# Crystal structures and solid-state reactivities of 1,4- and 1,2-bis-(5-hydroxypenta-1,3-diynyl)benzenes and 1-(5-hydroxypenta-1,3-diynyl)-4-ethynylbenzene

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Crystal structures and the solid-state polymerization of 1,4-bis(5-hydroxypenta-1,3-diynyl)benzene (**1**), 1,2-bis(5-hydroxypenta-1,3-diynyl)benzene (**2**) and 1-(5-hydroxypenta-1,3-diynyl)-4-ethynylbenzene (**3**) were investigated. The crystal structure of **1** depends on the recrystallization solvent. Crystals obtained from acetone–benzene mixtures polymerize when irradiated with γ-rays or heated. The colourless crystals become black and are insoluble in common organic solvents. Only one of the butadiynyl groups participates in the radiation-induced polymerization, whereas both do, in the thermal polymerization. Polymerization does not occur for crystals obtained from pure acetone. The polymerization reactivities are correlated to the crystal structures. Polymerizable crystals were not obtained from **2**. The arrangement of the butadiynyl groups in crystals of **2** is unfavorable for the polymerization. Crystals of **3**, obtained from hexane–acetone mixtures, polymerize upon γ-irradiation but not upon heating. In the radiation-induced polymerization of **3**, the propagation by the ethynyl and butadiynyl groups is considered to proceed independently along different crystal axes. The ethynyl groups are more reactive than the butadiynyl groups because they have a shorter intermolecular carbon–carbon distance through which the polymerization occurs. The difference in reactivity toward heating between **1** and **3** may also be interpreted in terms of intermolecular carbon–carbon distances of the butadiynyl groups.

## Introduction

We have previously reported on the reactions of γ-irradiated crystals of diethynylbenzene derivatives.[1–3] The crystal structures of the monomers were markedly affected by the nature of the substituents and their positions in the aromatic ring, leading to a variety of solid-state reactivities. Polymerization or dimerization occurred selectively depending on the crystal structures in contrast to the non-selective reactivities in solution. The present study is concerned with the crystal structures and solid-state polymerization of bifunctional derivatives having diacetylene moieties. The structures and the melting points of the monomers, 1,4-bis(5-hydroxypenta-1,3-diynyl)-benzene (**1**), 1,2-bis(5-hydroxypenta-1,3-diynyl)benzene (**2**) and 1-(5-hydroxypenta-1,3-diynyl)-4-ethynylbenzene (**3**), used in the present study, are shown in Fig. 1.

Solid-state polymerization of diacetylene derivatives has been extensively studied in connection with both the propagation processes and the π-conjugation properties of the product polymers, including nonlinear optical properties.[4–6] Recently, attempting the enhancement of π-conjugation properties, bifunctional diacetylene monomers and octatetraynes have been synthesized and their polymerization reactivities have been investigated.[7–14] Radiation-induced solid-state polymerization has been reported for 1,4-bis(octadeca-1,3-diynyl)-benzene, an analogue of **1**. However, there has been no report on the crystal structures of bifunctional diacetylene monomers. In the present study the crystallographic analysis was undertaken to elucidate the contribution of the two functional groups to the polymerization.

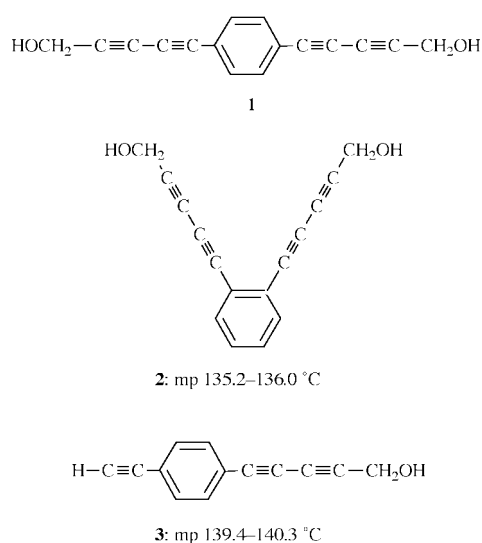The crystal structure of **1** depended on recrystallization sol-



Fig. 1 Structures of monomers.

vents. Changes in the recrystallization conditions of **1** revealed that it exists in two crystalline forms, designated as **1a** and **1b**. **1a** Crystals were obtained from acetone–benzene mixtures and **1b** crystals, from pure acetone. Upon γ-irradiation, **1a** polymerized so as to be insoluble in common organic solvents. Polymers were obtained neither from **1b**, nor from the crystals of **2**. Reactivities in polymerization are correlated to the monomer packings in the crystals. Polymerization was also examined for **3**.

**Table 1** Crystal data and experimental conditions

| Parameter | 1a | 1b | 2 | 3 |
|---|---|---|---|---|
| Empirical formula | $C_{16}H_{10}O_2$ | $C_{16}H_{10}O_2$ | $C_{16}H_{10}O_2$ | $C_{13}H_8O$ |
| Formula weight | 234.25 | 234.25 | 234.25 | 180.21 |
| Crystal dimensions/mm | $0.30 \times 0.25 \times 0.10$ | $0.30 \times 0.20 \times 0.20$ | $0.30 \times 0.30 \times 0.25$ | $0.40 \times 0.30 \times 0.15$ |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ | $P2_1/n$ | $P2_1$ |
| $a/\text{Å}$ | 4.104(3) | 17.669(3) | 8.179(2) | 4.041(1) |
| $b/\text{Å}$ | 5.427(6) | 8.058(3) | 8.826(3) | 5.641(3) |
| $c/\text{Å}$ | 26.816(2) | 9.354(3) | 17.338(2) | 21.062(4) |
| $\beta/°$ | 94.07(6) | 115.76(2) | 94.15(1) | 93.16(2) |
| $V/\text{Å}^3$ | 595.8(8) | 1199.5(5) | 1248.2(5) | 479.3(3) |
| $Z$ | 2 | 4 | 4 | 2 |
| $d_{calcd}/\text{g cm}^{-3}$ | 1.306 | 1.297 | 1.246 | 1.248 |
| $\mu(\text{Cu-K}\alpha)/\text{cm}^{-1}$ | 6.90 | | | |
| $\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$ | | 0.79 | 0.76 | 0.78 |
| $F(000)$ | 244.00 | 488.00 | 488.00 | 188.00 |
| No. of reflections, $m$ with $(I > 2\sigma(I))$ | 642 | 773 | 1719 | 911 |
| No. of variables, $n$ | 103 | 107 | 204 | 160 |
| $R^a$ | 0.042 | 0.060 | 0.050 | 0.040 |
| $Rw^b$ | 0.049 | 0.066 | 0.049 | 0.042 |
| $GOF^c$ | 3.32 | 1.51 | 1.69 | 1.59 |
| $\Delta\rho_{max}/\text{e Å}^{-3}$ | 0.14 | 0.18 | 0.16 | 0.10 |

$^a$ $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b$ $Rw = [\Sigma_\omega(|F_o| - |F_c|)^2/\Sigma_\omega|F_o|^2]^{1/2}$. $^c$ $GOF = [\Sigma_\omega(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Diffractometer: Rigaku AFC-5R. Crystal structure analysis: TEXSAN. Structure solution: direct method (SHELXS86). Refinement: full-matrix least-squares.

## Experimental

### Polymerization experiments

The monomers, **1** and **3**, were prepared by the coupling of 1,4-diethynylbenzene and 3-bromopropyn-1-ol by the literature method [15] and were purified by repeated recrystallization. Similarly, **2** was prepared from 1,2-diethynylbenzene and 3-bromopropyn-1-ol and was recrystallized. The diethynylbenzenes were prepared from 1,2- and 1,4-diiodobenzenes (Aldrich and Wako Chemicals, respectively) according to the literature. [16] 3-Bromopropyn-1-ol was prepared according to the literature. [17] The monomer crystals were sealed in Pyrex tubes under vacuum and were irradiated at room temperature with $\gamma$-rays from a $^{60}$Co source at a dose rate of 5.2 kGy h$^{-1}$ (1 Gy = 1 J kg$^{-1}$). The solid-state polymerization was followed by comparing the relative intensities of the stretching bands of the corresponding carbon–carbon triple bonds, –C≡C–H (3263 cm$^{-1}$) and –C≡C–C≡C– (2240 cm$^{-1}$), with those of the aromatic rings (832 cm$^{-1}$) of the FTIR spectra (KBr) of the original and irradiated crystals. The FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer. Fig. 2 shows the FTIR spectra of the original crystals of **1a** and **3**, which polymerized upon $\gamma$-irradiation or heating. Gel permeation chromatographic measurement was carried out by 262 nm absorption in tetrahydrofuran using a Shimadzu CR3A equipped with two 30 cm TSK-Gel G6000PWXL and G3000PWXL columns connected in series.

### X-Ray crystal structure analysis

The crystal data and experimental details are summarized in Table 1. X-Ray diffraction data were collected by a Rigaku AFC-5R diffractometer with graphite-monochromated Cu-K$\alpha$ radiation ($\lambda = 1.54178$ Å) up to $2\theta_{max}$ of 120.1°. All the crystallographic calculations were carried out by using the TEXSAN software package of the Molecular Structure Corporation. The crystal structures were solved by the direct method (SHELXS 86) and were refined by full-matrix least-squares. All the non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively.

Full crystallographic details (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC).
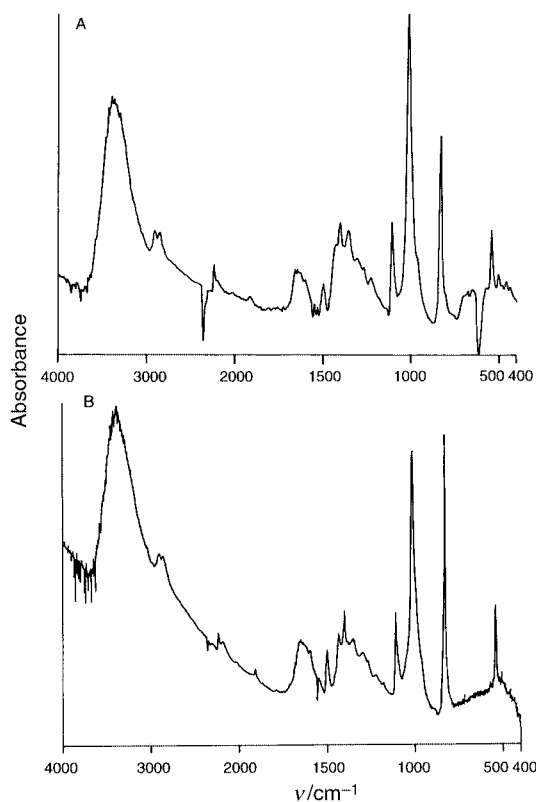
CCDC reference number 188/200.
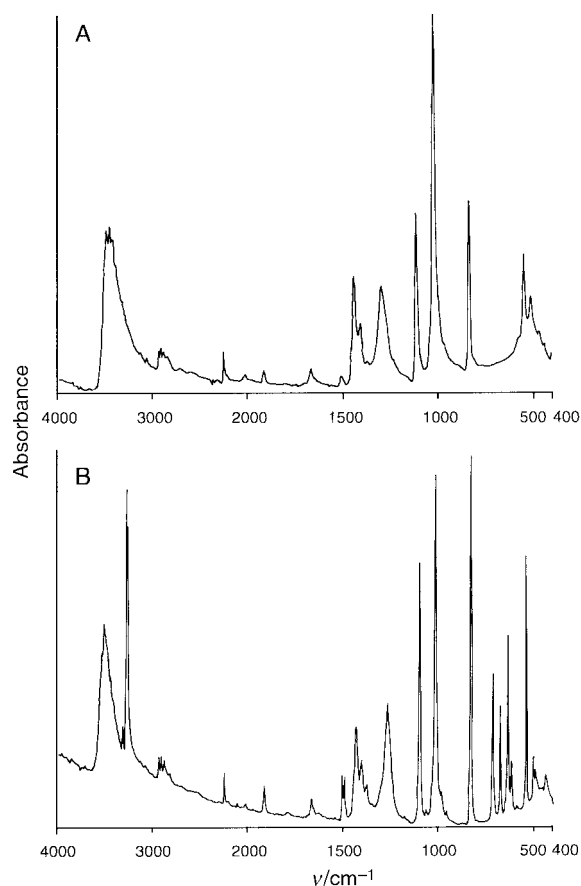
**Fig. 2** FTIR spectra of the original crystals of (A) **1a** and (B) **3**.

## Results and discussion

Upon heating **1a** crystals (obtained from acetone–benzene mixtures) turned black above *ca.* 120 °C and did not melt beyond 300 °C. When recrystallized from pure acetone, colouration of **1b** crystals was observed to begin at *ca.* 160 °C, and the black crystals melted at 210 °C. The melting point for crystals of **1** was therefore not determined because of the occurrence of polymerization upon heating.
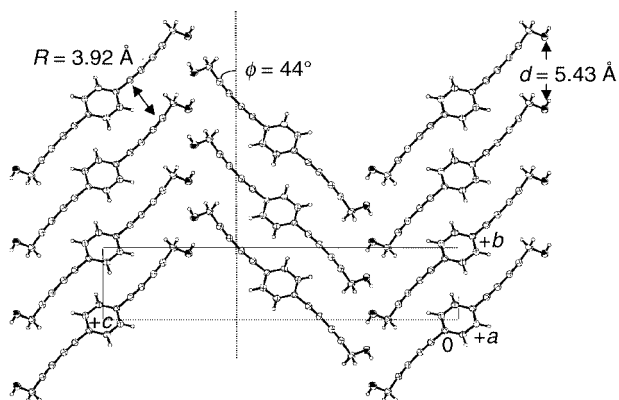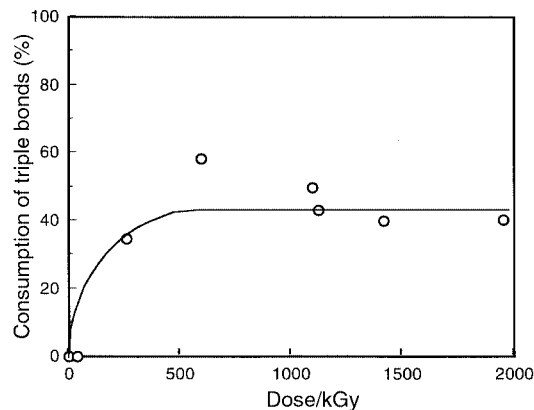
**Fig. 3** Crystal structure of **1a**, recrystallized from acetone–benzene mixtures, viewed down the *a* axis.
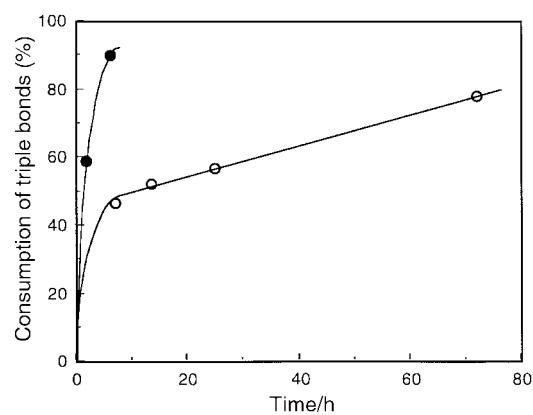


**Fig. 5** Consumption of the butadiynyl groups in the radiation-induced polymerization of **1a**, obtained from acetone–benzene mixtures.



**Fig. 4** FTIR spectra of **1a** (A) irradiated at a dose of 2.0 MGy and (B) heated at 100 °C for 25 h.



**Fig. 6** Consumption of the butadiynyl groups in the thermal polymerization of **1a**, obtained from acetone–benzene mixtures, at (○) 100 and (●) 150 °C.

The crystal structure of **1** depends on the recrystallization solvents. Fig. 3 shows the crystal structure of **1a**. The diacetylene groups are arranged regularly along the *b* axis. The regular arrangement along the *b* axis is formed by hydrogen bonding between neighbouring hydroxy groups.

To define the arrangement of diacetylene monomers, the following parameters are used.[6] They are intermolecular distance, *R*, between reacting carbons, stacking distance, *d*, between neighbouring monomers and the angle, $\varphi$, between diacetylene rod and stacking axis. In the crystal structure of **1a**, *R*, *d* and $\varphi$ are 3.92 Å, 5.43 Å and 44°, respectively; these parameters are in the range reported to be favorable for polymerization.[6] Thus, the solid-state polymerization in this crystal is considered to proceed along the *b* axis. The **1a** crystals polymerized so as to be insoluble in common organic solvents when irradiated with γ-rays or heated, and the colourless crystals became black, as expected from the crystal data. Fig. 4 shows the FTIR spectra of **1a,** irradiated with γ rays at a dose of 2.0 MGy and heated at 100 °C for 25 h. The absorption intensity of the –C≡C–C≡C– band at 2240 cm$^{-1}$ decreases and a new band appears at around

2190 cm$^{-1}$, which is assigned to conjugated acetylene.[8] Fig. 5 shows the consumption of the butadiynyl groups in the radiation-induced polymerization of **1a**. The consumption of the butadiynyl groups seems to be constant at below 50% above the irradiation dose of *ca.* 500 kGy. There was no appreciable change in the FTIR spectra at the high irradiation doses at least above 1.0 MGy. Therefore, the radiation-induced polymerization is considered to proceed by one of the diacetylene moieties. The arrangement of the remaining butadiynyl groups of the polymer should not be suitable for the further reactions of the pendants. Unfortunately, attempts at X-ray structure analysis of the samples in various stages of polymerization were unsuccessful because of the poor crystallinity of the samples, and the arrangement of the remaining butadiynyl groups of the polymer was not clarified.

Fig. 6 shows the consumption of the butadiynyl groups in the thermal polymerization at 100 and 150 °C. It is demonstrated that both of the diacetylene moieties participate in the thermal polymerization, resulting in the consumption of the butadiynyl groups above 50%. The FTIR spectral change around the 2240 and 2190 cm$^{-1}$ bands at 100 °C is illustrated in Fig. 7. After polymerization by one of the butadiynyl groups, a rearrangement of the polymer may occur to promote the reactions of the pendants at the high temperatures.

Fig. 8 shows the crystal structure of **1b.** It was found that the arrangement of the aromatic rings in the neighbouring mono- mer molecules is not parallel. The parameters *R*, *d* and $\varphi$ are 6.08 Å, 9.35 Å and 24°, respectively, which indicate that the arrangement of this crystal is not suitable for the polymeriz- ation. The crystals did not polymerize upon γ-irradiation, as expected. **1b** Crystals irradiated at a dose of 510 kGy were sub- mitted to gel permeation chromatography. Even low molecular
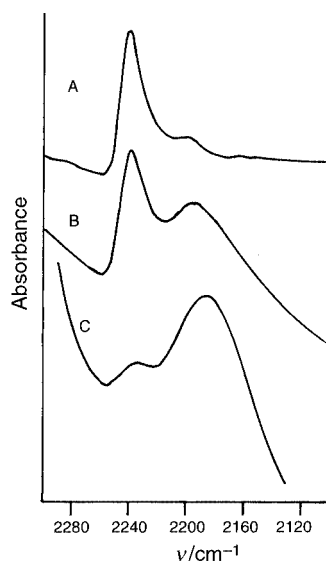
**Fig. 7** Change in the absorption intensities of the 2240 and 2190 cm$^{-1}$ bands of the **1a** crystals upon heating at 100 °C: the heating times are (A) 0, (B) 25 and (C) 72 h.
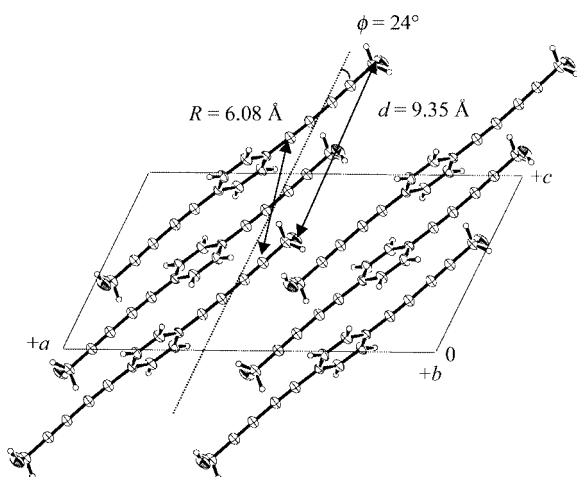


**Fig. 8** Crystal structure of **1b**, recrystallized from acetone, viewed down the *b* axis.

weight oligomers were not detected by the gel permeation chromatogram of the irradiated crystals. Neither did **1b** polymerize upon heating at up to 150 °C.

No crystals which polymerized upon γ-irradiation or heating were obtained from **2**. The melting point of the crystals obtained from ethyl acetate was 135.2–136.0 °C. Fig. 9 shows the structure of the inert crystals. The parameters *R*, *d* and *φ* are 6.19 Å, 8.83 Å and 34°, respectively, which indicate that the arrangement of crystal **2** is unfavorable for polymerization.[6]

Figs. 10A and 10B show the crystal structure of **3**, obtained from hexane–acetone mixtures. Considering the structure from the *a* axis projection of the crystal packing, the diacetylene groups are arranged along the *b* axis and their packing parameters *R*, *d* and *φ* are 4.02 Å, 5.64 Å and 42°, respectively (Fig. 10A). It was found that this crystal structure is quite similar to the crystal structure of **1a** and the crystals of **3** take suitable packing structures for solid-state polymerization. Therefore, it is expected that this monomer is polymerized along the *b* axis. The regular arrangement along the *b* axis is also formed by hydrogen bonding between neighbouring hydroxy groups. On the other hand, from the crystal packing projected along the *b* axis, it was found that the ethynyl moieties are regularly arranged along the *a* axis and the shortest carbon–carbon distance of the neighbouring ethynyl moieties is 3.79 Å (Fig. 10B). On the basis of the molecular arrangement, the solid-state
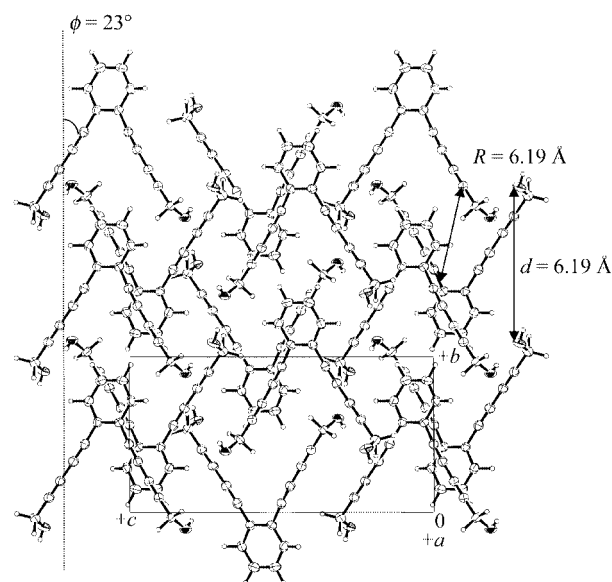


**Fig. 9** Crystal structure of **2** viewed down the *a* axis.
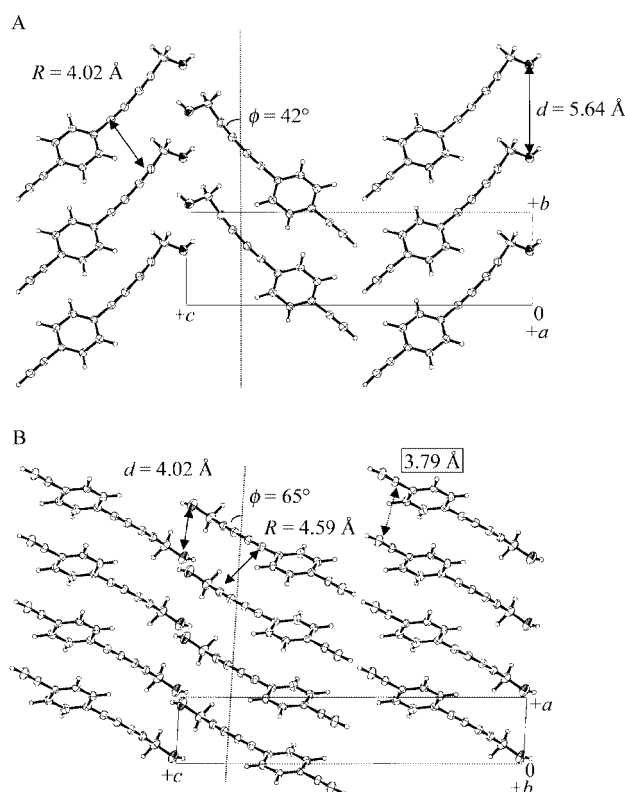




**Fig. 10** Crystal structure of **3** viewed down the (A) *a* and (B) *b* axes.

polymerization of **3** by the ethynyl moiety is expected to proceed, similarly to the case of 1,4-diethynylbenzene.[1,18] Thus, with respect to the crystals of **3**, the monomer arrangement is suitable for solid-state polymerization not only by the diacetylene moieties but also by the ethynyl groups. The distance between the reacting carbons is shorter for the ethynyl groups than for the diacetylene moieties. So polymerization is expected to be preferable for the ethynyl groups than for the diacetylene moieties. Irradiation of the crystals of **3** for a short time resulted in a poor crystallinity. This may be due to the scission of the hydrogen bonds between the neighbouring diacetylene moieties caused by the predominant bond formation between the ethynyl groups. Such a lowering of the crystallinity was not observed for the irradiated **1a** crystals, where the crystal lattice is held by the diacetylene polymerization.

Crystals of **3** polymerize upon γ-irradiation but not upon
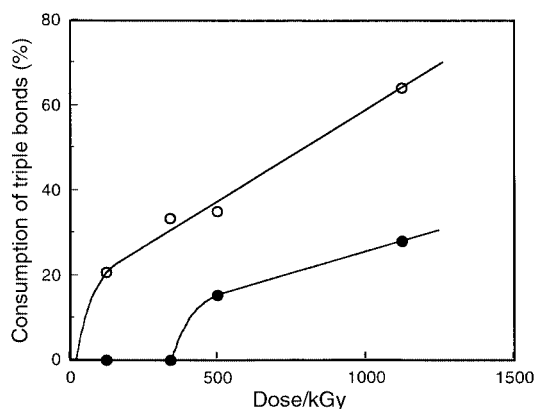
**Fig. 11** Consumption of the (○) ethynyl and (●) butadiynyl groups in the radiation-induced polymerization of **3**.

heating. A decrease in absorption intensity at 2240 cm$^{-1}$ was observed in the FTIR spectra of the irradiated crystals of **3**, as well as the appearance of a new band at 2190 cm$^{-1}$, similarly to the case of **1a**. In addition, the absorption intensity of the –C≡C–H band at 3263 cm$^{-1}$ decreased upon γ-irradiation. These results indicate that both of the ethynyl and butadiynyl groups participate in the polymerization, as expected from the crystallographic data. Fig. 11 shows the consumption of the ethynyl and butadiynyl groups in the radiation-induced polymerization of **3**. The consumption of the ethynyl groups is larger than that of the butadiynyl groups. Furthermore, the consumption of the butadiynyl groups of **3** is smaller than that of **1a**. These results can be interpreted in terms of the long distance between the reacting carbons of the butadiynyl groups of **3**, 4.02 Å, compared with that of **1a**, 3.92 Å. Polymerization by the butadiynyl groups may have an induction period (Fig. 11), although there may be some errors in the low yields in the early stage of the polymerization. On the basis of the molecular arrangement of the crystals, the two propagations by the ethynyl and butadiynyl groups of **3** are considered to proceed along the different axes of the crystals.

The relatively long distance between the reacting carbons of the butadiynyl group of **3** may be responsible for its inertness toward heating. The ethynyl groups may also be inert toward

heating. In our previous study,[1,2] 1,4-diethynylbenzene did not polymerize upon heating below the melting point, 94–95 °C, whereas it polymerized upon irradiation with γ-rays[1] and UV light.[18] The ethynyl groups attached to aromatic rings are considered to be inert in the thermal polymerization in crystalline states, since the melting points of various aromatic acetylenes have been determined.[18]

## References

1 M. Hagihara, Y. Yamamoto, S. Takahashi and K. Hayashi, *Radiat. Phys. Chem.*, 1986, **28**, 165.
2 Y. Kai, A. Yamamoto, D. Xu, N. Kasai, M. Hagihara, Y. Yamamoto, S. Takahashi and K. Hayashi, *Makromol. Chem.*, 1987, **188**, 3047.
3 Y. Yamamoto, T. Ueda, N. Kanehisa, K. Miyawaki, Y. Takai, S. Tagawa, M. Sawada and Y. Kai, *J. Chem. Soc., Perkin Trans. 2*, 1997, 734.
4 H. Basseler, *Adv. Polym. Sci.*, 1984, **63**, 1.
5 H. Sixl, *Adv. Polym. Sci.*, 1984, **63**, 49.
6 V. Enkelmann, *Adv. Polym. Sci.*, 1984, **63**, 91.
7 S. Okada, H. Matsuda, A. Masaki, H. Nakanishi and K. Hayamizu, *Chem. Lett.*, 1997, 1105.
8 S. Okada, H. Matsuda, H. Nakanishi and M. Kato, *Mol. Cryst. Liq. Cryst.*, 1990, **189**, 57.
9 S. Okada, K. Hayamizu, H. Matsuda, A. Masaki and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 857.
10 S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, N. Minami and H. Nakanishi, *Macromolecules*, 1994, **27**, 6259.
11 K. Hayamizu, S. Okada, T. Doi, H. Kawanami, N. Kikuchi, H. Matsuda and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 791.
12 S. Nezu and J. B. Lando, *J. Polym. Sci.: Part A: Polym. Chem.*, 1995, **33**, 2455.
13 W. S. Price, N. Kikuchi, H. Matsuda, K. Hayamizu, S. Okada and H. Nakanishi, *Macromolecules*, 1995, **28**, 5363.
14 H. Matsuzawa, S. Okada, H. Matsuda and H. Nakanishi, *Chem. Lett.*, 1997, 1105.
15 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988, ch. 10, p. 212.
16 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.
17 T. Ando, S. Shioi and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2611.
18 O. Rohde and G. Wegner, *Makromol. Chem.*, 1978, **179**, 2013.

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