Structure and solid state photopolymerization of pentaerythritol tetracinnamate

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Pentaerythritol tetracinnamate (PTC) was obtained in several different crystalline forms, and its solid state photopolymerization induced by u.v. irradiation, was carried out under two different experimental conditions. The structure of one crystalline form (α-PTC), the X-ray diffraction pattern of the photopolymerization product and the i.r. spectra before, during and after the u.v. irradiation are given as experimental evidence for a possible two-step mechanism of the photoreaction. This mechanism implies that the crystal structure of the monomer controls topochemically the reaction at least in its first step.

INTRODUCTION

It is well known that cinnamic acid and its derivatives undergo solid state dimerization under the action of u.v. radiation. Recently it was shown[1] that derivatives of cinnamic acid containing two double bonds per molecule can photopolymerize in the solid state giving linear high polymers with a regular structure. On the basis of these results and in the context of a research program aimed at defining the possibilities of formation of two- and three-dimensionally ordered polymers, we thought it worthwhile to prepare a polyfunctional derivative of cinnamic acid and to study its solid state polymerization. Pentaerythritol tetracinnamate was chosen as a suitable monomer, in view of the fact that its molecule could have a high symmetry.

EXPERIMENTAL AND RESULTS

Preparation of the monomer

Pentaerythritol tetracinnamate (PTC) C(CH₂OCOCH CHC₆H₅)₄ was obtained by heating an intimate mixture of pentaerythritol (1 mol) with molten cinnamoil chloride (5 mol) at ~120°C.

Heating was continued until no more hydrogen chloride was evolved. In typical preparations, the reaction product was triturated under cold ethanol, in order to eliminate the excess cinnamoil chloride, and then recrystallized from the same solvent: m.p. 126°C. Analysis found for $C_{41}H_{36}O_8$: C 75.03%, H 5.41% (calculated: C 75.00%, H 5.49%).

The i.r. spectrum of PTC (KBr pellet) is shown in *Figure 1*. The u.v. spectrum of PTC (in an ethanol solution) shows a λ_{max} at ~275 mm.

X-ray data on pentaerythritol tetracinnamate and determination of its crystal structure

PTC shows several different crystalline forms depending on the crystallization solvent. The X-ray diffraction patterns of three of these forms (α, β, and γ) are given in *Figure 2*.

Single crystals of the α-form, suitable for X-ray structural analysis, were prepared by slowly evaporating a solu-

tion of PTC in a 1:1 v/v acetone–toluene mixture. The crystal data are: $a = 21.15(2)$, $b = 16.90(2)$, $c = 5.75(1)$ Å, $\alpha = 102°55'$ (6'), $\beta = 89°19'$ (6'), $\gamma = 99°51'$ (6'), $Z = 2$, space group $P\bar{1}$.

The X-ray intensities were measured with a G.E. XRD6 diffractometer using Zr filtered MoKα radiation.

The structure was determined by application of a symbolic addition procedure and refined by anisotropic least squares down to a value of 0.12 for the conventional R index calculated on the basis of the 2581 observed reflections.

The atomic coordinates, bond distances and angles in the molecule have already been published[2] but no details of the molecular packing have yet been reported. *Figure 3* will be referred to in the discussion on the topochemically relevant features of this crystal structure.

Photopolymerization experiments

Two types of photopolymerization experiments were performed on PTC.

In order to check the photopolymerizability of the various crystalline forms of PTC, a few milligrams of the monomer in a KBr pellet were irradiated with a 500 W high pressure mercury lamp. The polymerization was followed by i.r. analysis. In all the examined samples a marked reduction was observed in the intensities of the peaks at ~1630 cm⁻¹ ($\nu_{C=C}$ aliphatic) and at ~980 cm⁻¹ (ν_{C-H}, trans H–C=C–H) which are well developed in the monomer spectrum (*Figure 1*). In *Figure 4* the variation of the i.r. spectrum in the range 1550–1850 cm⁻¹ as a function of the irradiation time is reported. Inspection of
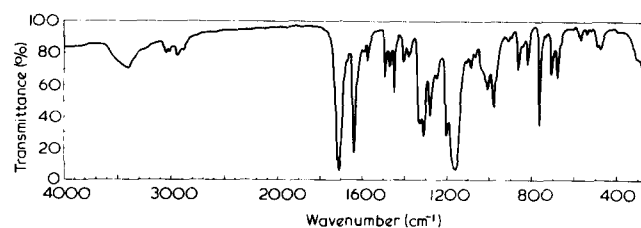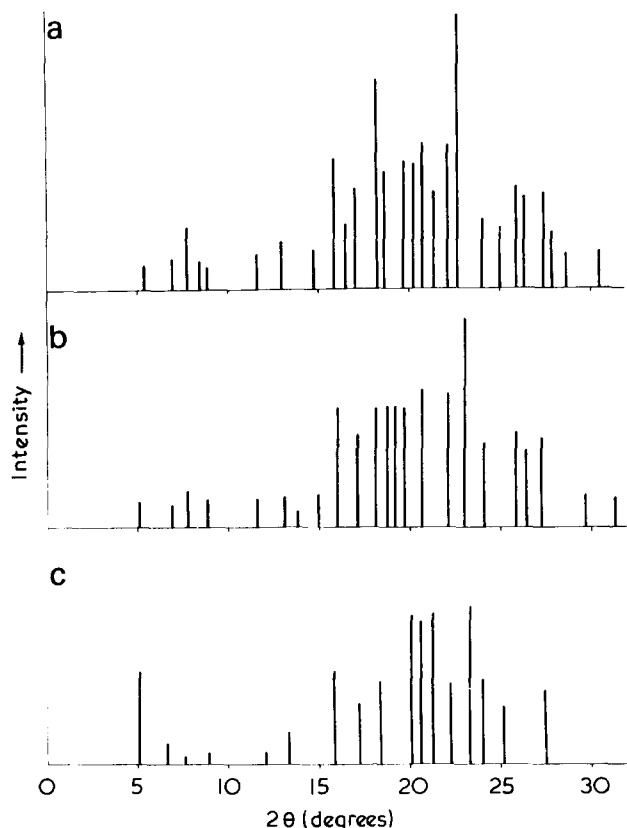

Figure 1 Infra-red spectrum of α-PTC

Figure 2 Schematic X-ray diffraction powder patterns of (a) α-PTC; (b) β-PTC; (c) γ-PTC

Figure 4 also shows that a shift of the 1710 cm^{-1} peak ($\nu_{C=O}$) to higher frequencies occurs simultaneously, which may be related to the transition from a conjugated structure to an unconjugated one. After u.v. irradiation all the samples gave the i.r. spectrum shown in *Figure 5*, thus proving that they give essentially the same photopolymerization product.

Further photopolymerization experiments were performed by irradiating a 2% w/v suspension of finely ground PTC in ethyl alcohol or n-heptane at temperatures ranging from −72° to +25°C with a 500 W mercury lamp. Similar experiments were performed by irradiating thin layers of finely powdered PTC in air or nitrogen.

In all cases, irrespective of the crystalline form of the starting monomer, a yellowish product was obtained in 5—35% yields, depending on the irradiation time. The product was insoluble in all the common solvents and was easily purified by extracting it with boiling toluene in a Soxhlet apparatus. By heating the product up to 320°C on a Kofler hot-stage apparatus no softening or melting was observed. The i.r. spectrum of the product (KBr pellet) was identical to the one shown in *Figure 5*. No evidence of crystallinity was found in the product by conventional X-ray diffraction methods.

DISCUSSION

As shown in *Figure 3*, in a crystal of α-PTC three of the four non-equivalent intermolecular distances between double bonds are 3.78, 4.79, and 8.14 Å, while the fourth distance is 5.75 Å, corresponding to the repeat distance along the c-axis of the triclinic unit cell. The two shortest distances are the ones between the double bonds facing

each other through the symmetry centres at (½ ½ 0) (the 3.78 Å distance) and (0 ½ ½) (the 4.79 Å distance). The value of 3.78 Å is well within the range estimated[3] for the occurrence of solid state photodimerization of cinnamic acid derivatives. The value of 4.79 Å, although slightly outside this range, must still be considered propitious for the cycloaddition reaction. In fact the actual conformation of the molecular branch near the inversion centre at (0 ½ ½) is such as to allow the approach of the two double bonds, whose π-orbitals are favourably oriented for the cycle formation. Therefore it is highly probable that the first step in the solid state photopolymerization of α-PTC is the cycloaddition of the double bonds about the inversion centres at (½ ½ 0) and (0 ½ ½) with the formation of polymeric regularly branched linear chains running parallel to the a-axis of the monomer unit cell.

However, the i.r. analysis of the photopolymerization products indicates (see above) that the olefinic character is strongly reduced after u.v. irradiation, and this implies that *all* the double bonds eventually participate in the cycloaddition reaction, and that, after the first step, the photoreaction continues by involving the other double bonds (two per monomeric unit) still present in the side branches of the linear macromolecules.

This assumption also corroborates with the above mentioned experimental observations of the absence of a melting point and of the insolubility of the polymerization product; these facts could not be easily explained if the final product of the photoreaction were a linear polymer.

It is conceivable that the structural rearrangements following the first step of the photochemical reaction may lead to a random shortening of the distances between pairs of double bonds along the c-axis of the monomer unit cell, thus allowing a second step of cycloaddition reactions with the formation of irregular polymeric bidimensional sheets approximately parallel to the ac-crystallographic plane of α-PTC.

However the formation of irregular blocks based on three-dimensional networks cannot be excluded on the basis of the available evidence, especially if one considered the possibility of local premelting phenomena leading to random conformations of the side branches of the initially formed linear macromolecules. The aggregation of these irregular sheets or three-dimensionally structured blocks must produce an amorphous material. In fact no evidence of crystal-
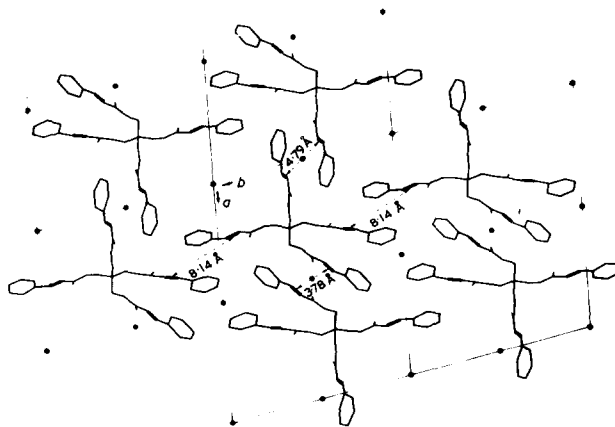

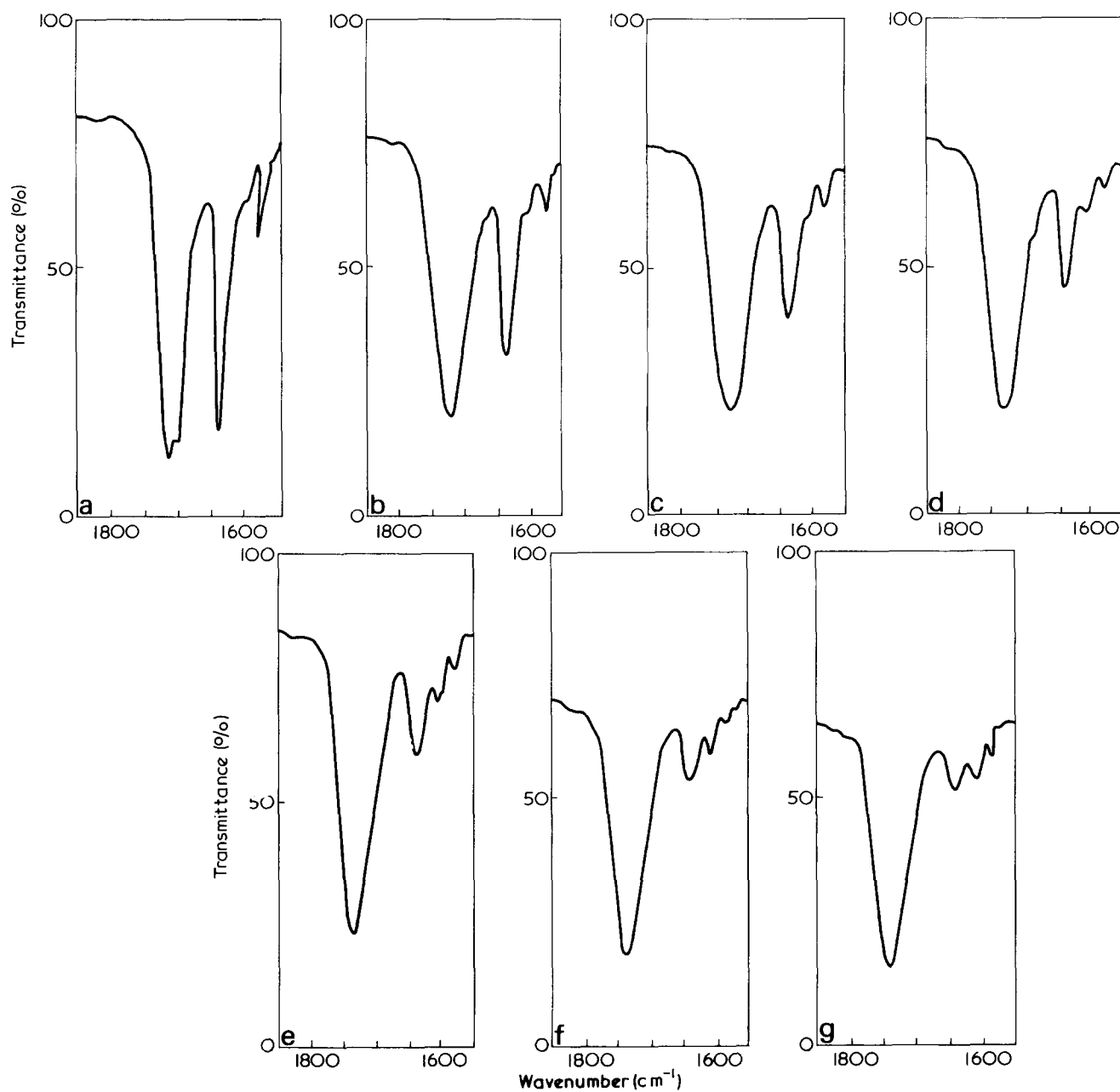*Figure 3* Triclinic projection of the structure of α-PTC onto the ab-plane

Figure 4 Time sequence of the i.r. spectra of one of the PTC samples during photopolymerization under the action of u.v. radiation. Only portions of the recorded spectra are given. Irradiation time: (a) 0 min; (b) 30 min; (c) 60 min; (d) 120 min; (e) 240 min; (f) 420 min; (g) 660 min
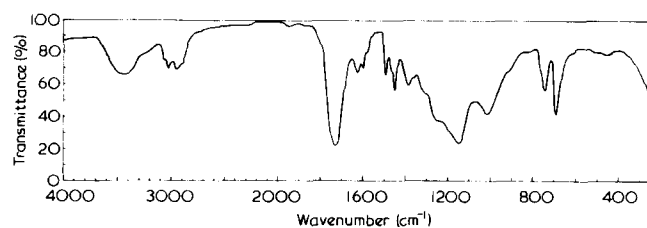

Figure 5 Infra-red spectrum of the photopolymerization product

linity (see above) was found in the X-ray diffraction pattern of the final photopolymerization product.

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