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Solid-State Co-crystallization of Diacetylenes and Its Topochemical Polymerization

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Mixed crystals of 2,4-hexadiynylene-di(*p*-toluenesulfonate) with -di(*p*-bromobenzenesulfonate) and with -di(*p*-chlorobenzenesulfonate) were formed by simple grinding of these monomer crystals. The formation of the mixed crystals was proved by X-ray powder diffraction and infrared spectral analyses as well as by their thermal behavior. These mixed crystals polymerized upon heating.

As a result of an extensive study on the topochemical photocopolymerization of mixed crystals of diolefin compounds we have succeeded in preparing photoreactive mixed crystals from several couples of diolefin compounds.1) It was recently found in our laboratory that a few mixed crystals of diolefins could be obtained not only by recrystallization from a solution, but also by simple grinding of two monomers with an agate mortar and pestle or an amalgamator.2) For example, the grinding of ethyl 4-[2-(2-pyrazyl)ethenyl]cinnamate and *S*-ethyl 4-[2-(2-pyrazyl)ethenyl]thiocinnamate crystals resulted in the formation of a mixed crystal, which showed a similar photopolymerizability to that obtained by recrystallization from a solution. On the basis of this result, the grinding was considered to be applicable for the formation of mixed crystals of other organic compounds. On the other hand, some of the diacetylene mixed crystals have been reported to undergo topochemical polymerization.3) All of the reported mixed crystals of diacetylenes were, however, prepared by recrystallization from solution.

In the present paper we report on the successful preparation of mixed crystals by simple grinding of two couples of diacetylene crystals and on the topochemical polymerization of these crystals.

2,4-Hexadiynylene-di(*p*-toluenesulfonate) (**TS**), -di(*p*-bromobenzenesulfonate) (**BBS**), and -di(*p*-chlorobenzenesulfonate) (**CBS**) were prepared by methods reported in the literature4) and recrystallized from CH_2Cl_2 at 5 °C. Two couples of pure crystals, **TS/BBS** and **TS/CBS**, with various molar ratios were agitated for 20 min at 5 °C by using an amalgamator to give the corresponding mixtures, **TS-BBS** and **TS-CBS**. The mixtures were highly crystalline, pale-orange-colored powders and were soluble in ordinary solvents such as acetone, $CHCl_3$, and CH_2Cl_2. As reference samples, each of three diacetylene compounds was separately ground using the same process. **TS**, thus obtained, was a red-orange-colored powder which included a few wt% polymer.

Figure 1 shows the X-ray powder diffraction patterns of **TS-BBS** (1.3:1), **TS**, and **BBS**. If the mixed system comprised a mixture of two monomer crystals, the X-ray diffraction pattern of **TS-BBS** should

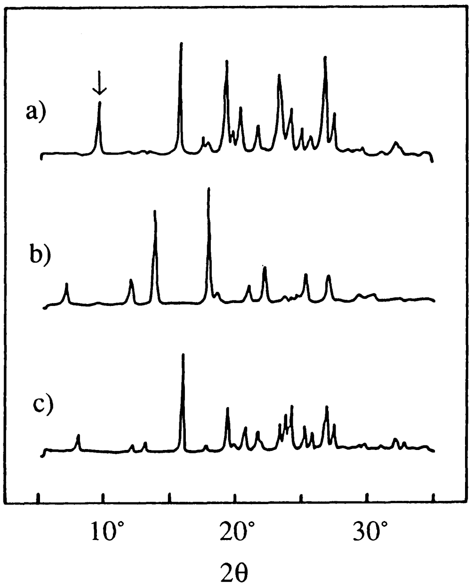

Fig. 1. X-Ray powder diffraction patterns of a) a mixed crystal of **TS-BBS** (1.3:1), b) **TS**, and c) **BBS** prepared by grinding.

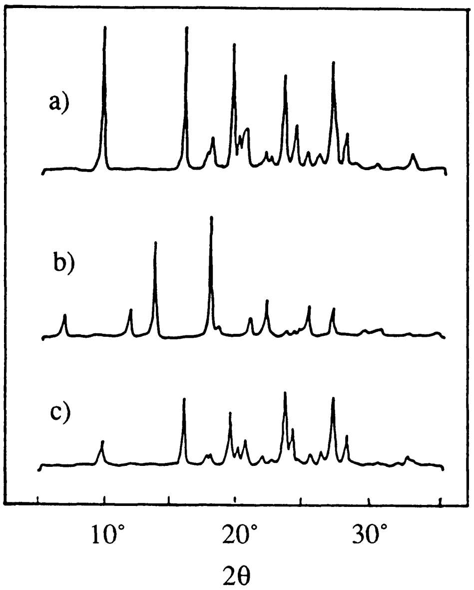

Fig. 2. X-Ray powder diffraction patterns of a) a mixed crystal of **TS-CBS** (1.1:1), b) **TS**, and c) **CBS** prepared by grinding.

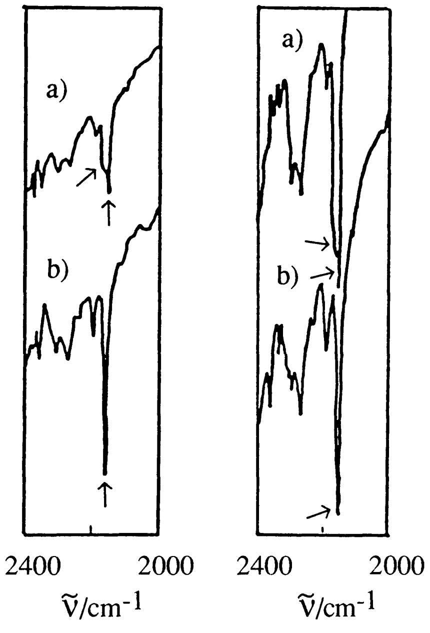

Fig. 3. IR spectra of the mixtures of **TS-BBS** (1.3:1), (left) and **TS-CBS** (1.1:1), (right): a) Samples prepared by simple mixing. b) Mixed crystals prepared by grinding.

overlap those of **TS** and **BBS**. The diffraction pattern of **TS-BBS** in the region from 2θ = 5° to 15° was, however, quite different from those of **TS** and **BBS**, and showed a new peak at 2θ = 9.4°. Moreover, in the diffraction pattern of **TS-BBS**, a new strong peak appeared at 2θ = 23°, and also the strongest peak at 2θ = 17.7° in the diffraction pattern of **TS** became very weak. In the region from 2θ = 19° to 30°, the pattern of **TS-BBS** was similar to that of **BBS**. A similar correlation was observed between the diffraction pattern of **TS-CBS** (1.1:1) and those of **TS** and **CBS** (Fig. 2). The pattern of **TS-CBS** was similar to that of **CBS** but quite different from that of **TS**.

Moreover, in their IR spectra, **TS-BBS** (1.3:1) and **TS-CBS** (1.1:1) showed only one peak at 2160 cm^{-1} for C≡C stretching, whereas **TS** showed a peak at 2170 cm^{-1}, and **BBS** and **CBS** at 2160 cm^{-1} (Fig. 3). The results of the X-ray diffraction pattern and IR spectra led to the conclusion that **TS** was incorporated in the crystal lattices of **BBS** and **CBS** by grinding in the crystalline-state, resulting in the formation of mixed crystals.

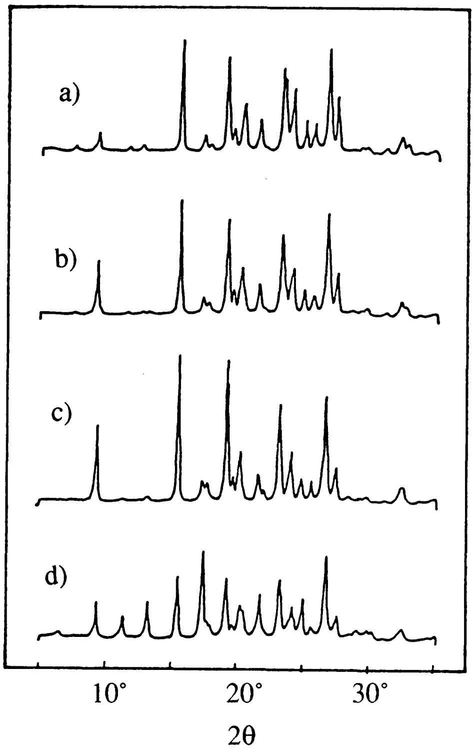

Fig. 4. X-Ray powder diffraction patterns of mixed crystals of **TS-BBS** with various molar ratios: a) 1 : 1.5, b) 1.3 : 1, c) 2.2 : 1, and d) 3.3 : 1.

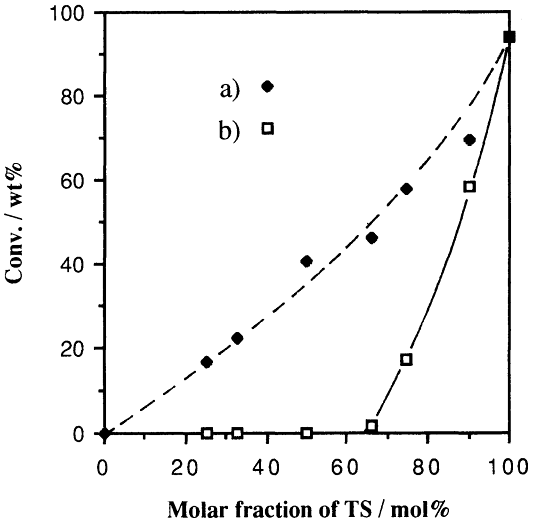

Fig. 5. Conversion curve for the thermal polymerization of the mixtures of **TS** and **BBS** with various molar ratios:
a) Sample prepared by simple mixing.
b) Mixed crystal prepared by grinding.
Thermal treatment ; 70 °C for 30 h.

The X-ray powder diffraction patterns of **TS-BBS** with various molar ratios (**TS** : **BBS** = 1:1.5 - 3.3:1) are shown in Fig. 4. The diffraction patterns of **TS-BBS** (1:1.5 - 2.2:1) were similar to each other, except that of **TS-BBS** (3.3:1), in which the patterns of **TS-BBS** and **TS** were simply overlapped. The X-ray diffraction patterns imply that **TS** and **BBS** formed a solid-solution in a molar ratio approximately from 1:1 to 2:1.

As the polymers derived from 2,4-hexadiynylene disulfonate derivatives have been reported to be insoluble in ordinary solvents such as acetone, MeOH, and $CHCl_3$,[4)] the insoluble part formed by a thermal treatment was roughly defined as being a polymer. The conversion of a thermal treatment at 70 °C for 30 h was determined gravimetrically on the basis of residual monomers extracted with $CHCl_3$. Figure 5 shows a conversion curve for the polymerization of mixtures of **TS** and **BBS** (prepared by grinding or by simple mixing) with various molar ratios.

Conversion to a polymer of the mixture (prepared by simple mixing) increased upon increasing the molar fraction of **TS**. On the other hand, that of mixtures prepared by grinding started to increase only when **TS** contained over 66 mol%. The conversion curve may be explained in terms of the fact that ground mixtures with a molar ratio of **TS** : **BBS** over 2:1 comprise two crystal compounds: a reactive **TS** crystal and a less reactive solid-solution of **TS - BBS** ; only the **TS** part transformed into a polymer. The conversion curve for

Table 1. Conversion for the Thermal Polymerization[a] of Mixed Crystals and Reference Samples

Sample	**TS-CBS** (1:1)	**TS-BBS** (1:1)	**CBS**	**BBS**
Conversion	15.1%[b]	4.0%	1.3%	0%

a) Thermal treatment; 70 °C for 30 h, then 80 °C for 90 h.

b) Molar ratio of residual monomer was 1:1.

simple mixing and ground mixtures of **TS** and **CBS** were very similar to those of **TS** and **BBS**.

Table 1 shows the final conversions of **TS-BBS** (1:1), **TS-CBS** (1:1), as well as that of reference samples, **BBS** and **CBS**, to those polymers undergoing thermal treatment at 70 °C for 30 h, followed by that at 80 °C for 90 h. Mixed crystals were converted into polymers in higher conversion than were reference samples. Furthermore, the molar ratio of residual monomers which were recovered from a thermally-treated sample of **TS-CBS** (1:1) did not change, compared to that before the thermal treatment. The final conversions and the molar ratios of residual monomers suggested that the mixed crystals transformed into coploymers upon undergoing thermal treatment.

All of the results in the present experiments lead to the conclusion that mixed crystals are formed by a simple grinding of two diacetylene derivatives in the crystalline state, strongly supporting that these mixed crystals polymerize upon undergoing a thermal treatment above 70 °C into the copolymers. The grinding procedure may be generally applicable for the preparation of topochemically reactive diacetylene mixed crystals, although the mechanism that produces these mixed crystals is not yet clear.

References

1) M. Hasegawa, Y. Endo, M. Aoyama, and K. Saigo, *Bull. Chem. Soc. Jpn.*, **62**, 1556 (1989); Y. Maekawa, S. Kato, and M. Hasegawa, *J. Am. Chem. Soc.*, in press.
2) Y. Maekawa, P. J. Lim, K. Saigo, and M. Hasegawa, to be published.
3) D. J. Ando, D. Bloor, and B. Tieke, *Makromol. Chem., Rapid Commun.*, **1**, 385 (1980); V. Enklemann, *J. Mater. Soc.*, **15**, 951 (1980); V. Enklemann, *Adv. Polym. Sci.*, **63**, 91 (1984).
4) G. Wegner, *Makromol. Chem.*, **145**, 85 (1971); D. J. Ando, D. Bloor, C. L. Hubble, and R. L. Willams, *Makromol. Chem.*, **181**, 453 (1980).

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