# Formation of a Topochemically Photoreactive Mixed Crystal by Grinding and Its Mechanistic Interpretation

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A mixed crystal of ethyl and propyl $\alpha$-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate was formed in the solid state by simple grinding. The mixed crystal formation was ascertained by the change in the X-ray diffraction pattern upon grinding and by $^1$H NMR and HPLC analyses of the photoproducts. According to several attempts, it was concluded that a mechanical treatment was necessary for the formation of the mixed crystal phase. The kinetic data concerning the analysis of the topochemical photoproducts revealed that the following growth of the mixed crystal phase was triggered by each of the mixed crystal nuclei and that the growth of the mixed crystal phase was accelerated by either thermal annealing or exposure in humidity. During the early stage of mixed crystal growth, the growth rate was nearly proportional to the surface area of the nuclei of the mixed crystal.

The topochemical photoreaction of unsymmetrically substituted diolefin crystals has been intensively studied in our laboratory from the viewpoints of stereospecific organic chemistry and new polymer synthesis. Since the topochemical photoreaction proceeds under the strict crystal-lattice-control, and since the molecular arrangement in crystals is strongly influenced by any slight modification of the chemical structure of the reactants, the topochemical behavior of unsymmetrically substituted diolefin crystals varies strikingly to give several types of monocyclic dimers, tricyclic dimers, oligomers, and/or polymers.[1,2]

In previous papers we have reported that each compound of ethyl 4-[2-(2-pyrazinyl)ethenyl]cinnamate[3] and *S*-ethyl-4-[2-(2-pyrazinyl)ethenyl]thiocinnamate[4] individually gave a crystalline linear polymer upon photoirradiation in the crystalline state, while these crystals formed a mixed crystal not only by co-crystallization from solution, but also by simple grinding of the two component crystals.[5] The photoreaction of the mixed crystal gave a highly crystalline copolymer with high molecular weight. Since the two components are isomorphous to each other at an X-ray crystallographic level,[3,4] the high tendency for mixed crystal formation seems to be caused by the similar crystal structure of the two components. In any event, this result indicates that simple grinding might become a general method for the preparation of mixed crystals as well as recrystallization from solution. On the other hand, ethyl and propyl $\alpha$-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates formed a mixed crystal upon recrystallization from solution, although their lattice constants are different from each other and the crystal structure of the mixed crystal is quite different from those of the homocrystals.[1]

In this paper, we report on the formation of a mixed crystal of ethyl and propyl $\alpha$-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates (**1a**, **1b**) by simple grinding, and discuss the influencing factors of the growth of a mixed crystal from a mechanistic point of view.

## Experimental

**General.** Infrared spectra were recorded on a JASCO IR-810 spectrophotometer, and $^1$H NMR spectra were measured on a JEOL PMX-60SI or a JEOL GX-400 instrument. The melting points were measured using a Laboratory Devices Mel-Temp and are uncorrected. DSC and TG curves were recorded on a Shimadzu DSC-50 and a TG-50 instrument, respectively, under a nitrogen stream with a heating rate of 10°C min$^{-1}$ for ca. 5 mg of the sample. X-ray powder diffraction analyses were carried out with a Rigaku Rotaflex RU-200 spectrometer ($\lambda$=1.54184 Å). High-performance liquid chromatography (HPLC) was performed on a steel column (4 mm×250 mm) packed with LiChrosorb Si 60 (7 μm; Merck and Co.) at a flow rate of 1.0 ml min$^{-1}$ using ethyl acetate as an eluent; the absorbance at 263 nm was monitored on a Shimadzu SPD-2A spectrophotometric detector. A calculation of the area was performed using a Hitachi D2500 Chromato-Integrator.

Compounds **1a** and **1b** were prepared by methods described in a previous paper;[6] **1a** and **1b** were recrystallized from ethanol and 1-propanol, respectively.

**Preparation of Mixed Crystal by Grinding.** A mixed crystal of **1a** and **1b** upon grinding (**1a·1b** (grinding)) was prepared from 244 mg (1 mmol) of **1a** and 256 mg (1 mmol) of **1b** by grinding together 3600 times with an agate mortar and a ceramic pestle at room temperature. The grinding rate was kept at one time per second. Sampling was undertaken after grinding 300, 450, 600, 750, 900, 1800, and 3600 times.

**Photoirradiation of the Ground Mixture.** A ground mixture (1—3 mg) was sandwiched between quartz plates and irradiated with a 500-W super-high-pressure mercury lamp (Ushio USH-500D) through a Kenko L42 filter (wavelengths>410 nm) until the yellow color of the mixture disappeared (30—60 min were required). The plates were cooled by an ice bath during the irradiation. The photoproduct was determined to be a mixture of dimers **2a**—**d**, **3a**, and **3b** by $^1$H NMR and HPLC analyses.[1] The molar fraction of the mixed crystal was calculated on the basis of the ratio of the dimers, since the topochemical photoreactions of either homocrystals, **1a** and **1b**, and mixed crystal **1a**·**1b** (solution) gave dimers **3a** and **3b**, and **2a**—**d** in quantitative yields, respectively.[1,7,8]

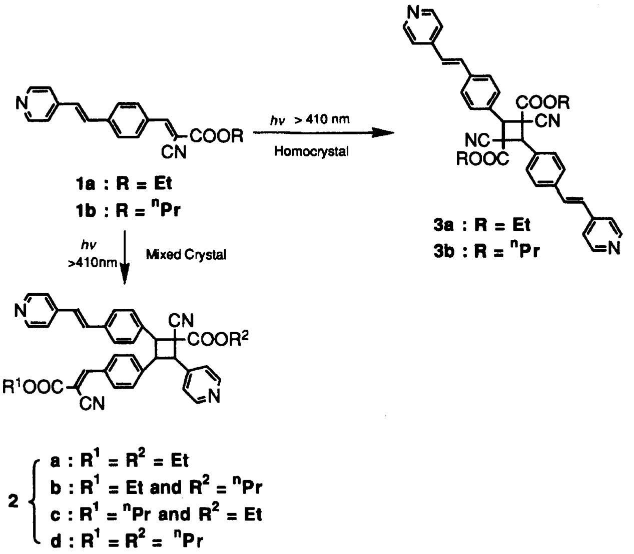
**Annealing of Ground Mixture.** A ground mixture (100 mg) was put into two-necked round-bottom flask filled with argon gas, and dried with $P_2O_5$. The flask was heated with an oil bath at 70±1 or 90±1°C. There observed no apparent change in the finely divided shape of the mixture after annealing. Samples were taken out from the top of the flask and irradiated with UV light, as described above.

**Humidity Effect.** Two portions of a 900-time ground mixture were separately put into two sample tubes. One of them was dried over silica gel; the other was filled with water-saturated air. The two tubes were kept in the dark at room temperature for one week; no apparent change in finely divided shape was observed for the samples upon standing. Then, the X-ray powder diffraction patterns were measured.

## Results and Discussion

**Mixed Crystal Formation by Grinding.** In our previous study concerning the topochemical behavior of ethyl 4-[2-(2-pyrazinyl)ethenyl]cinnamate[3] and *S*-ethyl-4-[2-(2-pyrazinyl)ethenyl]thiocinnamate,[4] we have found that a photoreactive mixed crystal could be prepared from the two compounds not only by recrystallization from solution but also by simple grinding of a mixture of the homocrystals in solid state.[5] Moreover, we have recently reported that recrystallization of a mixture of **1a** and **1b** from ethanol afforded mixed crystal **1a**·**1b** (solution) in a wide range of molar ratio, in which two molecules of **1a** and/or **1b** formed a pair, and that four kinds of bent-type dimer **2a**—**d** were quantitatively produced in a ratio of 1:1:1:1 upon photoirradiation of **1a**·**1b** (solution) comprising equimolar amounts of **1a** and **1b**,[1] although homocrystals **1a** and **1b** were quantitatively converted into linear-type dimers **3a** and **3b**, respectively, under the same conditions (Scheme 1).[7,8] On the basis of these facts, it is expected that a mixed crystal is also formed from **1a** and **1b** by simple grinding, as was observed for a combination of ethyl 4-[2-(2-pyrazinyl)ethenyl]cinnamate and *S*-ethyl-4-[2-(2-pyrazinyl)ethenyl]thiocinnamate.

When an equimolar mixture of **1a** and **1b** was ground 900 times by an agate mortar and a ceramic pestle and then irradiated with wavelengths longer than 410 nm, bent-type dimers **2a**—**d** (9% yield) and linear-type dimers **3a**, **b** (86% yield) were obtained, of which the structures were confirmed by comparing the high-performance liquid chromatogram (Fig. 1) and $^{1}$H NMR spectrum with those of authentic samples, although there was no change in the X-ray powder diffraction pattern before and after grinding (Figs. 2a and 2b) except for a broadening of the diffraction peaks due to atomization. The photochemical behavior of the ground mixture indicates that the formation of **2a**—**d** arises from a number of nuclei of mixed crystal formed by grinding, of which the X-ray powder diffraction peaks were hidden in the background of the ground mixture. Moreover, **3a** and **3b** might be derived from unchanged homocrystals **1a** and **1b**, respectively.



Scheme 1.

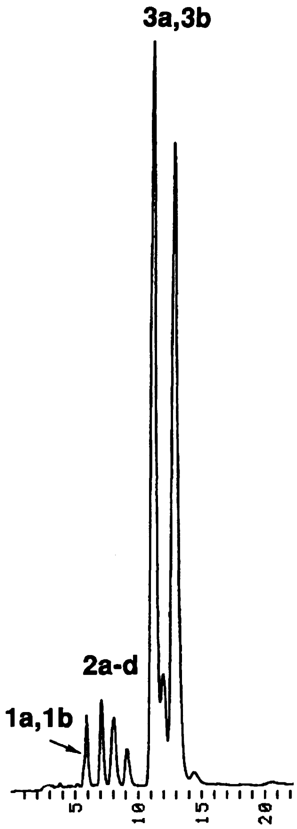


Fig. 1. HPLC chromatogram of the photoproducts of a mixture after grinding 900 rounds. There appeared three peaks derived from **2** in the chromatogram (the second peak did not resolved into two peaks).

Upon standing a ground mixture of **1a** and **1b** for 7 d at room temperature after grinding, new peaks appeared at $2\theta = 18.9°$ and 19.9° in the X-ray powder diffraction pattern (Fig. 2c). These peaks tended to coincide with the main peaks of ground **1a**·**1b** (solution)

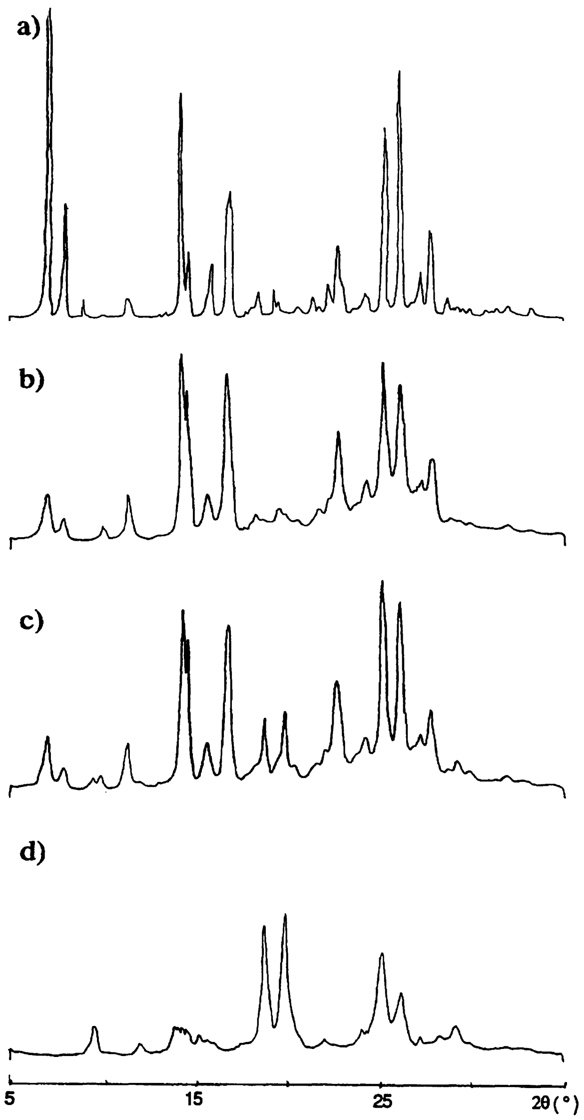


Fig. 2. Changes in the X-ray powder diffraction pattern of a ground mixture of **1a** and **1b** upon standing at room temperature; a) before grinding (simple mixture), b) just after grinding 900 rounds, c) after standing of the sample b) for 7 d, and d) mixed crystal **1a·1b** (solution) ground 900 rounds.

(Fig. 2d). All of these results concerning the X-ray powder diffraction patterns and the topochemical behavior of ground crystals strongly indicate that a number of mixed crystal nuclei are formed by simple grinding; then, upon standing at room temperature, they grow to 'crystals' which are detectable by X-ray diffraction analysis.

Although several papers have been written concerning the formation of complexes by grinding, such as quinhydrone crystal formation from 2,5-dimethylhydroquinone and *p*-benzoquinone crystals,[9] the formation of a mixed crystal *by grinding* is rare. In the formation of a complex such as quinhydrone by grinding, the driving force for the complex formation has been assumed to involve strong nonbonding interaction(s) between the two components, such as a hydrogen bond, an electrostatic interaction, and a charge-transfer interaction.[9,10] In contrast, in the formation of mixed crystal **1a·1b** (grinding), there should be no significant difference in the intermolecular interaction between the homocrystals and the mixed crystal, since the difference in the chemical structure is only of the ester group.

A DSC analysis of a simply blended equimolar mixture of homocrystals **1a** and **1b** showed a broad endothermic peak in the range 130—170°C with a heat of 3.6 kJ mol$^{-1}$.[11] On the other hand, a DSC analysis of mixed crystal **1a·1b** (solution) showed a single endothermic peak of the melting point at 145°C; the heat of fusion was 2.9 kJ mol$^{-1}$. The smaller endothermic value of heat absorption for the melt of mixed crystal **1a·1b** (solution), compared to that of a simply blended equimolar mixture of homocrystals **1a** and **1b** ($\Delta H$=0.7 kJ mol$^{-1}$), suggests that, during the formation of mixed crystal **1a·1b** (grinding), the entropical contribution is predominant in the change of the free energy, since mixed crystal **1a·1b** (solution) is less stable than a simply blended equimolar mixture of homocrystals **1a** and **1b** at room temperature. Therefore, the most possible driving force should arise from an increase in entropy, just as in the case of mixing two kinds of mutually soluble liquids.

**Effect of the Number of Grinding Times.** Since the nucleation of mixed crystal **1a·1b** was found to be caused by grinding, we examined the effect of the number of grinding times on the formation of mixed crystal **1a·1b** (grinding). Figure 3 shows plots of the number of grinding times ($N$) versus the molar fraction of mixed crystal **1a·1b** (grinding) in the ground mixture ($M$). The molar fraction was calculated as described in the experimental section on the basis of an analysis of the photoproducts. As can be seen from Fig. 3, the amount of mixed crystal **1a·1b** (grinding) in the ground mixture increased in proportion to the number of grinding times. In addition, after the mixture was ground 1800 times, very broad X-ray powder diffraction peaks were observed at $2\theta$=18.9° and 19.9°. These peaks were not observed during the early stage of grinding (Fig. 4), but became distinct after the mixture was ground 3600 times, indicating that the nuclei of mixed crystal **1a·1b** (grinding) increased and grew to a considerable extent.

Otsuka and Kaneniwa have reported that the crystal structures of chloramphenicol palmitate and indomethacin were transformed upon grinding due to polymorphism.[12] In contrast, the transformation of the crystal structures of homocrystals **1a** and **1b** in the present case was not detected by X-ray powder diffraction analyses, even after grinding 3600 times. Mixed crystal formation after a polymorphic transformation of **1a** and/or **1b** can thus be ruled out.

**Temperature Effect on Growth of the Mixed**

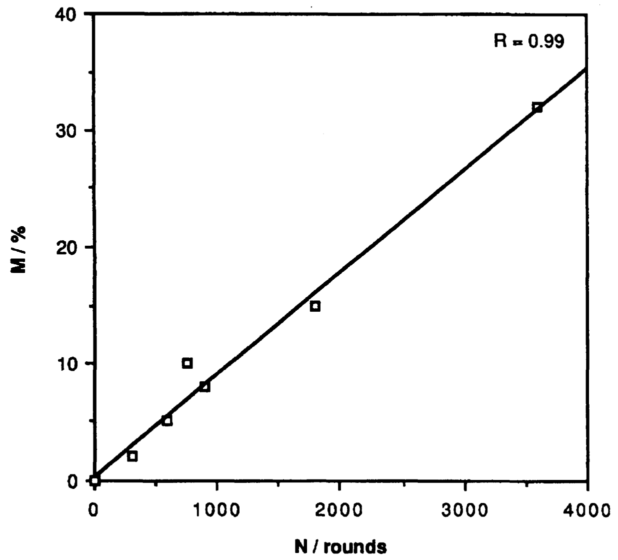


Fig. 3. Plots of the number of grinding times (*N*) versus the molar fraction of mixed crystal **1a·1b** (grinding) (*M*).

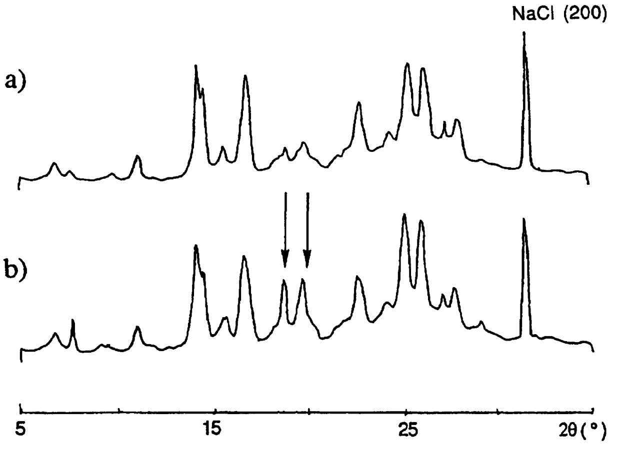


Fig. 4. Changes in the X-ray diffraction pattern during grinding; a) 1800 times, and b) 3600 times. NaCl was mixed as a reference.

**Crystal.** As is the case of crystal growth in solution, the temperature during standing of a mixture of **1a** and **1b** with the nuclei of mixed crystal **1a·1b** (grinding) may accelerate the growth rate of the mixed crystal. Table 1 shows the temperature (*T*) effect on the molar fraction of the mixed crystal (*M*) after annealing for 30 min at various temperatures. In each run, a mixture of **1a** and **1b** was ground 900 times at room temperature before annealing in order to prepare an appropriate amount of the nuclei of mixed crystal **1a·1b** (grinding) in the ground mixture. As the annealing temperatures are lower than the melting points of **1a**, **1b** and mixed crystal **1a·1b** (solution) (177.0—178.0°C, 148.5—151.0°C, and 145.5—151.0°C,[1,11] respectively), it is obvious that the annealing temperatures affected only the topochemical growth of mixed crystal **1a·1b** (grinding). The result in Table 1 shows that a higher temperature causes faster growth of the mixed crystal.

Table 1. Yields of the Mixed Crystal after Annealing for 30 min at Various Temperature[a)]

| $T$/°C | $M^{b)}$/% |
|---|---|
| 50 | 6 |
| 60 | 16 |
| 70 | 27 |
| 80 | 41 |
| 90 | 65 |
| 100 | 71 |

a) A mixture was ground for 900 times at room temperature before heat treatment. b) The yield was determined on the basis of the yields of the photoproducts after irradiation.

Figure 5 shows plots of the annealing period (*t*) versus the molar fraction of the mixed crystal **1a·1b** (grinding) (*M*) upon annealing at 70 and 90°C. The curves were logarithmic; the molar fraction of mixed crystal **1a·1b** (grinding) increased almost linearly to the annealing period during the early stage, but changed asymptotically after the middle stage.

Moreover, a sharpening of the diffraction peaks was generally observed upon annealing of ground mixed crystal **1a·1b** (grinding). When an equimolar mixture of **1a** and **1b** was ground 3600 times and then heated under an argon atmosphere for 2 h at 70°C, its X-ray powder diffraction pattern became nearly the same as that of mixed crystal **1a·1b** (solution), with quite weak diffraction peaks arising from trace amounts of homocrystals **1a** and **1b**. In contrast, when ground only 60 times, the diffraction peaks of mixed crystal **1a·1b** (grinding) was hardly detected, even after annealing for

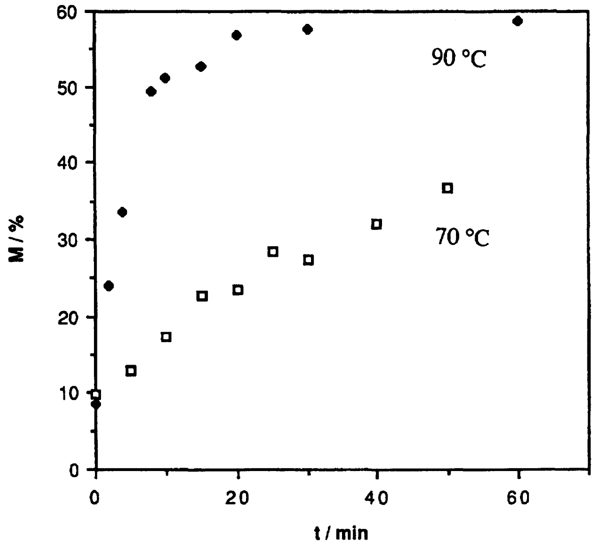


Fig. 5. Plots of the period for annealing (*t*) versus the molar fraction of the mixed crystal (*M*). □ : annealing at 70°C, ◆ : annealing at 90°C.

3 h at 80°C. These facts suggest that the upper limit of the growth of mixed crystal **1a·1b** (grinding) is determined by the initial amount of the nuclei of mixed crystal **1a·1b** (grinding) before annealing, and that the rearrangement of the molecules of **1a** and **1b** from each homocrystal to mixed crystal **1a·1b** (grinding) is the most important step for its growth and is accelerated upon heating.

**Effect of Humidity.** When ground mixtures of **1a** and **1b** were kept at room temperature for a week in two sample tubes, one of which was dried over silica gel and the other was filled with water-saturated air, the latter sample showed stronger X-ray diffraction peaks of mixed crystal **1a·1b** (grinding) than the former sample. These results indicate that water plays an accelerating role in the growth of mixed crystal **1a·1b** (grinding).

In contrast to the ordinary transformation of the crystal structure of an organic compound during dissolution,[13] the mixed crystal formation through dissolution may be ruled out in the present work, since both of **1a** and **1b** hardly dissolve in water. Although details of this phenomenon are still unsolved, moisture may have a certain lubricant effect on the formation and growth of mixed crystal **1a·1b** (grinding).[14]

**A Model for the Growth of Mixed Crystal 1a·1b (Grinding).** Patil and co-workers, and Dubey and Tiwari performed experimental analyses of the solid-state reactions of two components by using a capillary tube, in which one powdered component was placed on the other; they detected the formation of products by observing changes in the color around the boundary.[15,16] As a result, they concluded that the key step of these solid-state reactions can be rationalized to be a diffusional process of one component into the other. In each case, there were strong interaction(s) between the two components, such as a charge-transfer interaction, a hydrogen bond, and/or an electrostatic interaction, which can serve as a driving force(s) for mixing. As discussed before, however, in the case of the formation of mixed crystal **1a·1b** (grinding), the crystal structures solved by an X-ray crystallographic analysis showed that there is no distinct difference in the intermolecular interaction between each homocrystal and the mixed crystal.[1] This fact indicates that the present mixed crystal **1a·1b** (grinding) formation would be hard to explain in terms of the factor of intermolecular interaction, but by some other factor such as increase in entropy, which was suggested on the basis of DSC analysis as was mentioned before.

From the observed broadened diffraction peaks just after grinding of **1a** and **1b**, it is supposed that a disorder in or around the crystalline lattice of **1a** and **1b** in the ground mixture occurs to a large extent. In addition, a sharpening of the diffraction peaks with growth of mixed crystal **1a·1b** (grinding) on standing indicates that the molecular rearrangement from the disordered crystals to new ordered crystals is a rate-determining process for the formation of mixed crystal **1a·1b** (grinding). In a ground mixture, disordered microcrystals of **1a** and **1b** may exist as a fine conglomerate with a small amount of the nuclei of mixed crystal **1a·1b** (grinding). In the conglomerate, both **1a** and **1b** molecules would be smoothly supplied for the growth of mixed crystal **1a·1b** (grinding), since the disordered crystalline molecules are loosely trammeled and facile to move. Then, even though nucleation of mixed crystal **1a·1b** (grinding) is considered to be very slow, upon the formation of mixed crystal **1a·1b** (grinding), the growth of mixed crystal **1a·1b** (grinding) smoothly proceeds from these nuclei, in analogy with some crystal structure transformations brought about by grinding, in which nucleation is a prerequired step.[12] In other words, it is considered that the growth is initiated at the nuclei surface of the mixed crystal **1a·1b** (grinding); the growth rate of mixed crystal **1a·1b** (grinding) is represented as

$$\frac{\mathrm{d}M}{\mathrm{d}t} = KS, \tag{1}$$

where $M$ is the molar fraction of mixed crystal **1a·1b** (grinding) in a ground mixture, $t$ is time, $S$ is the surface area of mixed crystal **1a·1b** (grinding) at time $t$, and $K$ is a constant at a certain temperature.

Since the square root of the surface area of an object is proportional to the cubic root of its volume, and since $M$ should be proportional to the total volume of mixed crystal **1a·1b** (grinding) in a unit volume, Eq. 1 can be converted into

$$\frac{\mathrm{d}M}{\mathrm{d}t} = K'M^{\frac{2}{3}}, \tag{2}$$

where $K'$ is a constant at a certain temperature.

The solution of Eq. 2 thus gives

$$M^{\frac{1}{3}} = K''t + A, \tag{3}$$

where $K''$ and $A$ are constants at constant temperature.

As shown in Fig. 6 (plots of $M^{1/3}$ versus time ($t$) at 70°C), a linear correlation was observed up to a $t$ of around 15 min at 70°C. This result indicates that at the initial stage of growth of mixed crystal **1a·1b** (grinding) the growth rate at a certain temperature is in proportion to the surface area of the mixed crystal; namely, the growth rate is dependent only on the amount of mixed crystal **1a·1b** (grinding) in a ground mixture. When the molar ratio of mixed crystal **1a·1b** (grinding) increases to some extent, plots of $M^{1/3}$ versus time are off the straight line. This result may be explained in terms of the idea that as individual nuclei begin to come into contact with each other, the conditions for Eq. 1 are not fulfilled. Consequently, the rate of the growth is depressed by a saturation of the mixed crystal **1a·1b** (grinding) surface. Thus, these results strongly suggest that at the initial stage mixed crystal **1a·1b** (grinding) grows mainly from the surface of the nuclei.

As shown in Fig. 3 which gives a linear correlation

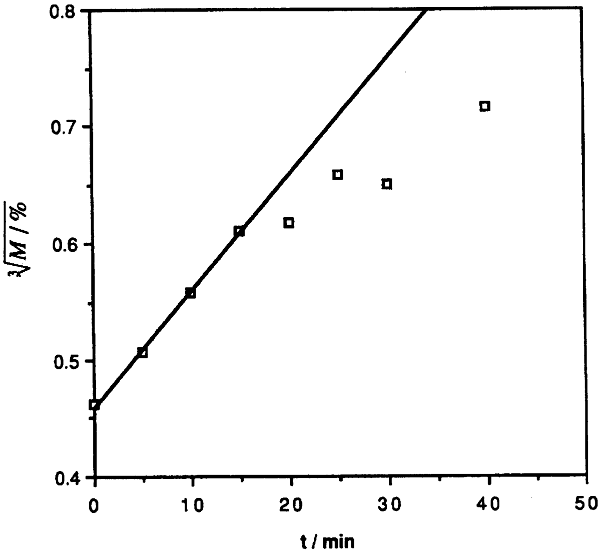


Fig. 6. Plots of the time ($t$) versus $M^{1/3}$. The temperature of annealing was 70°C. The $R$ factor of the straight line in first four plots is 1.00.

between the number of grinding times ($N$) and the molar fraction of mixed crystal **1a·1b** (grinding) ($M$), the initial amount of $M$ ($M_0$) should be dependent on $N$. Therefore, $M_0$ can be represented as

$$M_0 = BN, \tag{4}$$

where $B$ is a constant.

This correlation is preserved at least until $N$ becomes 3600 times.

On the other hand, the effect of temperature on the growth rate of the crystal is generally described[17] as

$$K = C\exp\,(-E/kT), \tag{5}$$

where $K$ is the rate of growth, $E$ is the energy for growth, $T$ is temperature, $C$ is a constant and $k$ is the Boltzmann constant.

Although it is possible to formulate the effects of the number of grinding times and the temperature by Eqs. 4 and 5, respectively, the effect of humidity cannot be correlated with the proper rate. We therefore represented the effect of humidity simply as $H$ based on the assumption that the humidity is constant. As a result, taking into account all of the factors which affect the growth of mixed crystal **1a·1b** (grinding), its behavior during the initial stage can be described by

$$M^{\frac{1}{3}} = H(C\exp\,(-E/kT)t + BN), \tag{6}$$

where the coefficients of $t$ and $HBN$ correspond to $K''$ and $A$ in Eq. 3, respectively. When ground for constant times, the total amount of mixed crystal **1a·1b** (grinding) can be represented by

$$M^{\frac{1}{3}} = D\exp\,(-E/kT)t + F, \tag{7}$$

where $D$ and $F$ are constants.

Pontius and Willis reported that during the initial stage of development, the growth rate of silver grains is in proportion to its surface area.[18] In the present study, the number of grinding times and the amount mixed crystal **1a·1b** (grinding) correspond to the exposure time on a film and to the amount of silver grain, respectively.

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11) A DSC analysis of **1a** showed two endothermic peaks at 143 and 175°C; the former arises from polymorphic transformation and the latter from the melting point. In DSC curve of **1b**, two endothermic peaks appeared at 146 and 147°C in a similar manner, which also arise from polymorphic transformation and the melting point, respectively. From the peak area, the sum of the heats of polymorphic transformation and melting for **1a** and **1b** were assumed to be 4.0 kJ mol$^{-1}$ and 3.8 kJ mol$^{-1}$, respectively.

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