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Kiyoshige Fukuda[a]; Yoshio Shibasaki[a]; Hiroo Nakahara[a]
[a] Department of Chemistry, Saitama University, Urawa, Japan

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Polycondensation of Long-Chain Esters of α-Amino Acids in Monolayers at Air/Water Interface and in Multilayers on Solid Surface

KIYOSHIGE FUKUDA, YOSHIO SHIBASAKI, and HIROO NAKAHARA

Department of Chemistry
Saitama University
Urawa, 338, Japan

ABSTRUCT

Polycondensations of long-chain esters of glycine and alanine in the monolayers spread at air/water interface and in the multilayers deposited on solid surface have been investigated by surface viscosity and IR spectra. These compounds form stable monolayers on neutral and alkaline subphases. The polycondensation can occur rather quickly in the monolayers at room temperature without any catalyst or initiator. The polymerization rate is markedly influenced by the area per molecule and the maximum polymerizability is obtained at the area somewhat larger than the condensed region. Furthermore, polymerizability in the multilayer prepared by Blodgett's technique is superior to those in the bulk powder at the same temperature and in the molten state at higher temperature. These results lead to the conclusion that the polycondensation is accelerated by the regular arrangement of the monomer molecules at the interface, where the functional groups are concentrated and situated most effectively for the reaction. Two probable mechanisms for the polycondensation of the long-chain esters of α-amino acids in the Y-type multilayer have been proposed.

INTRODUCTION

Polymerization reactions at the interface are of particular interest with respect to the effects of molecular orientation on the reaction rates and on the configuration or conformation of the resultant macromolecules [1-6].

This paper deals with polycondensation of long-chain esters of α-amino acids in the monolayers spread on water surface and in the multilayers deposited on solid surface. From the quantitative analysis of the reaction by infrared spectra, it has been found that the polycondensation is markedly accelerated by regular arrangement of the monomer molecules at the interface.

EXPERIMENTAL

Materials

Materials used in this study are given in Table 1.

These compounds were prepared by alcoholysis of the corresponding methyl esters in hydrochlorinated form with hexadecanol or octadecanol, followed by dehydrochlorination with ammonia and purified by repeated recrystallizations from ethanol solutions. The melting points of the racemic compounds are somewhat higher than those of the optical isomers.

Procedures

Monolayers of these compounds were spread from benzene solutions on aqueous subphases. Surface pressure was measured by a film balance of hanging plate type; its sensitivity was within

Table 1. Long-Chain Esters of α-Amino Acids

Compounds		Abbrev.	mp(°C)
Glycine hexadecyl ester	$NH_2CH_2COOC_{16}H_{33}$	Gly-C_{16}	51.3 - 51.8
Alanine hexadecyl ester	$NH_2\underset{CH_3}{CH}COOC_{16}H_{33}$	d-Ala-C_{16}	32.0 - 32.5
		dl-Ala-C_{16}	36.0 - 36.5
Alanine octadecyl ester	$NH_2\underset{CH_3}{CH}COOC_{18}H_{37}$	l-Ala-C_{18}	37.3 - 38.4
		dl-Ala-C_{18}	39.1 - 39.4

0.025 dyn cm^{-1}. Polymerization process in the monolayers was followed by the increase of surface viscosity and also by the analysis of infrared spectra of the scraped films. Surface viscosity was measured by the damping of rotatory oscillation of a platinum ring suspended on the monolayer covered water surface.

Multilayers were prepared by Langmuir-Blodgett's technique on calcium fluoride plate which had been precoated with ferric stearate monolayer. Under appropriate conditions, it was possible to deposit more than 300 layers of glycine hexadecyl ester in the alternating Y-type film within 15 minutes, during this period no appreciable polymerization has yet proceeded. Deposition conditions were as follows: the substrate water contains 10^{-3}M calcium chloride, the pH is adjusted in the range of 9 to 10 with ammonium hydroxide, the piston pressure is 30 dyn cm^{-1} and temperature is below 15°C. With alanine esters, succesive deposition of the multilayers is somewhat difficult. It was necessary to dry up water included between adjacent two layers before next dipping, unless a higher salt concentration, a higher pH value of about 11 and a lower temperature below 10°C were used. Polycondensation in the multilayers was followed by infrared spectra.

RESULTS AND DISCUSSION

Monolayer Properties

Surface pressure-area isotherms of the long-chain esters of α-amino acids depend markedly on pH values of the aqueous subphase, as shown in Fig.1. These compounds can form stable monolayers on neutral and alkaline subphases, but on acidic subphase the films tend to expand and to become unstable because of increasing solubility due to ionization of the amino group. The monolayer of glycine ester is a condensed type, whereas those of alanine derivatives are somewhat expanded and the transition from the expanded to the condensed films occurs at the molecular area of about 30 $Å^2$ or more. Some differences are observed between the racemic com-

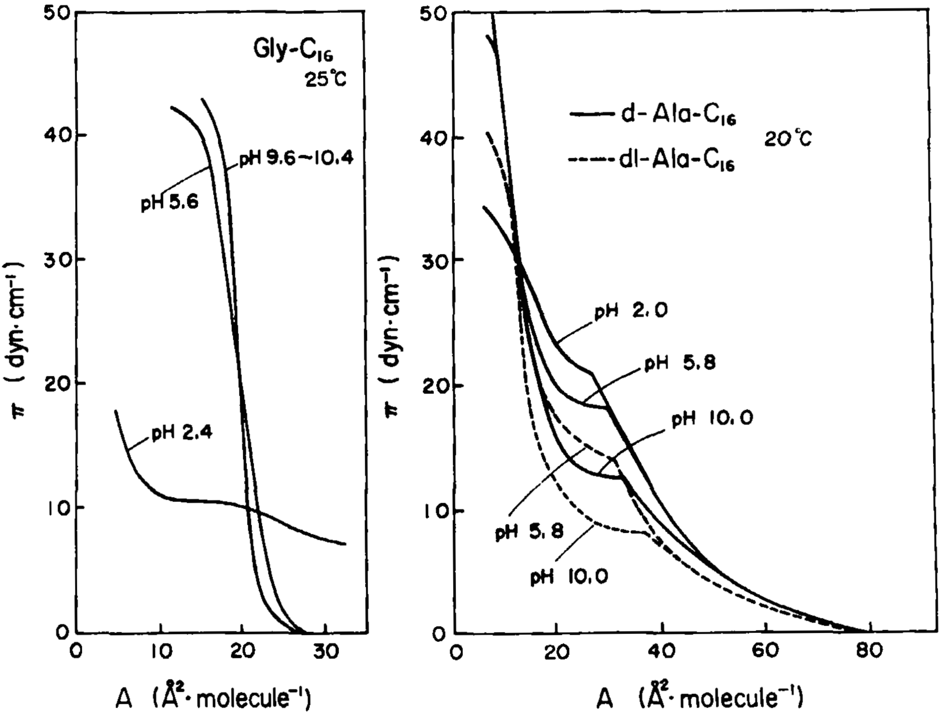


Fig.1. Surface pressure-area isotherms for hexadecyl esters of glycine (A) and alanine (B).

pound and the optical isomer; the racemic compound seems to be packed more closely.

Polycondensation in Multilayers

In Fig. 2, surface viscosity η_s is plotted as a function of time for hexadecyl esters of glycine and alanine spread on distilled water at various area per molecule. A remarkable increase of surface viscosity indicates that the polycondensation can occur rather quickly in the monolayers at the air/water interface without any catalyst or initiator. When the area per molecule was changed, the most significant increase of surface viscosity was

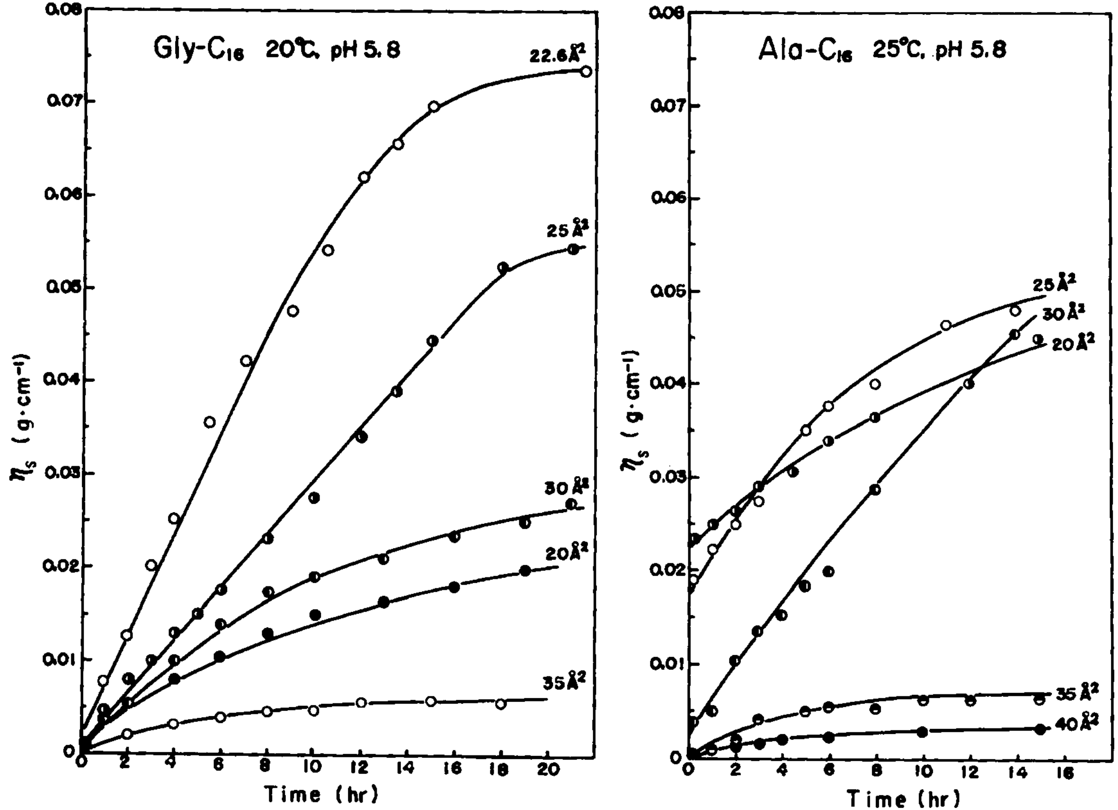


Fig.2. Change of surface viscosity (η_s) with time for hexadecyl esters of glycine (A) and alanine (B) spread on distilled water at various areas per molecule.

observed at the area of 22.6 Å^2 for glycine ester (A). On the other hand, with alanine ester (B) the rate of viscosity change was highest in the region of 25 to 30 Å^2 per molecule. On further compression or expansion of the monolayers, the increase of surface viscosity was retarded. These results suggest that there is an optimum condition of packing for monomer molecules to polymerize. However, the quantitative relation between the surface viscosity and the extent of polymerization is unknown at the present time. Therefore, infrared spectroscopy seems to be usefull for the kinetic study of the monolayer polymerization.

At different intervals of time, the monolayers were collapsed and scraped up from the interface onto the calcium fluoride plates and their IR spectra were obtained. Fig.3 shows the change of infrared spectra with time for glycine hexadecyl ester spread on distilled water. Of major importance is disappearance of the ester carbonyl stretching band at 1743 cm^{-1} and simultaneous appearance of the broader bands at 1645 and 1550 cm^{-1} which can be assigned to the amide I and amide II bands of polypeptide. With alanine octadecyl ester on neutral subphase at pH 7 to 8, similar changes of infrared spectra were observed. These spectral changes indicate a progress of the polycondensation with elimination of the long-chain alcohol in the monolayer, as shown schematically in Fig. 4. However, when the subphase is in more basic region from pH 10 up, appearance of the amide bands was not clear in spite of decreasing of the ester band. This suggests that hydrolysis of the long-chain ester may occur in competition with the polycondensation in higher pH region.

In order to use infrared spectroscopy as a quantitative measure of the polymerization, a series of artificial mixtures of the reactant (long-chain ester of amino acid) and products (poly-amino acis plus long-chain alcohol) in various compositions corresponding to the percentages of polymerization was examined by KBr disc method. The results showed that the integrated intensity of the ester band decreases linearly with increasing extent of polymeri-

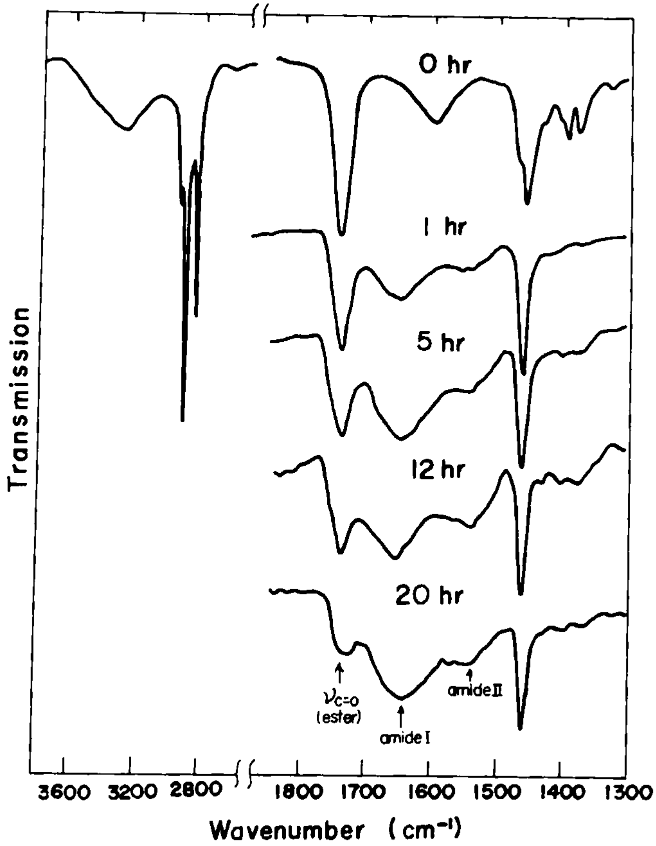


Fig.3. IR spectra for monolayer of glycine hexadecyl ester spread on distilled water and scraped up at different time intervals.

zation while that of the amide I band increases. With amide I band, however, the measurement of band intensity is less accurate because of an overlap with NH_2 deformation band of the monomer. On the basis of these data, the percentage of polymerization can be estimated by the quantity $100(A_0 - A_t)/A_0$, where A_0 and A_t are the integrated intensities of the ester band at start and time t,

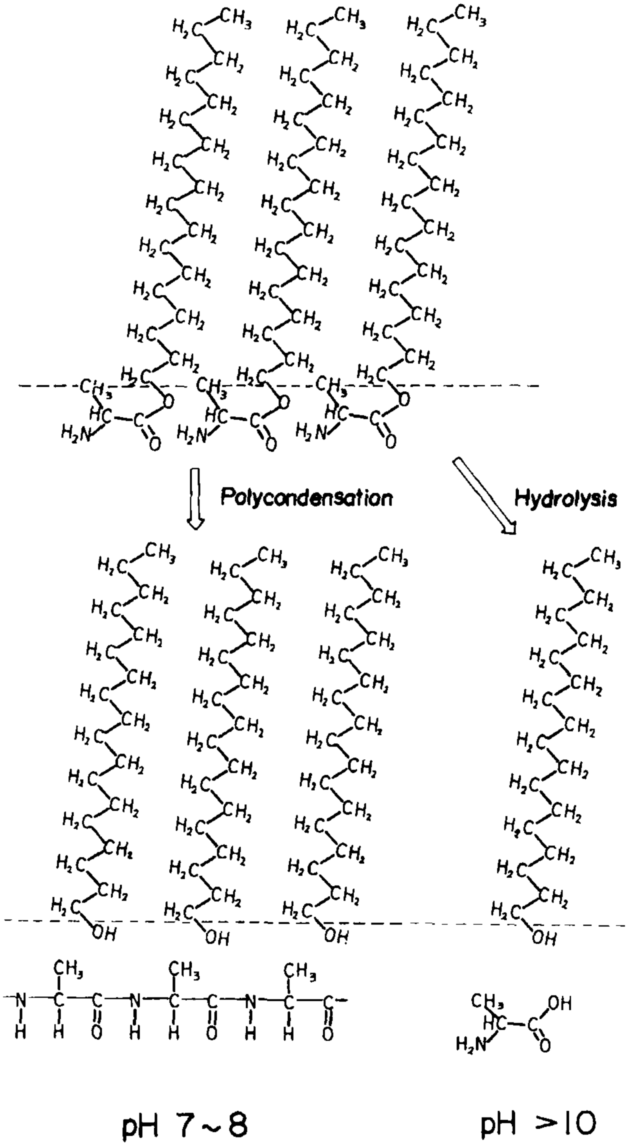


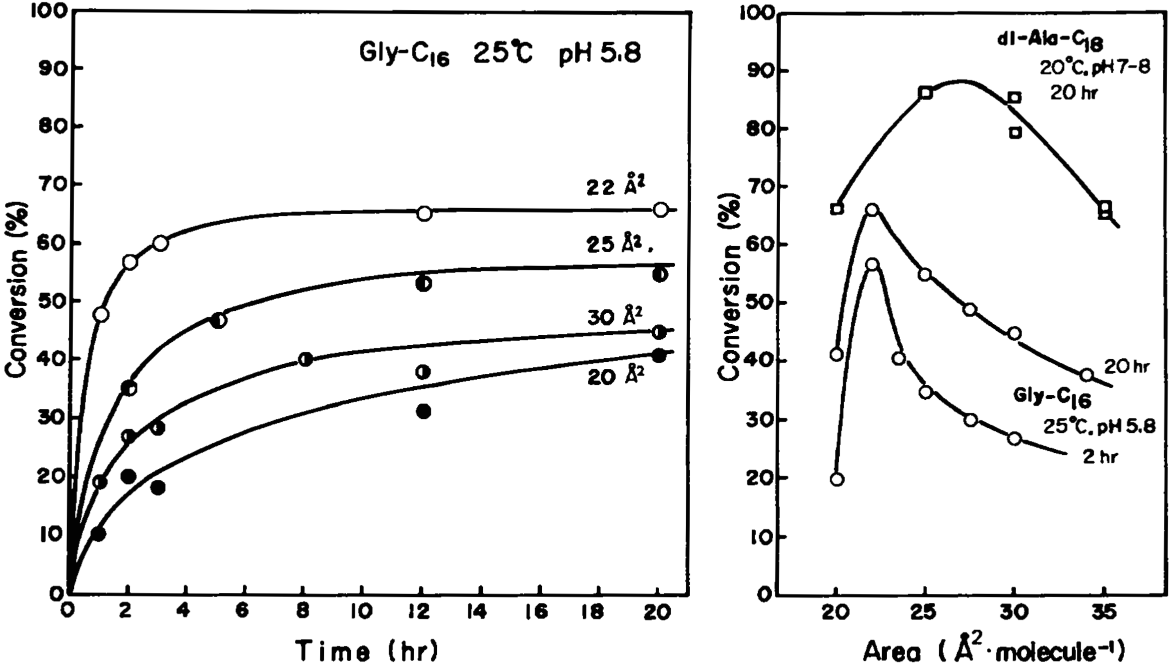
Fig.4. Schematic illustration for two probable reactions in the monolayer of long-chain ester of α-amino acid.

respectively. Thus, polymerization curves under various conditions can be compared.

In Fig.5(A), the percent conversion are plotted against the reaction time for glycine hexadecyl ester spread on distilled water at various areas per molecules. It is found that the rate of polymerization in the monolayer is markedly influenced by the molecular packing. In Fig.5(B), the conversions at 2 and 20 hours after spreading are plotted as functions of the area per molecule. The maximum polymerizability was obtained at the area of about 22 Å^2 for glycine hexadecyl ester. On the other hand, in the case of dl-alanine octadecyl ester the maximum polymerizability was observed in the region of 25 to 30 Å^2 per molecule. These results are in well agreement with those obtained from surface viscosity measurements. Thus, it has been confirmed that there is an optimum condition for the polymerization with respect to the packing and orientation of the monomer molecules at the interface, which corresponds to just before the condensed region, in other words, to the nearly close packing but with some freedom. Particular orientation and suitably close packing together with some rotational freedom of the monomer molecules in the monolayer seem to be very favorable for the polymerization reactions.

Polycondensation in Multilayers

Fig.6 shows the change of IR spectra for the multilayers of glycine hexadecyl ester kept at 40°C for various time periods. In the top trace obtained immediately after the deposition, the ester band at 1743 cm^{-1} is very strong, indicating no appreciable polymerization at this stage. As time advances the amide bands appear and increase at the expense of the ester band. These spectral changes represent a progress of the polycondensation in the multilayers. The bottom trace (full line) shows the spectrum obtained after dipping of the polymerized film into n-hexane for two minutes, in which the characteristic bands due to hydrocarbon chain are markedly diminished; this indicates the dissolution of unreacted



(a) (b)

Fig.5. Polycondensation in the monolayer of glycine hexadecyl ester spread on distilled water at various areas per molecule (A). Effect of molecular area on the polycondensation in the monolayers of long-chain esters of glycine and alanine (B).

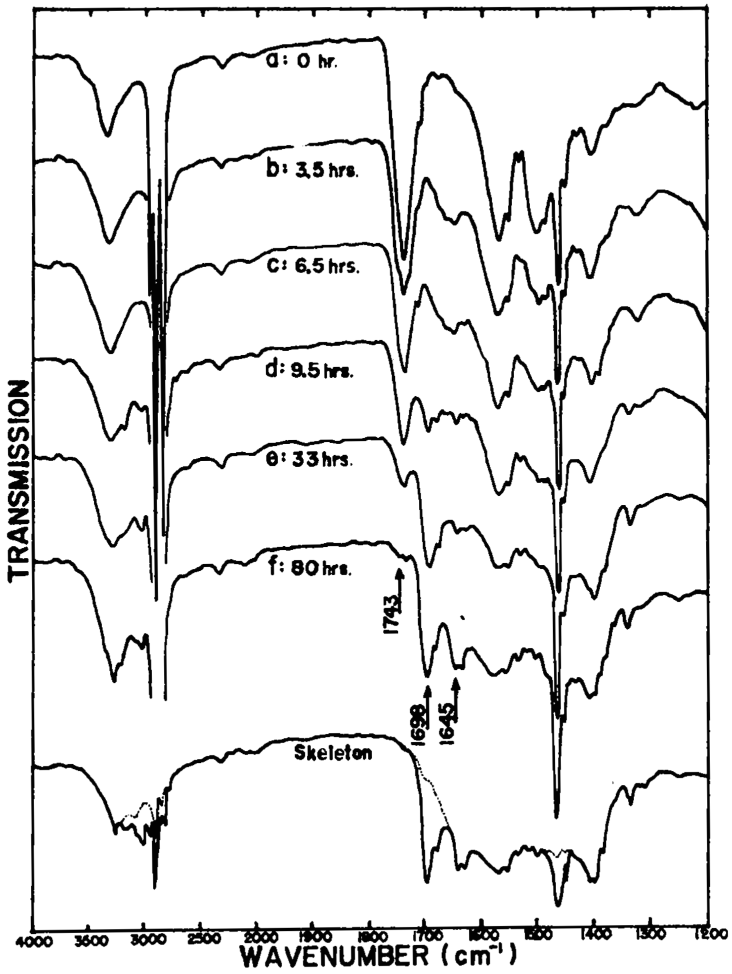


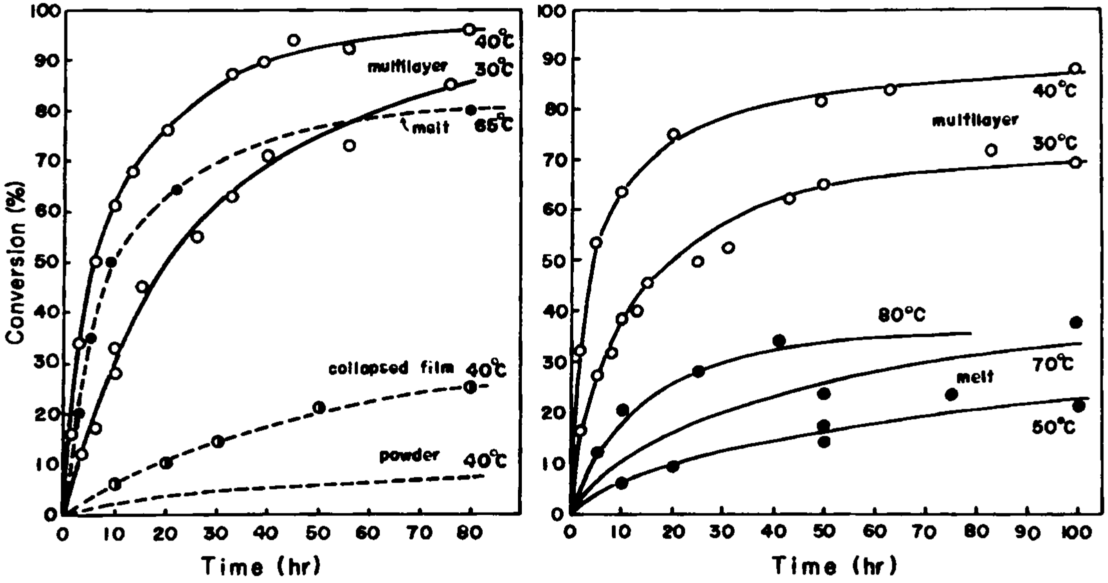
Fig.6. Change of IR spectra with time for the multilayer of glycine hexadecyl ester kept at 40°C.

monomer and resultant hexadecanol. Furthermore, in the spectrum obtained after additional dipping into ethanol for two minutes (dotted line) the band at 1698 cm^{-1}, as well as $-CH_2-$ bands, almost disappears, whereas the amide I and II bands remain invariably. From these facts, the band at 1698 cm^{-1} may be assigned to the oligomers of glycine.

In Fig.7, the rates of polymerization in various physical states are compared with each other by plotting the extent of conversion against the reaction time. Glycine hexadecyl ester in the multilayer shows a remarkable polymerizability at 30 to 40°C, below its melting point (52°C), whereas the rates of polycondensation in the bulk powder and in the collapsed film at the same temperature are very slow [Fig.7(a)]. Furthermore, it should be noted that the polymerizability in the multilayer at lower temperature (40°C) is superior to that in the molten state at higher temperature (65°C). Similar results were obtained with alanine octadecyl ester. The polymerizability in the built-up multilayer at 30 to 40°C is much higher than that in the melt at 50 to 80°C [Fig.7(B)]. These results lead to the conclusion that the polycondensation is accelerated by the regular arrangement of the monomer molecules at the interface, where the functional groups are concentrated and situated most effectively for the reaction.

On the other hand, the polymerization rate in the built-up multilayer is rather slow as compared with that in the spread monolayer on water surface at the optimum area (described in previous section) because the molecules in the multilayer deposited under high compression may be packed more closely than the optimum condition. Collating all the results, it is suggested that the best condition for the polymerization resembles a liquid crystalline state, which is very interesting in connection with the function of biomembrane.

Next, the reaction kinetics has been examined. As shown in Fig.8, when logarithms of the ratio of the initial and the remaining concentrations of the monomer [$\log(A_o/A_t)$] are plotted against the time, approximately straight lines are obtained up to about 70 % conversion for both the polycondensations of alanine octadecyl ester in the monolayer (A) and of glycine hexadecyl ester in the multilayer (B). Therefore, the polycondensation in the interfacial films is considered to proceed by the first-order reaction mechanism at least in the initial stage. The rate constant k at



(a) (b)

Fig.7. Comparison of the rates of polycondensation in various physical states for glycine hexadecyl ester (A) and alanine octadecyl ester (B).

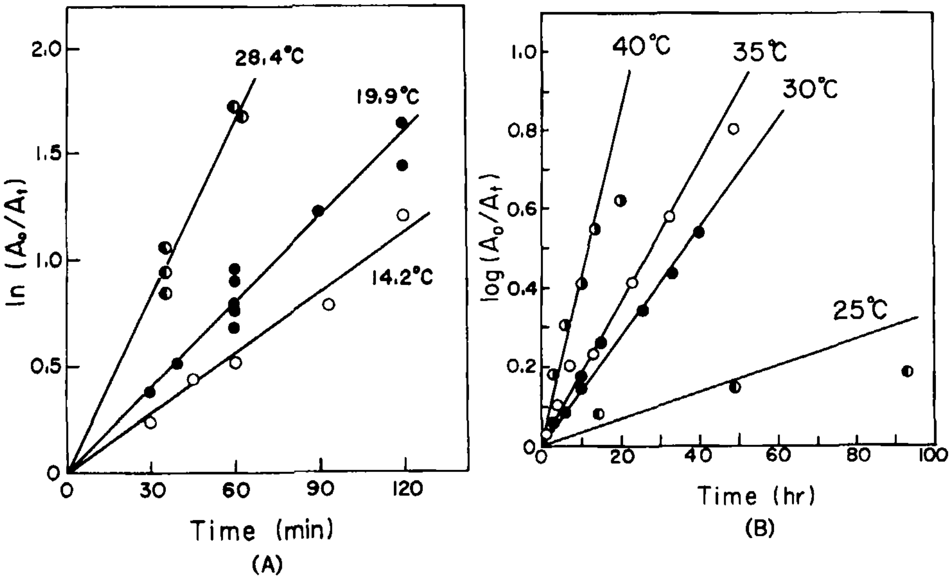


Fig.8. Plots of first-order reaction kinetics for the polycondensation of alanine octadecyl ester in the monolayer at 30 Å^2 per molecule (A) and glycine hexadecyl ester in the multilayer (B).

various temperatures can be estimated from the slope of these lines. From the Arrhenius plots of ln k versus 1/T, the activation energies were estimated at 14 kcal mol^{-1} for the polycondensation of alanine ester in the monolayer and at 20 kcal mol^{-1} for that of glycine ester in the multilayer. These values seem to be of same order with those of the corresponding reactions in the bulk system. Thus, it can be concluded that the acceleration of polycondensation in the interfacial films is attributed mainly to the frequency factor or the term of activation entropy.

Finally, two probable mechanisms for the polycondensation of the long-chain esters of α-amino acids in the Y-type multilayer have been proposed, as shown schematically in Fig.9. If the reaction propagates in a manner of sewing up alternately the functional

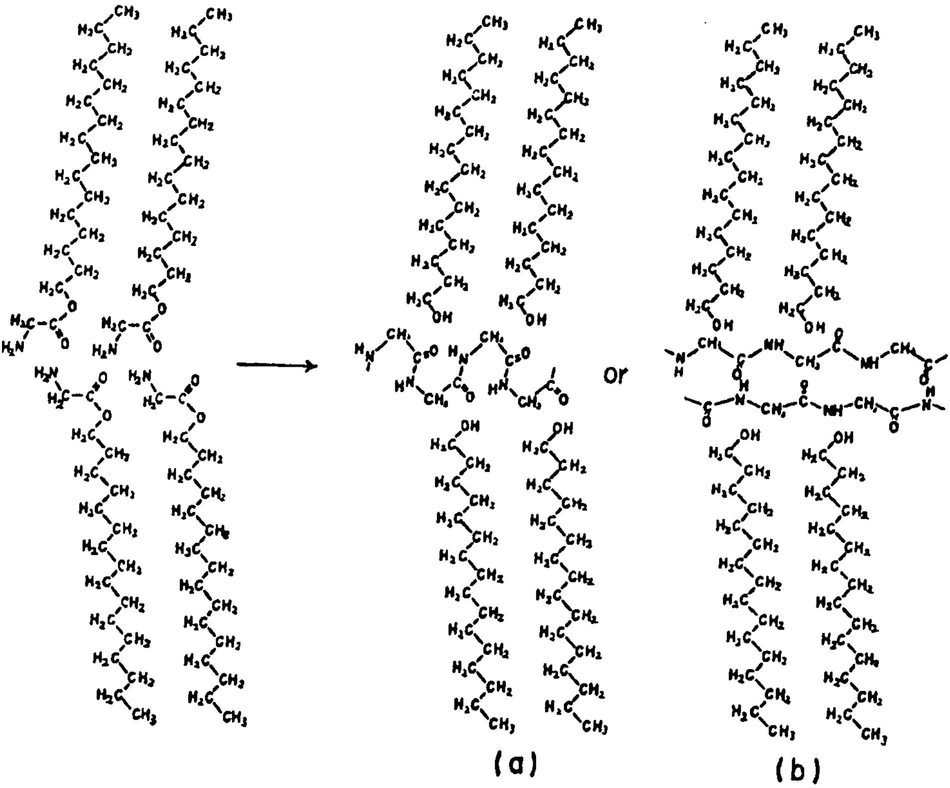


Fig.9. Schematic illustration of two probable mechanisms for the polycondensation in Y-type multilayer of long-chain ester of α-amino acid.

groups aligned head to head in the two adjacent layers, polypeptide chains of some helical structure are expected to be obtained (a). On the other hand, when the polycondensation can proceed two-dimensionally in each single layer of the built-up multilayer, as well as in the monolayer on water surface, poly-amino acids of extended zig-zag chain (β-form) may be formed (b). In fact, the amide I band in IR spectra for the multilayers after polymerization was observed at two different wave numbers, 1635 and 1645 cm^{-1}, depending on the deposition conditions. This seems to reflect the difference in chain conformation of the poly-amino acid obtained, but the details on this are left to problems in the future.

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