

Synthesis of Ultra Pure Long Normal Alkanes to Hexacohectane, Their Crystallization and Thermal Behavior

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ABSTRACT: Ultra pure long chain normal alkanes (abbr.: C_n , where n is the number of carbon atoms in a chain), C_{80} , C_{102} , C_{120} , C_{160} , were synthesized by Wurtz condensation. For samples of C_{120} and C_{160} , a once-folded chain crystal was formed by solution crystallization; thicknesses of the layer lamella were on an average 7.8 nm for C_{120} , and 10.0 nm for C_{160} , which equals to a half of the extended chain length for each molecular weight. In the DSC thermograms of the C_{160} crystals, an exothermic peak which indicates recrystallization to extended chain crystal following to melting of once-folded chain crystal, appeared clearly. Consequently, folding of normal alkane molecular chain was found to take place from about C_{120} .

KEY WORDS Higher Normal Alkane / Homologous Purity / Gel Permeation Chromatography / Wurtz Condensation / Once-Folded Chain Crystal / Extended Chain Crystal / Hexacohectane / Eicosahectane

One remarkable characteristic of flexible polymers is that they crystallize by chain folding. Since the first report on chain folding in solution crystallization of polyethylene (PE)¹ 40 years ago, many studies have been made on crystallization behavior and resulting crystal structures using well-characterized PE and also normal alkanes (abbr., n -alkanes) as model compounds. To elucidate the characteristics of the chain folding phenomenon ultra long n -alkanes such as C_{384} and C_{390} were synthesized by Wegner *et al.*² and Whiting *et al.*,³ respectively 1985. Unfortunately they could not give a definite answer enough yet, owing to limited amounts of the synthesized products and insufficient homologous purity.

Takamizawa *et al.*⁴ sought solution to the same problem by studying higher-order crystalline structure on low molecular PE fractions ($M_w/M_n=1.01-1.03$) located in the transition region from extended chain crystal to folded chain crystal. The relationship between average molecular weight and X-ray long period L for PE single crystals is in Figure 1. Dotted lines show lamella thickness corresponding to the number of folding, $f=0, 1, \text{ and } 2$, calculated from chain length. In this calculation, contribution of the folded portions to the thickness is neglected. At the low molecular weight end, the long period linearly increases, regardless of the crystallization solvent, with the chain length, and L is nearly in accordance with the calculation shown as dotted lines. However, L suddenly decreases when the molecular weight exceeds a critical value depending on the crystallization solvent; *i.e.*, the effects of chain folding are clearly recognized. As a whole, PE single crystals appear to have higher-order structures with integer numbers of folding following the calculated line except single crystals from fractions of 2000—2400. Takamizawa⁴ printed out that this discrepancy was attributable to polydispersity of samples.

It is very difficult to get a fraction with very narrow

distribution of molecular weight from simple fractionation. Thus, we synthesized ultra pure n -alkanes with chain length as long as possible as the model compound of PE. First, n -alkanes were synthesized by the Wurtz condensation of polymethylene-dihalide following a report of Carothers *et al.*⁵ Owing to insufficient purity of the carboxylic acid used as starting material, report⁶ was made only on the pressure dependence of the melting point of n -alkanes.

This paper reports the synthesis of high purity n -alkanes of C_{80} and C_{102} whose chain lengths are in the region corresponding to the lamella thickness of folded chain crystal of PE as well as C_{120} ⁴ and C_{160} where chain folding starts. The melting behavior of the prepared crystals is discussed based on results concerning the morphology, as well as higher-order structure of folded chain crystals.

EXPERIMENTAL

Materials

For sample synthesis, purified linear carboxylic acid and dicarboxylic acid free of homologue were used as starting materials with consideration to elongation of

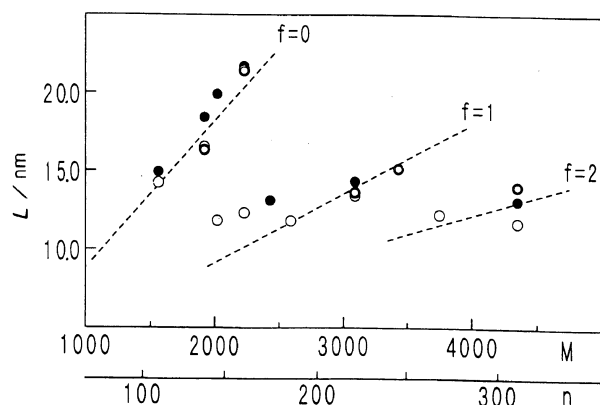


Figure 1. Correlation of long periods with molecular weights of polyethylene fractions. Crystallization solvents: ○, *p*-xylene (PX); ●, iso-amylacetate (IAAC); ⊙, hexadecane.

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* Sadly passed away. Will be greatly missed.

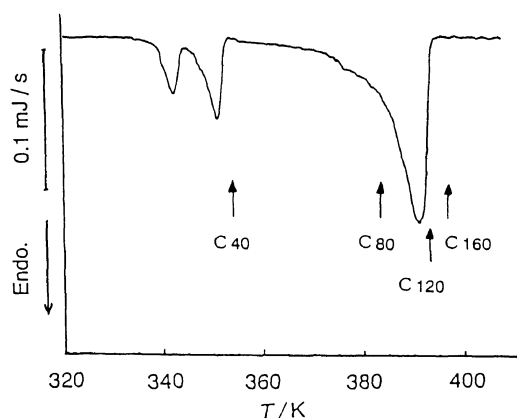
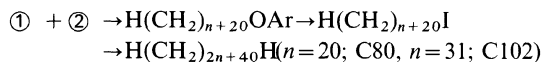
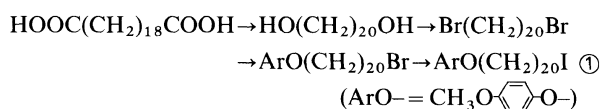


Figure 2. DSC thermograms for synthetic products by Wurtz condensation.

length by the Wurtz condensation⁵ of iodides. Icosanedioic acid (Okamura Seiyu Co.), as the starting material was purified as methyl ester by reported molecular distillation and recrystallization. Homologous purity was determined by a capillary gas chromatograph (GC) as 99.9% or higher.

The reaction scheme is as follows.



This is a coupling reaction of 1-iodo-20 (*p*-methoxyphenoxy)icosane $\textcircled{1}$ and iodo-alkane $\textcircled{2}$. Since difference of adsorption is large between the by-products ($\text{ArO}(\text{CH}_2)_{40}\text{OAr}$, $\text{H}(\text{CH}_2)_{40}\text{H}$) and unreacted materials, separation is possible by a column method. In this way, C80 and C102 were obtained with high purity.

For synthesis of C120 and C160, the iodide of the by-product $\text{ArO}(\text{CH}_2)_{40}\text{OAr}$, 1,40-diiodotetracontane was subjected to the Wurtz condensation for chain extension.

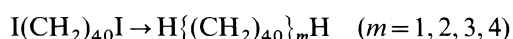


Figure 2 shows DSC thermograms of the alkanes prepared. The arrows indicate melting points of the corresponding *n*-alkanes. The mixture was refined by an adsorption column and GPC to get C120 and C160. Separation in GPC was performed at column temperature higher than 90°C using toluene or xylene as the elution solvent, and the 0.1% solution was isolated.

Homologous purity was analyzed by a Shimadzu GC14A capillary GC equipped with a column of SGE 25A Q5-HT-5-0.15 and data processor C-R6A. Carefully programmed temperature operation on the capillary GC ensured that an upper limit of the number of carbon atoms for *n*-alkanes to be analyzed by the capillary GC is located at around 110.⁸ The samples used in this work was found to have the following purities; C80, 99.4%; C102, 99.1%; C120 and C160, unanalyzable, while $\text{I}(\text{CH}_2)_{40}\text{I}$ before the condensation was of 98.9% purity.

Table I. Long periods and melting temperatures of ultra long *n*-alkanes^a

<i>C_n</i>	<i>L</i>	<i>L_{cal}</i>	<i>T_m</i>	<i>T_{mcal}</i>
	nm	nm	K	K
C80	10.6	10.5	382.8	382.8
C102	13.1	13.3	388.3	389.0
C120	7.8*			
	(15.0*)	15.6	(392.4)	392.7
C160	10.0*			
	(20.2*)	20.7	(397.5)	398.1

^a *L_{cal}*, *T_{mcal}*: the calculated from Broadhurst's equation. * Determined from shadow length on TEM photographs () determined from IAAC solution (*T_c* 365 K).

Measurements

DSC measurements were performed by a Rigaku DSC-8240B with a TAS-100 controller. The standard scanning rate of 0.5 K min⁻¹ and sample mass of about 1.00 mg were used. The temperature and heat of transition were calibrated as reported previously.⁷

The X-ray long period *L* for layered mat of the solution crystal was measured with a Rigaku Geigerflex 2027 diffractometer using Ni filtered Cu-*K_α* radiation.

TEM and SEM were made for observation of morphology with a Hitachi MS-5 and Nihondenshi JSM-T100, respectively.

RESULTS AND DISCUSSION

X-Ray Long Period and Melting Point of *n*-Alkanes

Table I gives values of X-ray long periods *L* and melting temperatures (*T_m*) of C80 crystal and C102 crystal prepared from 0.1% heptane solution by slow cooling method. Agreement of *T_m* values with those calculated from Broadhurst's equation⁹ indicates that the molecular chains were crystallized as the extended form. Figure 3(a) and (b) show TEM photographs of C160 and C120 crystals from 0.05% *p*-xylene (PX) solution (a) and the crystals from 0.05% isoamyl acetate (IAAC) solution (b) at 365 K. The crystals from PX solution were lozenge shaped, and their thicknesses determined from shadow length measurements of TEM photographs were with average 10.0 nm for C160 and 7.8 nm for C120 crystals, or half the extended chain length for each molecular weight. Long periods of C160 crystal and C120 crystal could not be measured due to insufficient sample amount, but formation of once-folded chain crystal was confirmed. The crystals of C160 and C120 from IAAC were like tree leaves, and similar to the extended chain crystals which Takamizawa *et al.*¹⁰ obtained previously from low molecular weight PE fractions. Toda¹¹ and Frank¹² reported that round-shaped PE crystals were obtained from solution crystallized at high temperature, and discussed the mechanism of crystallization. The values marked by * in Table I were obtained from the shadow length measurement of TEM photographs. Crystal thickness was on an average 20.0 nm for C160 and 15.0 nm for C120 crystals, corresponding to molecular chain length. This means the growth of extended chain crystals in IAAC.

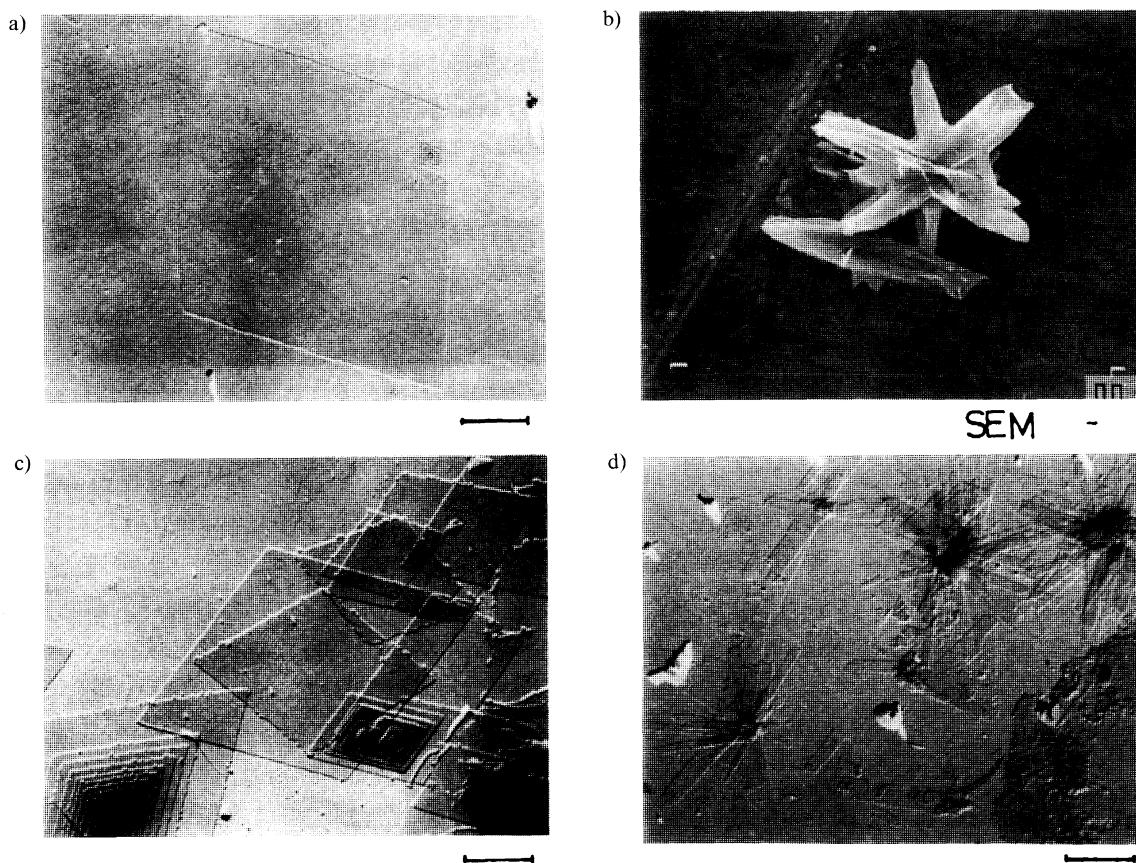


Figure 3. TEM and SEM photographs for the solution-crystallized samples. (a) C160 (PX); (b) C160 (IAAC); (c) C120 (PX); (d) C120 (IAAC) bar indicate 2000 nm.

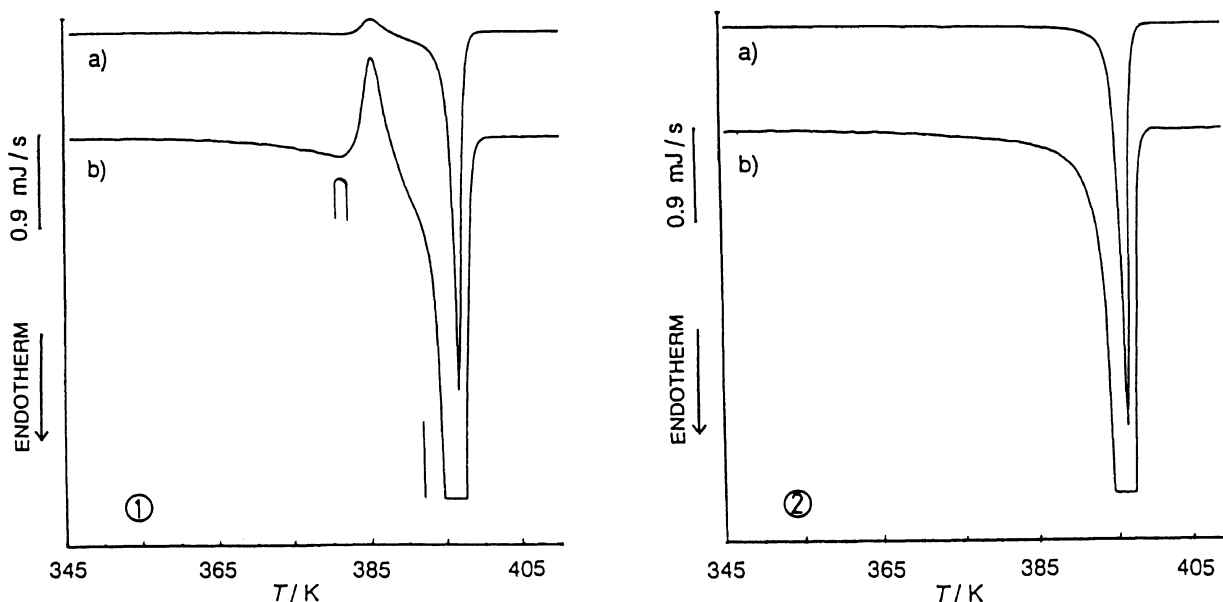


Figure 4. DSC thermograms for solution-crystallized samples of C160 heating rate 3 K min^{-1} . Crystallization-solvents: ① PX; ② IAAC. (a) normal drawing; (b) enlarged drawing ($\times 25$).

Polymorphism of Melting Process for Once-Folded Crystals of C160 and C120

Figure 4 shows DSC thermograms of the C160 crystals from PX (①) by quenching and from IAAC (②) solutions. Enlarged curves (b) are also shown for distinction of detailed thermal features, taking into account results of TEM observation. The peak at lower tempera-

ture side in Figure 4① should indicate the melting of folded chain crystal, and the following exothermic peak, the crystallization of extended chain form, which melted at a somewhat higher temperature. Ungar *et al.*¹³ reported similar results in the case of bulk crystals of $n\text{-C}_{294}\text{H}_{590}$. Figure 4② is the DSC thermogram for the crystal prepared from isothermal crystallization

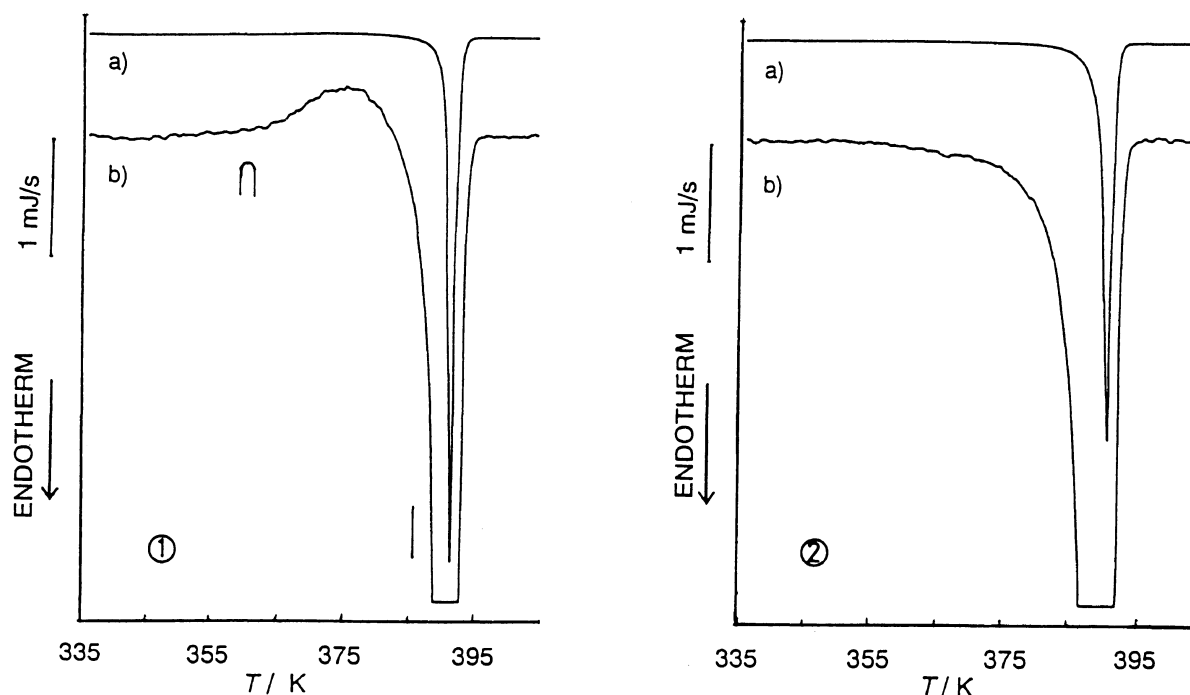


Figure 5. DSC thermograms for solution-crystallized samples of C120 heating rate 3 K min^{-1} . Crystallization-solvents; ① PX; ② IAAC. (a) normal drawing; (b) enlarged drawing ($\times 25$).

at the IAAC solution at 92°C for 216 hours, where the enlarged curve also indicates a single endothermic peak at 394.5 K . This T_m is higher by 2.3 K than that of the previous synthetic product⁶ and proves the effects of purification of starting material. The growth of extended chain crystals is confirmed. Figure 5 shows DSC thermograms for the C120 crystals when the sample was subjected to crystallization at the conditions as in the case of C160. The thermal behavior for C120 crystals was similar to that of C160; *i.e.*, the formation of once-folded chain crystal was confirmed to occur in the case of C120. The heating rate was 3 K min^{-1} as the case of C160 crystal. With the standard heating rate of 0.5 K min^{-1} , the endothermic peak of once-folded chain crystal became ambiguous, which suggests that stabilization from a metastable state of once-folded chain crystal to the extended chain crystal gradually occurs at such a slow heating rate. From this point of view, cross-linking experiment¹⁴ for amorphous parts was made by γ -ray irradiation for the purpose of inhibiting melt-recrystallization. However, this experiment was unsuccessful for C160 and C120 crystals due to the absence of a double bonds in the parts to be crosslinked. The C120 crystals from IAAC solution had an endothermic peak temperature of 392.4 K , which agrees with 392.7 K calculated from the Broadhurst's equation⁹ as in the case of C160 from IAAC solution.

Effects of Heat Treatment for Once-Folded Chain Crystals

Estimation of the melting point of once-folded chain crystals was made by heat treatment method since γ -ray irradiation was not applicable as mentioned above. Figure 6 shows DSC thermograms for heat treated C160 crystals and the C160 crystal as grown. The endothermic peak, indicated by the arrow, of the once-folded chain crystals became sharp and peak temperature became

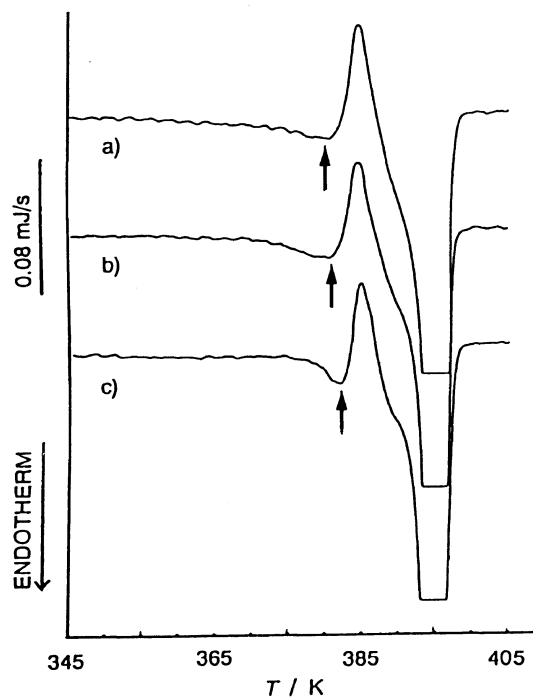


Figure 6. DSC thermograms for annealed samples of the solution-crystallized C160. Heating rate 3 K min^{-1} . (a) as grown sample compared with (b),(c); (b) $T_a 94^\circ\text{C}$, 30 min. (c) $T_a 104^\circ\text{C}$, 30 min.

higher with annealing time. The once-folded chain crystal here is considered "as grown" type shown schematically in Figure 7 which is a metastable state containing various defects during crystallization process indicated by arrows. Highly stable crystals like C1 can be measured directly for the crystal from IAAC as shown in Figure 4② and Figure 5②. In less stable crystals of C2, C3, and C4 which have Gibbs's free energy G in the order $G_{C4} > G_{C3} > G_{C2} > G_{C1}$,¹⁵ thermal motion starts at a considerably low temperature during heating and the

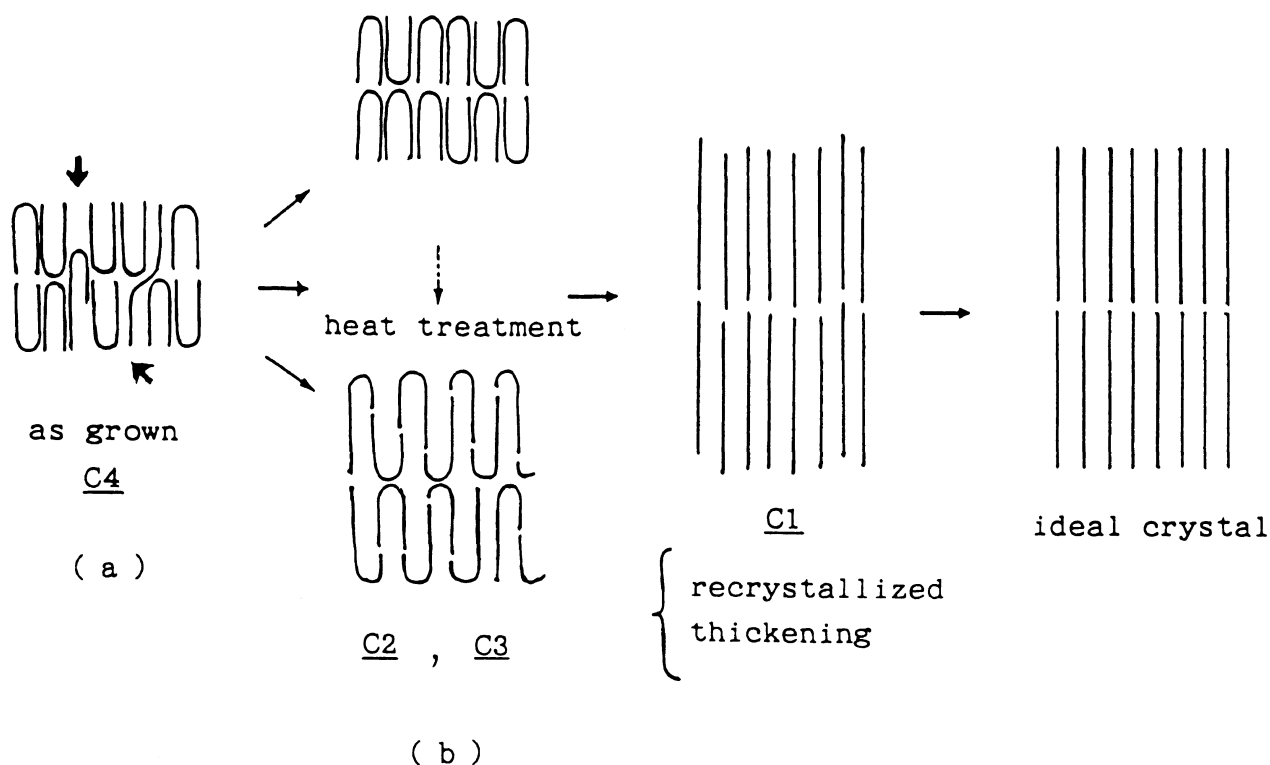


Figure 7. Schematic representation of molecular structure of once-folded chain crystals. (a) as grown type; (b) annealed type.

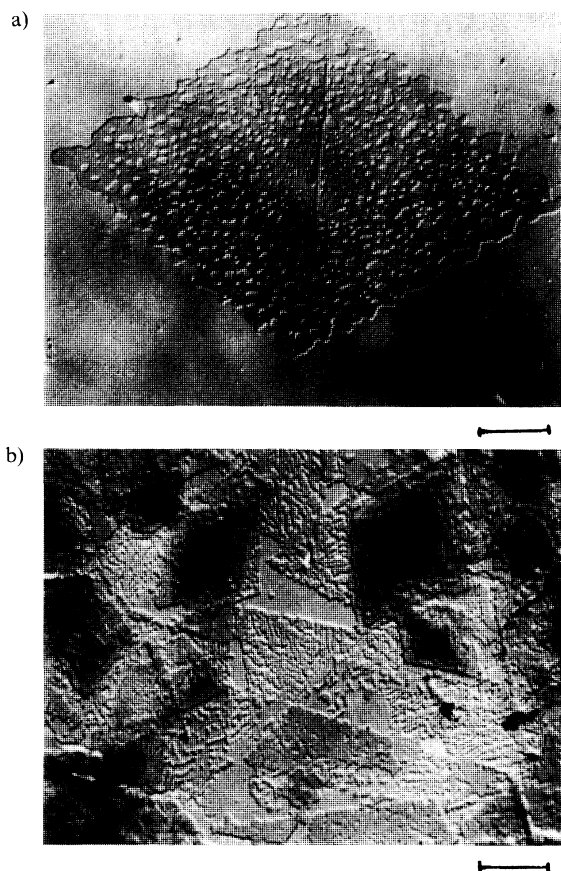


Figure 8. TEM photographs for annealing samples of solution-crystallized C160 and C120. (a) C160, T_a 94°C, 30min; (b) C120, T_a 84.5°C, 30 min bar indicate 2000 nm.

metastable crystals transform to more stable structure (C4→C3, C2) through the reorganization before melting. The enlarged DSC curve suggests that the rearrangement occurs at considerably low temperature. TEM photographs showing morphology of C160 and C120 crystals after heat treatment are shown in Figure 8. The specimens were prepared by hanging a crystal suspension on carbon film on mesh, drying the solvent of suspension enough, and subjecting this sheet mesh to heat treatment in an ample. Holes representing thickening of layer lamella observed by Hirai *et al.*¹⁶ in TEM were observed at many sites on the crystal surface. Thickness determined from shadow for C160 was about 7 nm larger than folded chain length. This might be ascribed to structural change accompanied by thickening although confirmation by the long period measurement of the heat treated crystal is required. The melting point of recrystallized sample (extended chain crystal) at higher temperature changed little with heat treatment, but the endothermic peak temperature rose, and enthalpy of fusion increased. It is quite possible that thickening of layer lamella occurs and subsequent recrystallization after melting, and remelting follows. Hence, determination of the melting point of once-folded chain crystal is considered to require change of structure (highly stable state) by heat treatment at a substantially low temperature. Discussion is possible without regarding partial melting or other matters frequently observed for a poly-disperse sample because of the high purity in this study.

CONCLUSIONS

C80, C102, C120, and C160 of high purity were synthesized by Wurtz condensation. For C120 and C160,

once-folded chain crystals were formed by solution crystallization. Folding of *n*-alkane molecular chain was found to take place from C120. The thickness of layer lamella was on an average, 7.8 nm for C120 and 10.0 nm for C160, or half the extended chain length. In the DSC thermograms of C160 crystals, an exothermic peak indicates recrystallization to extend crystal chain length following melting of once-folded chain crystals, which melted at some what higher temperature.

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REFERENCES

1. A. Keller, *Phil. Mag.*, **2**, 1171 (1957); W. W. Fischer, *Z. Naturforsch.*, **129**, 753 (1957); D. H. Till, Jr., *J. Polym. Sci.*, **24**, 301 (1957).
2. K. S. Lee and G. Wegner, *Makromol. Sci. Rapid Commun.*, **6**, 203 (1985).
3. L. Bidd and M. C. Whiting, *Chem. Commun.*, 543 (1985).
4. K. Takamizawa, *Netsusokutei*, **16**, 112 (1989); K. Takamizawa, Y. Urabe, and M. Hashiguti, *Polym. Prep. Jpn.*, **21**, 571 (1972).
5. W. H. Carothers, J. W. Hill, J. W. Kibby, and R. A. Jacobson, *J. Am. Chem. Soc.*, **52**, 527 (1930); W. Heitz, Th. Wirth, R. Peters, G. Strobl, and E. W. Fischer, *Makromol. Chem.*, **162**, 63 (1972).
6. K. Takamizawa, Y. Sasaki, K. Kono, and Y. Urabe, *Rep. Progr. Polym. Phys. Jpn.*, **19**, 285 (1976).
7. K. Takamizawa, T. Sonoda, and Y. Urabe, *Engineering Science Reports Kyushu University*, **10**, 363 (1989).
8. Y. Urabe and K. Takamizawa, *Polym. J.*, **26**, 283 (1994).
9. M. G. Broadhurst, *J. Res. Natl. Bur. Stand.*, **66A**, 241 (1962).
10. K. Takamizawa, Y. Urabe, and T. Hara, *Rep. Progr. Polym. Phys. Jpn.*, **12**, 179 (1969).
11. A. Toda, *Faraday Discuss.*, **95**, 127 (1993).
12. F. C. Frank, *J. Cryst. Growth*, **22**, 233 (1974).
13. G. Ungar, J. Stejny, A. Keller, and I. Bidd, M. C. Whiting, *Science*, **229**, 386 (1985).
14. K. Takamizawa, Y. Fukahori, and Y. Urabe, *Makromol. Chem.*, **128**, 236 (1969).
15. K. Takamizawa, "Series of Functional Polymer Materials," Vol. 3, Kyoritsu Publishing Co., Tokyo, 1993, p 296.
16. N. Hirai, T. Mitsuhashi, and Y. Yamasita, *Kobunshi Kagaku*, **189**, 33 (1961).