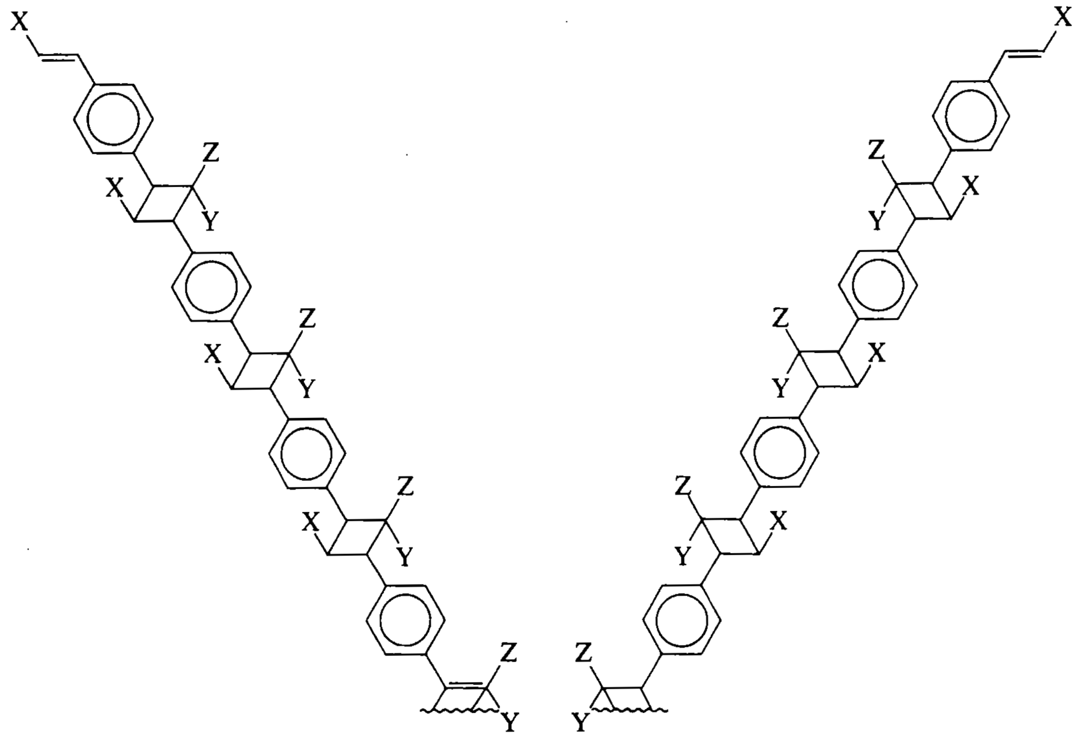
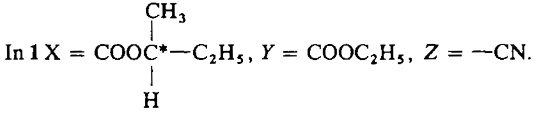


FIGURE 1 Schematic representation of the stack structures and polymerisation reactions in enantiomeric crystals [A and B] such as those of **1**.



$$\text{In } \mathbf{1}\ X = \mathrm{COO}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^*}}\text{—}C_2H_5,\ Y = COOC_2H_5,\ Z = \text{—}CN.$$

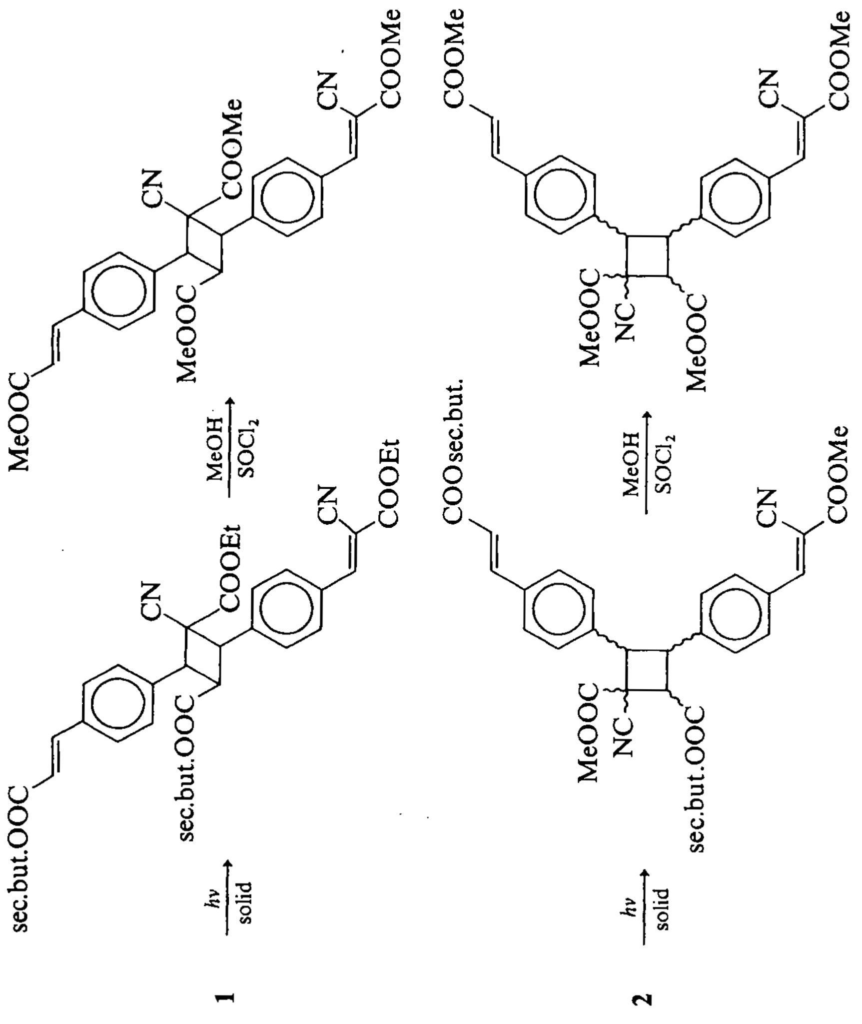
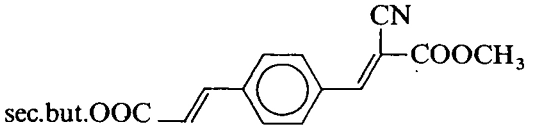


FIGURE 2 Structure of dimers of **1** and **2** and of the transmethylated compounds.

dimensions and X-ray diffraction intensities, similar but not identical to those of the pure chiral (**1**), and from D.S.C. analysis, it has been concluded that the racemate forms a solid solution of the two enantiomers, disordered with respect to the chiral sec.-butyl group.[4] In the racemate therefore, every enantiomeric single crystal of kind (A) or (B) of Figure 1 contains an equal number of *X*'s of opposite chiralities. The probability of crystallising in each of the two enantiomeric structures is the same. A large crystal of this solid solution, grown from the melt, part of which was shown to be optically inactive when dissolved, yielded on irradiation optically active dimers and low M.W. polymers.

The case opposite to that of (**1**) is represented by monomer (**2**). The racemate of (**2**) crystallises in the racemic space group $P2_1/a$, with $a = 9.67$, $b = 25.73$, $c = 8.15$ Å; $\beta = 123°$, $Z = 4$. Optically pure (**2**) is dimorphic: one of its two crystal structures is isomorphous with that of racemic composition, crystallising in space group $P2_1$, pseudo $P2_1/a$. Irradiation of optically pure monomer (**2**) in this structure gave chiral dimers and polymers which, after transmethylation, proved to be optically inactive, in the limits of instrumental error, as expected on the basis of the symmetrical structure of the monomer crystal.



(**2**)

These facts show unambiguously that the asymmetric induction is due to the influence of the chiral environment of the reaction site, and not to the influence of the chiral handle, and that in principle we can get by this kind of polymerisation optically active polymers from any achiral monomer, provided it crystallises in an asymmetric structure, and with correct contacts.

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3. F. Nakanishi and H. Hasegawa, *J. Pol. Sci. A-1*, **8**, 2151 (1970), and references therein.
4. This is one of several cases in which we found disorder in the crsytal involving enantiomeric sec. butyl groups (M. Lahav, F. Laub, L. Leiserowitz, and L. Roitman, unpublished results).