Stereospecific Polymerisation of Diethyl (*Z,Z*)-Hexa-2,4-dienedioate in the Crystalline State

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On exposure to UV light a crystal of diethyl (*Z,Z*)-hexa-2,4-dienedioate yielded an ultra-high molecular mass, highly stereoregular polymer, which was shown to have a tritactic structure by ^{13}C NMR spectroscopy.

The importance of chemical reactions in molecular crystals has been recognised by many organic chemists,[1,2] although most organic reactions are carried out in the liquid- or gaseous-state. A topochemcial reaction yields products whose structure is controlled by the crystal lattice of the reactant.[3] Only two kinds of polymers with a highly controlled structure (high stereoregularity and high crystallinity) have been prepared by topochemical polymerisation, *i.e.*, polymers from 2,5-distyrylpyrazine and its analogous diolefinic crystals,[4,5] and those from diacethylenic derivatives.[6] The former polymerisations proceed *via* stepwise [2 + 2]topochemical photopolymerisation and the latter gives a 1,4-polymer by a chain-reaction mechanism.

Recently we discovered that crystals of diethyl *cis,cis*-muconate [diethyl (*Z,Z*)-hexa-2,4-dienedioate] **1** yield a crystalline polymer with a highly regulated stereochemical structure on irradiation with UV light (Scheme 1), although stereoregular diolefinic polymers have always been obtained with transition metal initiator systems.[7] Here, we deal with a novel stereospecific polymerisation, which we believe is the first example of topochemical 1,4-polymerisation of 1,3-diene derivatives.

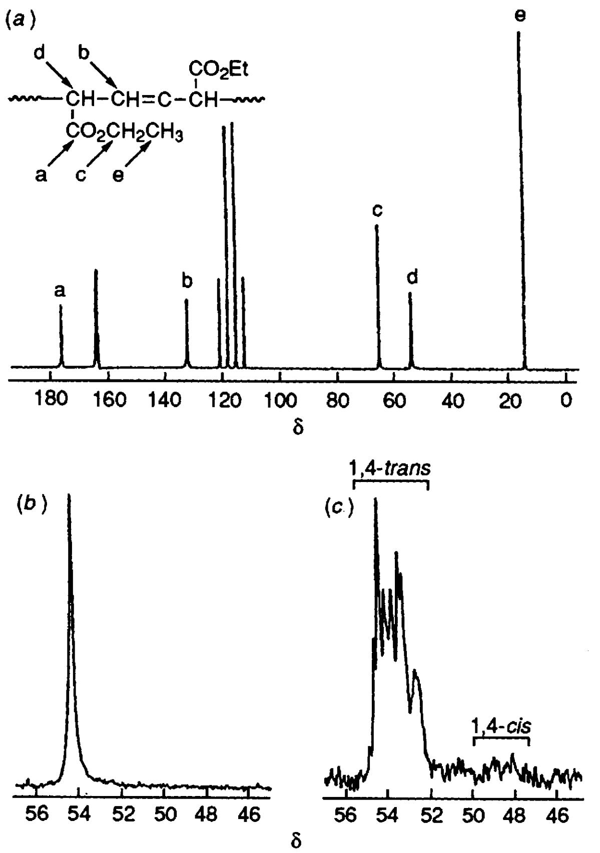


Fig. 1 ^{13}C NMR spectrum of the polymer produced from crystalline **1** under photoirradiation (*a*) and the expanded spectrum (*b*). The spectrum (*c*) is of the polymer prepared by radical polymerisation in the melt at 70 °C. [$^2H_1$]Trifluoroacetic acid solvent. Ambient temperature.

Monomer **1** was prepared by conventional methods, *i.e.*, the reaction of *cis,cis*-muconic acid and diethyl sulfate in the presence of potassium carbonate in acetone at room temperature or by esterification of the acid in ethanol with a catalytic amount of sulfuric acid under reflux. Colourless needles were obtained by recrystallisation from methanol or hexane; mp 53–54 °C. In repeated recrystallisations part of the crystal became insoluble when stored in a desiccator for one day. The colourless solid obtained was insoluble in common organic solvents except trifluoroacetic acid and 1,1,1,3,3,3-hexafluoropropan-2-ol. Based on viscosity measurements in trifluoroacetic acid at 30 °C, the intrinsic viscosity ([η]) of this material was found to be 185 cm^3 g^{-1}, indicative of a high molecular mass polymer. We hence studied the polymerisation of **1** in the crystalline state to clarify the polymerisation mechanism and the structure of the resulting polymer.

The results of the polymerisation of crystalline **1** under various irradiation conditions are shown in Table 1. When crystalline **1** was irradiated with a high-pressure mercury lamp at 0 °C for 4 h, the polymer was produced in 46.5% yield, but no reaction occurred in the dark. With direct sunlight, a yield of 71.4% was achieved with 4 h irradiation. Light at *ca.* 300 nm effected the polymerisation as shown by experiments with irradiation through filters. This polymerisation proceeds irrespective of the atmosphere, *i.e.*, *in vacuo*, in air, or even under water, as long as the crystal was exposed to UV light. **1** did not polymerise in solution, *e.g.*, in methanol, hexane, or toluene. The reaction was unique for the diethyl ester with the *cis,cis*-configuration; diethyl esters with *cis,trans*- and *trans,trans*-configurations, and the methyl or cyclohexyl esters did not polymerise under similar conditions. The non-formation of the dimer and/or oligomers during the polymerisation supports the belief that the polymerisation proceeds *via* a chain reaction. The polymers obtained are of ultra-high molecular mass, estimated from [η] as high as 10^3 cm^3 g^{-1} (Huggins constant 0.56–0.65).

The polymer obtained was shown to be crystalline from

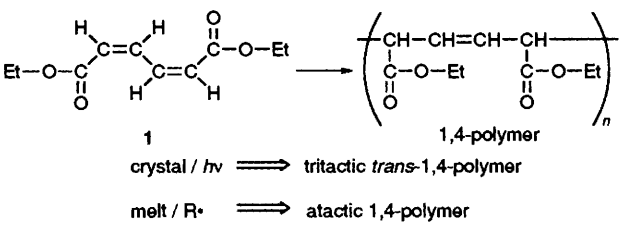
Table 1 Polymerisation of the crystal of **1** under photoirradiation

Light source	Atmosphere	*T*/°C	*t*	Yield/ (%)	[η]^a/ cm^3 g^{-1}
Hg lamp	In degassed Pyrex tube	0	4 h	46.5	939
Hg lamp	In unsealed Pyrex tube	0	4 h	20.3	—
Hg lamp (>280 nm)	In degassed Pyrex tube	0	4h	41.6	—
Hg lamp (>360 nm)	In degassed Pyrex tube	0	4h	10.5	—
Hg lamp (>390 nm)	In degassed Pyrex tube	0	4h	1.3	—
Sunlight	In air	room temp.	4h	71.6	—
Sunlight	In air	room temp.	5d	88.7	1170
Sunlight (310–410 nm)	In air	room temp.	5d	90.8	—
Sunlight (390–590 nm)	In air	room temp.	5d	27.9	—

[a] In trifluoroacetic acid at 30 °C.

observations with polarized light. In a DSC thermogram, no transition was observed below the onset temperature of decomposition (253 °C) in the first heating cycle, but endothermic and exothermic peaks were observed at 239 and 226 °C, respectively, during the heating and cooling cycles, after preheating to 250 °C and subsequent quenching. In the cooling cycle, the formation of spherulite was observed.

Fig. 1(*a*) shows the ^{13}C NMR spectrum of the polymer obtained from crystalline **1**. All the resonances are narrow, whereas the spectrum of the polymers which were prepared by radical polymerisation of **1** in the bulk (melt) at 70 °C with dimethyl 2,2′-azo(isobutyrate) as an initiator is more complicated because of inhomogeneity of the stereochemical structure [Fig. 1(*c*)]. The polymers produced by radical polymerisation of **1** in the melt or in solution are atactic 1,4-polymers. The ratios of the *trans*- and *cis*-configurations of these polymers are in the range 6.4–15.0 : 1, depending on the polymerisation temperature.[8] There are four possible structures of the repeating units of the tritactic polymers from **1** through the crystalline state polymerisation, *i.e.*, tacticities of a double bond and two methine carbons. The chemical shift of the methine carbon at δ 54 in Fig. 1(*b*) suggests that this polymer might be of *meso*-diisotactic or *meso*-disyndiotactic but not of *racemo*-structure.[9]



Scheme 1

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References

1 *Reactivity in Molecular Crystals*, ed. Y. Ohashi, Kodansha-VCH, Tokyo, 1993.
2 J. D. Wright, *Molecular Crystals*, 1987, ch.7.
3 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
4 M. Hasegawa, *Chem. Rev.*, 1983, **83**, 507.
5 W. L. Dilling, *Chem. Rev.*, 1983, **83**, 1.
6 G. Wegner, *Z. Naturforsch.*, 1969, **246**, 824.
7 L. Porri, A. Giarrusso and G. Ricci, *Prog. Polym. Sci.*, 1991, **16**, 405.
8 A. Matsumoto, T. Matsumura and S. Aoki, in preparation.
9 W. R. Hertler, T. V., RajanBabu, D. W. Ovenall, G. S. Reddy and D. Y. Sogah, *J. Am. Chem. Soc.*, 1988, **110**, 5841.
10 G. Friedman, M. Lahav and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1974, 428.
11 B. S. Green, M. Lahav and G. M. J. Schmidt, *J. Chem. Soc. B*, 1971, 1552.