Synthesis and Solid-state Polymerization Properties of Symmetrical and Unsymmetrical Diacetylene Derivatives containing a 'Polymerogenic' Side Group

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The ability of a benzyl urethane side group (R^1O) to promote the solid-state polymerization of diacetylenes $R^1OCH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OR^2$ has been demonstrated on the basis of chemical and *X*-ray structural data.

The topochemical polymerization of certain crystalline diacetylenes $R{-}C{\equiv}C{-}C{\equiv}C{-}R'$, such as the PTS ester (**1a**) (PTS = *p*-toluenesulphonic acid) and analogous compounds, yields crystalline materials containing oriented conjugated polymer chains;[1] systems of this type are potentially useful for the design of linear and non-linear optical devices.[2] However, as was recently reported,[2c] the reaction being strictly controlled by the monomer packing, it is generally impossible to predict whether a given compound will undergo polymerization or not, and the discovery of new reactive diacetylenes still largely remains a matter of chance, rather than the outcome of a planned molecular design. Also, little is known about the solid-state structure and properties of unsymmetrical diacetylenes, a class of compounds which is the object of much interest as a potential source of non-centrosymmetric crystals [*e.g.*, (**1c**)].[3—5]

In connection with previous studies in this area,[3,6] we report the synthesis and some properties of a new series of symmetrical and unsymmetrical polymerizable derivatives of hexa-2,4-diyne-1,6-diol (**2**). These compounds [(**3**)—(**14**) in

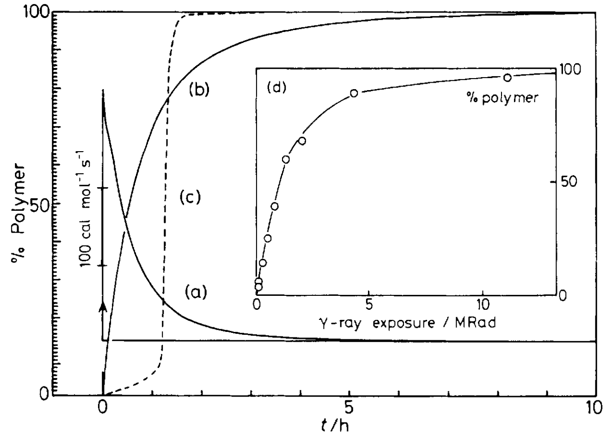

Figure 1. (a) Isothermal polymerization exotherm for a 18 mg polycrystalline sample of (**4**) at 363 K (Perkin-Elmer DSC2 calorimeter); (b) time–conversion curve corresponding to isotherm (a); (c) time-conversion curve for PTS (**1a**) at 363 K (from ref. 6); (d) time–conversion curve for γ-ray induced polymerization of (**4**).

Table 1. Structures and properties of new diacetylenes (**3**)—(**15**) and related compounds.[a]

R^1–OCH_2–C≡C–C≡C–CH_2O–R^2

	R^1	R^2	solvent[b]	M.p./ °C	Polym.
(**1a**)	*p*-$MeC_6H_4SO_2$	$=R^1$		96	(+)[6,8]
(**1b**)	*p*-$MeOC_6H_4SO_2$	$=R^1$		120	(+)[9]
(**1c**)	*p*-$MeC_6H_4SO_2$	*p*-$FC_6H_4SO_2$		71	(+)[3,4]
(**1d**)	*p*-$CF_3C_6H_4SO_2$	$=R^1$		105	(−)
(**1e**)	*p*-$ClC_6H_4SO_2$	$=R^1$		102	(−)[10]
(**2**)	H	H		113	[c]
(**3**)	$PhCH_2$–NHCO	H	tl	69	(+)
(**4**)	$PhCH_2$–NHCO	$=R^1$	tl/an	140	(+)
(**5**)	$PhCH_2$–NHCO	Ph–SO_2	ie/dm	71	(+)
(**6**)	$PhCH_2$–NHCO	*p*-$MeC_6H_4SO_2$	et/me	68	(+)
(**7**)	$PhCH_2$–NHCO	*p*-$CF_3C_6H_4SO_2$	an/al	99[d]	(+)
(**8**)	$PhCH_2$–NHCO	*p*-$FC_6H_4SO_2$	dm/me	90	(+)
(**9**)	$PhCH_2$–NHCO	*p*-$ClC_6H_4SO_2$	an/al	87	(+)
(**10**)	$PhCH_2$–NHCO	*p*-$MeOC_6H_4SO_2$	ie/dm	75	(+)
(**11**)	$PhCH_2$–NHCO	*p*-$NO_2C_6H_4SO_2$	ie/dm	98	(+)
(**12**)	$PhCH_2$–NHCO	*p*-$NO_2C_6H_4$NHCO	ea/dm	146	(−)[e]
(**13**)	$PhCH_2$–NHCO	*p*-$MeC_6H_4SO_2$NHCO	ea	168	(+)
(**14**)	$PhCH_2$–NHCO	*S*-PhCH*(Me)NHCO	dm/al	73	(+)[f]
(**15**)	*S*-PhCH*(Me)NHCO	$=R^1$	al	120	(−)

[a] Satisfactory ^{1}H n.m.r. spectra (200.13 MHz) and combustion analyses (C, H) have been obtained for all new compounds (**3**)—(**15**); m.p.s were measured on a Kofler hot bench and/or by differential scanning calorimetry (d.s.c.) [b] al: ethanol; an; acetone; dm: dichloromethane; ea: ethyl acetate; ee: diethyl ether; ie: di-isopropyl ether; me: methanol; tl: toluene. [c] See ref. 11. [d] Another unreactive crystal modification was occasionally observed (m.p. 100 °C). [e] Unreactive on thermal annealing and γ-ray exposure. [f] Probably incomplete polymerization.

Table 1] have in common the presence of a benzyl urethane side group R^1, which, to our knowledge, has not been tried so far for this purpose [a few other polymerizable urethane derivatives of (**2**) have been described].[7]

For the preparation of the symmetrical diacetylene (**4**), diol (**2**) and 2 equiv. of benzyl isocyanide were refluxed in toluene under nitrogen for 48 h. Purification of (**4**) by column chromatography on silica gel [dichloromethane–ether, 95 : 5 (v : v), as the eluant] followed by recrystallization from toluene or acetone, gave (*ca.* 70%) slightly blue-violet coloured crystals (the colour is due to the unavoidable formation of trace amounts of polymer during crystallization). By using 1 equiv. of benzyl isocyanide and a 24 h reflux time, the mono-urethane (**3**) was the major reaction product, and could be isolated (46%) by chromatography [dichloromethane–acetone, 9 : 1 (v : v), as the eluant]. This compound, which polymerizes slower than does (**4**), was a convenient starting material for the synthesis of the unsymmetrical diacetylenes (**5**)—(**14**).

The bis(urethane) derivatives (**12**) and (**14**) were obtained (70 and 50% yield) from the reaction of (**3**) and 1 equiv. of the corresponding isocyanide in refluxing toluene (24 h), whereas (**13**) was prepared by the reaction of (**3**) and 1 equiv. of toluene-*p*-sulphonyl isocyanide in dichloromethane (20 °C, 1 h, 70%). The sulphonyl esters (**5**)—(**11**) were prepared in *ca.* 70% yield as follows: to a solution of (**3**) (10 mmol) and the required sulphonyl chloride (11 mmol) in acetone (25 ml) was added dropwise (0 °C) 5.5 ml of 2 M sodium hydroxide. Water was then added and the desired product was purified by chromatography (dichloromethane as the eluant) and eventually recrystallized as indicated in Table 1.

With the exception of (**12**), diacetylenes (**3**)—(**14**) were found to polymerize in the crystalline state upon thermal annealing or exposure to light, u.v., or γ-radiation, yielding in most cases dark crystalline materials with a golden metallic reflectance. It is noteworthy that the isothermal polymerization exotherm of (**4**) at 363 K, and the corresponding time–conversion curve, shown in Figure 1(a) and (b), respectively, indicate the absence of an induction period. The same feature was observed when (**4**) was polymerized under γ-ray irradiation [Figure 1(d)]. This behaviour is similar to that of (**1b**),[9] but contrasts with that of PTS (**1a**) and of several of its congeners,[1a,b] which display a well defined two-stage process consisting of a comparatively long induction period followed by a fast autocatalytic polymerization, resulting in a typical S-shaped time–conversion curve such as that shown in Figure 1(c), for (**1a**) at 363 K.[6]

The absence of an induction period makes these compounds interesting photosensitive materials. For instance, a colourless spot of monomer (**4**) deposited on a piece of paper (from a drop of solution, air-dried in the dark) was instantly made visible (deep blue-violet colour) on exposure to u.v. light or sunlight.

The thermal polymerization of polycrystalline samples of monomers (**4**) and (**7**) was studied by differential microcalorimetry,[6] using isothermal [*e.g.*, Figure 1(a)] and non-isothermal methods. For both compounds, the plot of ln*k vs.* 1/*T* was linear up to 70% conversion; relevant data are assembled in Table 2, together with the corresponding figures for PTS,[6] and some preliminary results for a microcrystalline powder of (**9**). Although (**4**) and the unsymmetrical derivative (**7**) exhibit essentially similar kinetics, the latter reacts slightly faster, and is almost as reactive as PTS during its autocatalytic polymerization stage; (**9**) follows the same trend as (**7**). The high reactivity of these diacetylenes seems to be due to their large positive activation entropies (as compared with the large negative value for PTS), which almost offset the influence of their larger activation enthalpies.

The polymerization properties of the other new diacetylenes were only studied qualitatively, and the results are indicated in Table 1. It should be noted that the symmetrical bis(sulphonyl) esters (**1d**) and (**1e**) are unreactive, whereas the corresponding unsymmetrical compounds (**7**) and (**9**), containing the benzyl urethane side group, polymerize readily. The 'polymerogenic' effect of this group is also supported by the fact that the optically active unsymmetrical diacetylene

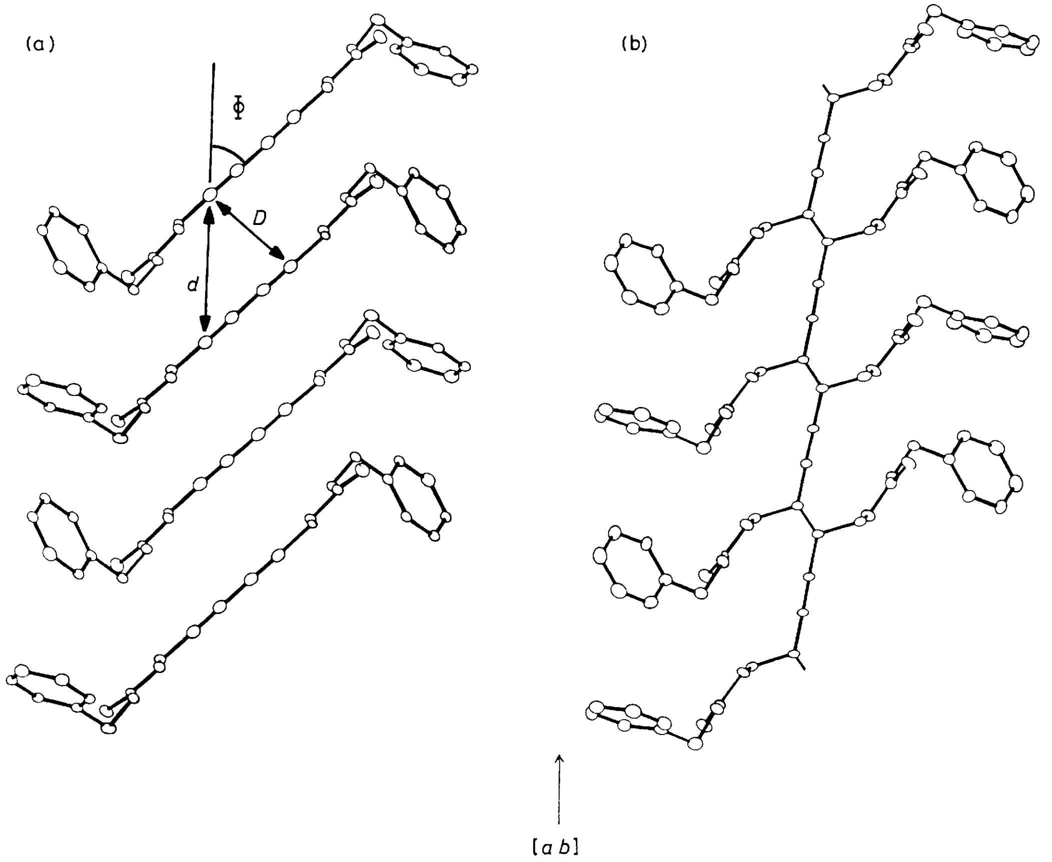

Figure 2. Projection of the crystal structure of (**4**) on the *ab* plane; (a), monomer, and (b), polymer.

(**14**) shows a moderate reactivity, whereas the analogous symmetrical derivative (**15**), with two (*S*)-α-methylbenzylurethane side groups, is unreactive.

Crystals of (**4**) suitable for an *X*-ray structure determination were grown from acetone at 4 °C. A plate 0.3 × 0.3 × 0.1 mm in size could be studied at 143 K, a temperature at which the *X*-ray induced polymerization is very slow. The same crystal was then annealed at 60 °C for 48 h, and the structure of the polymer at room temperature was determined.†

Table 2. Heat of reaction and activation parameters for the thermal polymerization of (**1a**),[6] (**4**), (**7**), and (**9**).

	ΔH_p/ kcal mol^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	k/s$-^1$ (363 K)	$t_{\frac{1}{2}}$/min (363 K)
(**1a**)					
	−37.5(4)	25.7[a]	−10[a]	1.4×10^{-5}	
		21.6[b]	−11[b]	3.0×10^{-3}	
(**4**)	−35.3(2)	29.0(6)	+5(3)	2.3×10^{-4}	50
(**7**)	−36.1(8)	30.3(4)	+11(3)	1.3×10^{-3}	9
(**9**)	−34.8[c]	29.2[c]	+8[c]		

[a] Induction period. [b] Autocatalytic range. [c] Preliminary data.

Projections of the monomer and polymer structures on the *ab* plane are shown in Figure 2(a) and (b). Each monomer molecule is H-bonded to the neighbouring molecules along the *c* direction (*i.e.*, above and below the plane of Figure 2), thus forming flat ribbons that are roughly perpendicular to the *ab* plane. Polymerization takes place along the *ab* diagonal; the repeat distance, $d = 4.82$ Å, the separation of the reacting carbon atoms, $D = 3.77$ Å, and the angle between the diacetylene rods and *ac* diagonal, $\Phi \approx 47°$, entirely fulfill the geometrical criteria for polymerizability ($d < 5$ Å, $D < 4$ Å, $\Phi \approx 45°$).[1a]

The important feature, which perhaps explains the high reactivity of (**4**) and its 'polymerogenic' properties, is the fact that the polymerization direction is different from, and independent of the H-bonding network which holds the molecules together and probably governs the packing. As a

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† *Crystal data:* monomer (**4**) at 143 K and polymer at room temperature; both structures were isomorphous, triclinic, space group $P\bar{1}$, $Z = 2$. The asymmetric unit consists of one monomer molecule ($C_{22}H_{20}N_2O_4$) or of the equivalent polymer fragment; monomer $a = 5.789(9)$, $b = 7.734(9)$, $c = 22.02(1)$ Å, $\alpha = 101.85(1)$, $\beta = 100.2(2)$, $\gamma = 90.36(8)°$, $U = 949(4)$ Å^3, $D_c = 1.317$ kg dm^{-3}; polymer $a = 5.631(6)$, $b = 7.960(6)$, $c = 21.316(4)$ Å, $\alpha = 99.38(6)$, $\beta = 92.65(7)$, $\gamma = 90.30(7)°$, $U = 941.2$ Å^3, $D_c = 1.33$ kg dm^{-3}. Neither the monomer nor the polymer showed any phase transition from room temperature down to 130 K. Data were collected on an automatic 4-circle Enraf-Nonius diffractometer. For monomer (**4**) at 143 K (cold N_2 gas stream), a total of 3181 reflections were collected, of which 2027 having $I > \sigma(I)$ were used in the structure solution. The structure was solved by direct methods (scale factor refinement and two Fourier differences). After isotropic ($R = 0.10$) then anisotropic ($R = 0.081$) refinements, the H atoms were located with a Fourier difference then refined to a final R value of 0.034. For the polymer at room temperature, 3419 reflections [1679 with $I > \sigma(I)$] were collected. The structure was solved by direct methods (all the H atoms were located) and refined as described above to a final R value of 0.052.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

consequence the H-bonding pattern is almost completely unaffected on going from the monomer to the polymer, and the reaction can proceed smoothly to completion without causing any lattice strain or mismatch at any stage. The absence of induction period might be explained in the same way. This behaviour is in contrast with that of bis(phenylurethane) analogous of (**4**), in which the polymerization direction and the H-bonding network coincide.[7d] These compounds are generally partially reactive (or unreactive), because the structural changes that occur during the reaction take place within the H-bonded ribbons, in such a way that the packing of the unreacted monomers progressively deviates from the conditions allowing polymerization.

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References

1 (a) V. Enkelmann in 'Polydiacetylenes,' ed. H. J. Cantow; *Adv. Polym. Sci.*, 1984, **63**, 91, and references therein; (b) H. Bässler, *ibid.*, 1984, **63**, 1.

2 (a) A. F. Garito, C. C. Teng, K. Y. Wong, and O. Zammani-'Khamiri, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 219; (b) G. M. Carter, Y. J. Chen, J. Georger, Jr., J. Hryniewicz, M. Rooney, M. F. Rubner, L. A. Samuelson, D. J. Sandman, M. Thakur, and S. Tripathy, *ibid.*, 1984, **106**, 259; (c) M. Schott and G. Wegner, in 'Non-linear Optical Properties of Organic Molecules and Crystals,' eds. D. S. Chemla and J. Zyss, Academic Press, Orlando (Florida), 1987, vol. 2, Ch. III-1.

3 M. Bertault, L. Toupet, J. Canceill, and A. Collet, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 443.

4 P. Strohriegl, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 437.

5 P. Strohriegl, H. Schultes, and E. Dorman, Abstracts of the 31st IUPAC Macromolecular Symposium, Merseburg, G.D.R., 1987, p. 208; J. Veciana, A. Galán, J. Riaza, O. Armet, E. Molins, and C. Miravitlles, Abstracts of the 8th International Congress on the Chemistry of the Organic Solid State, Lyon, France, 1987, p. 140.

6 M. Bertault, M. Schott, M.-J. Brienne, and A. Collet, *Chem. Phys.*, 1984, **85**, 481.

7 (a) C. Galiotis and R. J. Young, *Polymer*, 1983, **24**, 1023; (b) V. Enkelmann, *J. Chem. Res.* (*S*), 1981, (*S*) 344; (*M*) 3901; (c) E. Hädicke, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, *Angew. Chem., Int. Ed. Eng.*, 1971, **10**, 266; (d) A. Whuler, P. Spinat, and C. Brouty, *Acta Crystallogr., Sect. C.*, 1983, **40**, 693; C. Brouty, P. Spinat, and A. Whuler, *ibid.*, 1983, **39**, 594; 1984, **40**, 1619.

8 G. Wegner, *Makromol. Chem.*, 1971, **145**, 85; G. Wegner and V. Enkelmann, *Angew. Chem.*, 1977, **89**, 432; P. A. Albouy, P. Keller, and J.-P. Pouget, *J. Am. Chem. Soc.*, 1982, **104**, 6556.

9 D. J. Ando, D. Bloor, C. L. Hubble, and R. Williams, *Makromol. Chem.*, 1980, **181**, 453; G. N. Patel, Y. P. Khanna, D. M. Ivory, J. M. Sowa, and R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17**, 899; D. Bloor, D. J. Ando, C. L. Hubble, and R. L. Williams, *ibid.*, 1980, **18**, 779.

10 J. J. Mayerle and T. C. Clarke, *Acta Crystallogr., Sect. B*, 1978, **34**, 143.

11 E. Hädicke, K. Penzien, and H. W. Schnell, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 940.