is enriched in ^{13}C at the 1 position,[23] moderately strong signals should be observable from the 4-carbon of b. (The strongest signals will of course be produced from the 1-carbon of a.) In THF, the ^{13}C NMR spectrum of enriched I shows a strong signal at $\delta_{Me_4Si} = 57.4$ ppm and a weaker one at $\delta_{Me_4Si} = 48.2$ ppm, neither strong enough to be visible in preparations made using normal isoprene. These can be plausibly assigned to trans and cis 4-carbons respectively of structure b with trans predominating, using chemical shift correlations developed by Dorman et al.[24] Further work on b is clearly necessary, but the possibility that significant amounts of trans-1,4 units (as well as 1,2 units) in the polymer are produced from "reversed addition" active centers in polar solvents must be recognized.

The increase in rate of propagation with counterion size in diethyl ether is typical of diene polymerization in polar solvents and is the behavior expected of contact pairs. The principal cause is a decrease in activation energy. Once again it should be noted that two types of active center can occur in polar solvents which may have different reactivities toward monomer. If their proportion varies with counterion, this also could affect relative polymerization rates.

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Self-Stereoselective Polymerization of Racemic β-Chloroalkyl-β-propiolactones in the Solid Phases on Irradiation

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ABSTRACT: Ring-opening polymerizations of racemic β-dichloromethyl-β-propiolactone (DCPL) and racemic β-trichloromethyl-β-propiolactone (TCPL) in the solid phases on γ-ray or X-ray irradiation provide important information upon the effect of the monomer crystal lattices on the solid-state polymerizations, especially on the propagation step of polymerizations. Racemic DCPL and TCPL both form achiral crystals of the space group $P2_1/b$; two rectus (R) and two sinister (S) molecules in the unit cell compensate the optical activity. However, unlike isotactic poly(DCPL) and atactic poly(TCPL) obtained in solutions with organometallic catalysts, the racemic DCPL and TCPL crystals undergo solid-state polymerization to form new crystalline polymers, most likely syndiotactic poly(DCPL) and isotactic poly(TCPL). The distinct self-stereoselective polymerizations in both crystals are explainable in terms of the effect of the manner of molecular packing in the monomer crystals on the propagation of polymerizations. No detectable polymer is obtained from racemic β-monochloromethyl-β-propiolactone. Classification of solid-state polymerization modes for such racemic monomers is presented.

To date, extensive studies on radiation-induced solid-state polymerizations of a variety of cyclic monomers have been reported. We have investigated solely from the structural viewpoint characteristic features of the solid-state polymerizations of cyclic oligomers of formaldehyde $(-CH_2O-)_m$, where $m = 3$,[1] 4,[1,2] 5,[3,4] and 6,[5] diketene,[6] and β-propiolactone.[7] These monomers in the single-crystal states have been shown to yield three-dimensionally-oriented or uniaxially-oriented crystalline polymers on γ-ray or X-ray irradiation; the morphological structures of the resulting polymers, such as orientation of polymer chains and twin structure of polymer crystallites, reflect individually the crystal structures of the monomers. The process of "solid-state polymerization" is, however, complicated. It involves initiation, propagation, and termination steps of polymerization, and subreactions if they exist, followed by aggregation (crystallization) of polymer chains in a restricted environment. Therefore, we have been unable to obtain direct evidence concerning the way in which the propagation of polymerization may take place in the crystals at the molecular level. Two contrasting ideas are that (1) propagation of polymerization is really subjected to a monomer crystal lattice control and (2) that propagation takes place at local defect

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Scheme I

$[R_{\mathrm{mol}}]_{\mathrm{cryst}} \rightarrow \{RRRRRRR\ldots\}_{\mathrm{poly}}$ (isotactic) (1)

$[S_{\mathrm{mol}}]_{\mathrm{cryst}} \rightarrow \{SSSSSSS\ldots\}_{\mathrm{poly}}$ (isotactic) (2)

Scheme II

$[R_{\mathrm{mol}} + S_{\mathrm{mol}}]_{\mathrm{cryst}} \longrightarrow$

$\{RRRRRR\ldots\}_{\mathrm{poly}} + \{SSSSSS\ldots\}_{\mathrm{poly}}$ (isotactic) (1)

$\{RSRSRSRSRSRS\ldots\}_{\mathrm{poly}}$ (syndiotactic) (2)

$\{RRSSRRSSRRSS\ldots\}_{\mathrm{poly}}$, etc. (other regular) (3)

$\{RSSRSRRRSSRSS\ldots\}_{\mathrm{poly}}$ (atactic) (4)

sites; dislocations and stacking faults have been found to be crucially important in the dimerization reactions of anthracene and its derivatives.[8] In many vinyl monomers, monomer molecules in the vicinity of the end of a growing polymer chain seem to be released from the lattice control with a growing of the polymer chain.[9,10]

In this study, the attention will be focused on more direct information which will serve to clarify the role of monomer crystal lattices in the propagation of polymerization. One of the most suitable materials for this purpose would be a racemic monomer (mixture of optical isomers), because rectus (R) and sinister (S) molecules labeled with an asymmetric carbon atom, which we can distinguish from each other in the crystal lattices, will enable us to inspect the route of propagation of polymerization at the molecular level from the regularity of the monomer sequence in the resulting polymer chain. The materials examined in this study are racemic β-monochloromethyl-β-propiolactone (MCPL), β-dichloromethyl-β-propiolactone (DCPL), and β-trichloromethyl-β-propiolactone (TCPL). Among them, DCPL and TCPL were found to yield crystalline stereoregular polymers distinct from corresponding polymers obtained in solutions with organometallic catalysts. No detectable polymer was obtained from MCPL.

The present paper is concerned with the basic features of these solid-state polymerizations.

Scheme of Solid-State Polymerization of Racemic Monomer

Solid-state polymerization of such racemic monomers will be classified as follows.

Racemic monomers are crystallizable in two ways.

$$(R_{\mathrm{mol}} + S_{\mathrm{mol}})_{\mathrm{liq\ or\ solu}} \begin{array}{l} \nearrow\ [R_{\mathrm{mol}}]_{\mathrm{cryst}} + [S_{\mathrm{mol}}]_{\mathrm{cryst}} \qquad (\mathrm{I}) \\ \searrow\ [R_{\mathrm{mol}} + S_{\mathrm{mol}}]_{\mathrm{cryst}} \qquad (\mathrm{II}) \end{array}$$

If a racemic monomer forms mixed chiral crystals (optical resolution) (Scheme I), solid-state polymerization of these crystals yields an enantiomorphous pair of isotactic polymers so long as the polymerization takes place in a definite mode. This process makes it possible to obtain an optically active polymer without the help of a stereoelective catalyst, if the antipode monomer crystals are separated. On the other hand, if a racemic monomer forms achiral crystals (racemic lattice) (Scheme II) the resulting polymer assumes one of several configurations depending on the propagation route of polymerization in the monomer crystal; strictly speaking, the regularity of the resulting polymer would be polymerization-temperature sensitive and also depend on the degree of conversion. In the last three polymers, 2, 3, and 4, racemization is attained in the polymer chain itself. On the other hand, in the first polymer, 1, racemization will be achieved, as in the case of racemic monomer, either in the crystal lattice or between an enantiomorphous pair of whole crystallites depending on the crystallization scheme. Therefore, the case of Scheme II is especially of much interest for the present purpose.

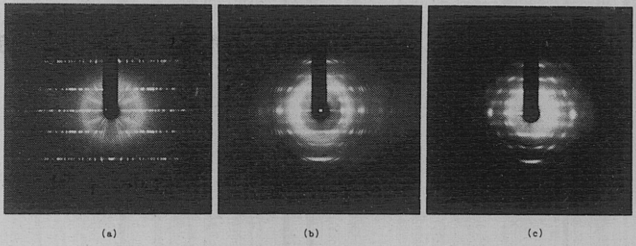
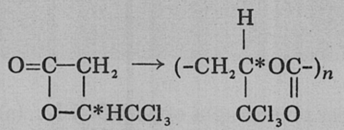


Figure 1. X-ray rotation photographs of TCPL: (a) pure monomer, (b) monomer + polymer (one of the as-polymerized materials), and (c) polymer (after removal of the residual monomer). The c axis of the original monomer crystal is the rotation axis in all photographs.

Solid-State Polymerization of β-Chloroalkyl-β-propiolactones

Ohse and Cherdron[11] reported that polymerization of TCPL in the melt with a variety of initiators gave a β-polyester. Tani and his co-workers[12] investigated stereoselective polymerizabilities of many kinds of racemic β-substituted-β-propiolactones by the use of organoaluminum and organozinc catalysts in solutions. According to their study, the isotacticities of poly(β-chloroalkyl-β-propiolactones) decrease with an increase in the number of chlorine atoms; the poly(MCPL) has the highest isotacticity and the poly(DCPL) is also isotactic, but the poly(TCPL) is eventually atactic.



$$\begin{array}{l} \mathrm{O{=}C{-}CH_2} \\ \quad | \qquad | \\ \mathrm{O{-}C^{*}HCCl_3} \end{array} \longrightarrow \left(\mathrm{-CH_2}\overset{\mathrm{H}}{\underset{\mathrm{CCl_3}}{\mathrm{C^{*}}}}\mathrm{O}\underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\mathrm{-}\right)_n$$

Experimental and Results

Racemic monomers, MCPL, DCPL, and TCPL, were kindly supplied by Tani laboratory. Slightly flat needle-like crystals of DCPL and TCPL were grown by sublimation or from ether solutions. MCPL was not obtained as single crystals available for the X-ray structure analysis. Solid-state polymerizations of these monomers were carried out at −78 °C for MCPL and at 0 and −78 °C for DCPL and TCPL with γ-rays from a cobalt-60 source of the Radiation Laboratory of this university at a dose rate of either 1.2×10^5 or 5×10^5 rad/h and for an irradiation time of 24 h. Unreacted monomers were then extracted, if necessary, with methanol. The relative polymerizabilities of these monomers in the solid phases are, at least qualitatively, proportional to those in solution.[12]

$$\mathrm{TCPL > DCPL \gg MCPL}$$

Actually no detectable polymer was obtained from MCPL under the experimental conditions used. However, the poly(TCPL) obtained in the solid phase is highly crystalline, differing from the poly(TCPL) obtained in solution, which is atactic and hence exhibits an amorphous X-ray pattern. The poly(DCPL) obtained in the solid phase is again crystalline when annealed as shown later but gives an X-ray fiber pattern different from that of the poly(DCPL) obtained in solution.

The X-ray photographs of the monomers and the resulting polymers were taken with nickel-filtered Cu Kα radiation. Especially, the X-ray photographs of the TCPL crystal for the crystal-structure analysis were taken at −100 °C in order to prevent polymerization on X-ray irradiation. Infrared spectra of these polymers were obtained by using the KBr-disk technique.

The solid-state polymerizations of DCPL and TCPL are characterized by the following structural features.

(1) Polymerization of a TCPL single crystal is accompanied by only a minor breaking up of the crystal (from Figure 1a to Figure 1b). The resulting polymer is highly crystalline and is uniaxially oriented along the c axis of the monomer crystal (Figure

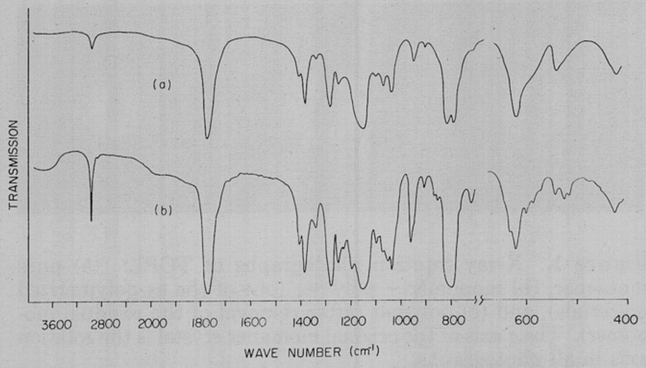


Figure 2. Infrared spectra of poly(TCPL): (a) atactic polymer obtained in solution, and (b) polymer obtained in the solid phase.

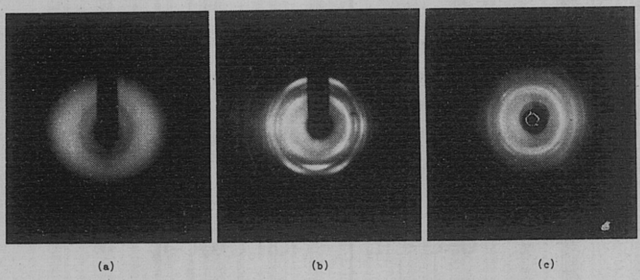


Figure 3. X-ray photographs of poly(DCPL): (a) as-polymerized polymer on X-ray irradiation at 15 °C, (b) after annealing of sample a, and (c) isotactic polymer obtained in solution.

1c). The fiber period of this polymer, 11.27 Å, is twice the *c* dimension of the monomer crystal, 5.602 Å. A comparison of an infrared spectrum of the polymer with that of the atactic polymer obtained in solution indicates that the polymer is again the β-polyester and exhibits many characteristic crystalline absorption bands (Figure 2).

(2) The polymerizability of DCPL in the solid phase is smaller than that of TCPL, but it is polymerization-temperature sensitive as are many other cases of cyclic monomers. Therefore, in addition to the γ-ray irradiated polymerization, the conversion to polymer on X-ray irradiation was followed at 15 °C, a few degrees below the melting point of DCPL, by taking successive X-ray photographs. A single crystal of DCPL tended gradually to break up to some extent on X-ray irradiation as exhibited by diketene[10] and finally, about 20 h later, gave a poor crystalline or rather amorphous X-ray pattern (Figure 3a). However, crystallization of this polymer on annealing above room temperature clearly showed that the polymer chains are aligned parallel to the *b* axis of the monomer crystal (Figure 3b). The fiber period of this polymer, 7.89 Å, does not bear reference to the *b* dimension of the monomer crystal, 6.32 Å. In addition, this X-ray fiber pattern is distinct from that of the isotactic polymer obtained in a solution whose fiber period is 11.55 Å (Figure 3c).

Structures of Monomer Crystals

The crystal data for racemic DCPL and TCPL are listed in Table I. The crystal structures of racemic DCPL and TCPL are shown in Figures 4 and 5, respectively. The details of the structure analyses will be reported in the near future. Both monomers crystallize into the monoclinic system of the space group $P2_1/b$ (first setting). This indicates unequivocally that crystallization of both monomers occurs in Scheme II; two *R* and two *S* monomer molecules in the unit cell compensate the optical activity. Despite the fact that both monomers crystallize into the same space group, the direct intermolecular C(O)···O contact in the TCPL crystal (3.12 Å) is between molecules of the same chirality, while in the DCPL crystal it is between molecules of opposite chiralities (3.15 Å); it has been recognized that the bond cleavage in lactone rings takes place at the C(O)–O bond in the formation of β-polyesters.[13,14] No other direct C(O)···O contacts are found

Table I
Crystal Data of Racemic DCPL and TCPL

	DCPL (10 °C) O=C-CH$_2$ | | O-C*HCHCl$_2$	TCPL (−100 °C) O=C-CH$_2$ | | O-C*HCCl$_3$
crystal system	monoclinic	monoclinic
space group	$P2_1/b$ ($hk0$, k = even; $00l$, l = even)	$P2_1/b$ ($hk0$, k = even; $00l$, l = even)
a (Å)	6.28	9.921
b (Å)	6.32	12.130
c (Å)	18.02	5.602
γ (deg)	117.0	93.77
N	4	4
density (calcd), g/cm^3	1.62	1.88

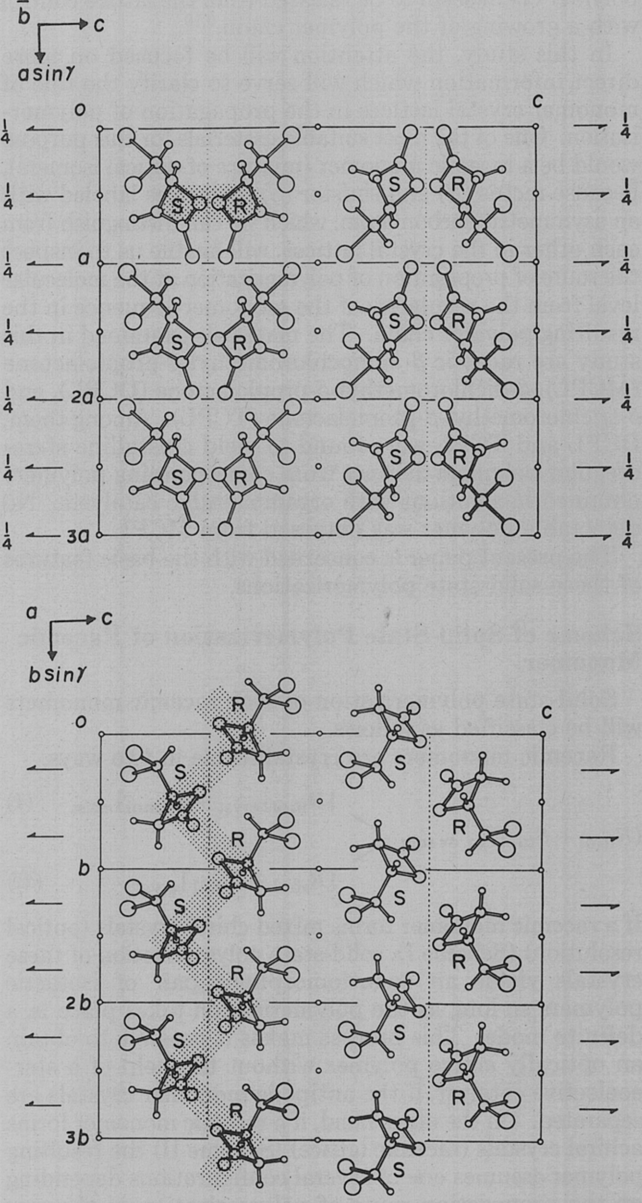


Figure 4. Crystal structure of DCPL: (top) *b* projection, and (bottom) *a* projection. Atoms are distinguished by the radii of circles, which decrease in order of Cl, O, C, and H.

for other molecular pairs in both crystals; the side groups, especially bulky chlorine atoms, prevent such direct contacts of the lactone rings. If the nearest neighbors are connected successively, as can be seen in Figures 4 and 5, by half-tone shadow, a route is formed along the *b* axis in DCPL, following a sequence of *SRSRSRSR*. . . (syndio-

Table II
Characteristics of Monomers and Polymers

	racemic MCPL	racemic DCPL	racemic TCPL
mp, °C	−11	21	43
monomer crystal	unknown	monoclinic $P2_1/b$ (racemic lattice)	monoclinic $P2_1/b$ (racemic lattice)
polymer obtained in solid phase	none detectable	syndiotactic, crystalline (uniaxially oriented along *b* axis of monomer crystal)	isotactic, crystalline (uniaxially oriented along *c* axis of monomer crystal)
polymer obtained in solution	isotactic, crystalline	isotactic, crystalline	atactic, amorphous

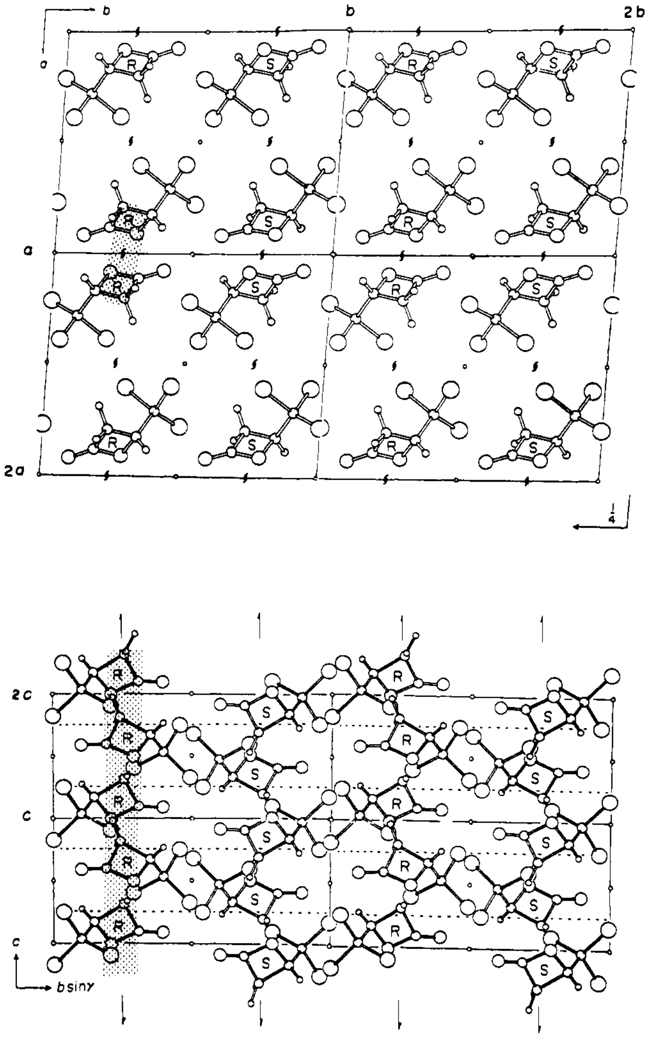


Figure 5. Crystal structure of TCPL: (top) *c* projection, and (bottom) *a* projection.

tactic), and along the *c* axis in TCPL, following a sequence of *RRRRRRR*... and of *SSSSSSS*... (isotactic). Both directions are in accordance with the observed polymer chain directions.

Stereoregularities of Resulting Polymers

Although detailed crystal structure analyses of both polymers obtained by the solid-state polymerizations will be necessary to verify their stereoregularities because of the absence of solvents for NMR measurement, the following considerations suggest that the poly(DCPL) is syndiotactic while the poly(TCPL) is isotactic.

(1) Figure 6 shows infrared spectra of three different samples of poly(DCPL): a, isotactic polymer; b, atactic fraction of sample a; and c, polymer obtained by the solid-state polymerization. These spectra are essentially the same, but distinct differences are seen in two regions of 1200–1300 and 500–650 cm^{-1}, in which samples a and c exhibit individually characteristic bands whose absorption intensities increase on crystallization. The spectrum of the atactic polymer exhibits an intermediate feature between a and c inclining toward c. These features therefore suggest that the poly(DCPL) obtained by the solid-state polymerization is syndiotactic. The fiber period of 7.89 Å composed of two monomer units is different from that of 11.55 Å composed of four monomer units in the isotactic polymer. This suggests that the fiber period of 7.89 Å in the solid-state polymerized polymer is composed of a pair of *S* and *R* monomer units. As we noted earlier, syndiotactic polymerization along the *b* axis of the monomer crystal is favorable from the consideration of the molecular packing in the monomer crystal. Therefore, it seems to be quite all right to consider that the solid-state polymerization of racemic DCPL takes place in Scheme II, eq 2.

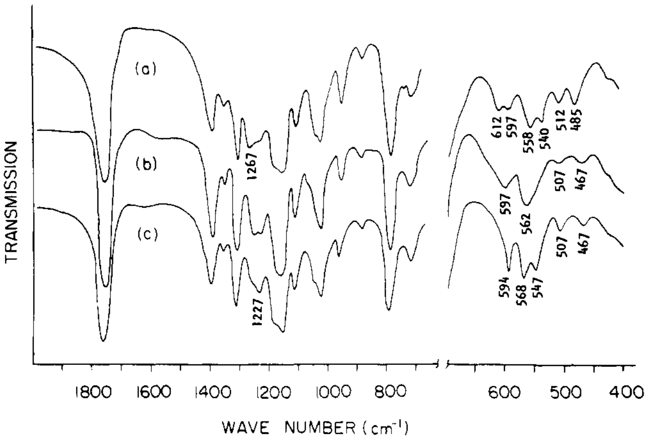


Figure 6. Infrared spectra of poly(DCPL): (a) isotactic polymer, (b) atactic polymer, and (c) polymer obtained by solid-state polymerization.

(2) The fiber period of 11.27 Å for the poly(TCPL) obtained by the solid-state polymerization seems an indication of a similar conformation of this polymer to the isotactic poly(DCPL) obtained in solution with the fiber period of 11.55 Å. Isotactic polymerization along the *c* axis of the TCPL crystal is quite favorable, as already mentioned. The polymerization scheme of racemic TCPL therefore appears to be Scheme II, eq 1. Alternatively, if the propagation of polymerization occurs at a specific defect site at which another type of polymer will be formed, what kind of polymer is expected? Referring to Figure 5, the most plausible defect, which will produce a stacking fault at which a different type of polymer will be formed, is a slip plane in the (100) plane with a Burgers vector of $^1/_2$[010], probably involving a slight change of the molecular orientation and of the position. This slip system will be generated by insertion or removal of a half-plane parallel to the (010) plane. In this slip system, *R* molecules on one side of this slip plane contact *S* molecules on

another side of this slip plane, instead of the contact between *S* and *S* (or *R* and *R*) molecules in the regular TCPL crystal. In this case again, the polymer chain will grow up along the *c* axis on the slip plane but assume syndiotactic configuration. However, there is no evidence that the resulting poly(TCPL) is syndiotactic.

In any event, the high crystallinities of both polymers obtained by the solid-state polymerizations, which are indicative of high stereoregularities of both polymers, tell us that the propagation of polymerization occurs in the definite routes extended over a considerably long distance. Especially in the case of DCPL, the pitch of monomer unit in the resulting polymer chain in the crystalline state (fiber period/2 = 3.95 Å) appreciably misfits the pitch of monomer molecule along the *b* axis of the DCPL crystal ($b/2$ = 3.16 Å). This might be greatly responsible for the breaking up of the monomer crystal due to polymerization to some extent and also compel the as-polymerized polymer chains to assume distorted conformations prior to crystallization on annealing. Another indication is that the crystal orientation of the poly(DCPL) is inferior to that of the poly(TCPL) in which the pitch of the monomer unit (fiber period/4 = 2.82 Å) fits quite well the monomer interval in the TCPL crystal ($c/2$ = 2.80 Å) (cf. Figures 1c and 3c). All of these arguments do not contradict the experimental results. Nevertheless, the sharpness of the X-ray reflections of the poly(DCPL) indicates that the regular syndiotactic sequences are extended, on the average, over 50 Å.

Because of the difficulty of preparing single crystals of MCPL, the crystal structure of MCPL is still unknown. It is therefore uncertain whether the infeasibility of solid-state polymerization of MCPL is the result of the molecular packing in the MCPL crystal or a reduced polymerizability of the MCPL molecule itself. Table II summarizes the characteristics of MCPL, DCPL, and TCPL concerning polymerizations in the solid phase and in solution.

The present finding is merely of the basic features on the solid-state polymerizations of racemic β-chloroalkyl-β-propiolactones. It is most likely that solid-state polymerizations take place preferentially at any crystal defects, as has already been pointed out by many workers, and yet the present study shows the major effect that the molecular arrangements in monomer crystals play in polymerization. In particular, the crystallographic dimensions of DCPL and of the resulting polymer do not bear reference to each other; from this aspect the reaction is not topotactic. Nevertheless, the formation of the high stereoregular polymer suggests to us that solid-state polymerizations of many other monomers can yield a variety of stereoregular polymers. More detailed studies on the solid-state polymerizations of the racemic β-chloroalkyl-β-propiolactones will be continued in order to find out functions which operate on these polymerizations.

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