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SURFACE EFFECTS ON PHASE TRANSITION BEHAVIOR AND THERMAL POLYMERIZATION OF LONG-CHAIN DIYNOIC ACIDS IN MICRO DSC MEASUREMENTS

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Effects of metal surfaces, such as aluminium, silver and gold, on the melting behavior and thermal polymerization of long-chain diynoic acids having a diacetylene group at different positions were investigated by thermal analyses using DSC, TG and other methods. The surface effects of metals were significant in the order of Ag, Al and Au. These effects are attributable to the anchoring of carboxyl group on the surface by chemisorption, which leads to unfavorable condition for polymerization of heptadeca-2,4-diynoic acid. In the case of tricosa-10,12-diynoic acid, containing a flexible methylene chain inserted between COOH and C≡C–C≡ C groups, the anchoring of COOH on the metal surface causes rather favorable effect on the polymerization.

Keywords: diynoic acids, phase transition, surface effects, thermal polymerization

Introduction

Molecular arrangements and thermal properties of long-chain diynoic acids in thin solid films are of interest in connection with their polymerizabilities and non-linear optical properties of the resultant polydiacetylene films. Their thermal properties can be different from those of the bulk phase, because the ratio of surface-area to bulk-volume is very high. Recently, surface effects in the micro DSC measurements of long-chain vinyl compounds [1], stearic acid [2], and *n*-alkane [3] have been reported. In order to clarify the surface effects of various metals, such as Al, Ag and Au, this paper deals with the influence of sample weight on the phase transition behavior and thermal polymerization of diynoic acids containing a diacetylene group at different positions.

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Experimental

Heptadeca-2,4-diynoic acid:
$CH_3(CH_2)_{11}$–C≡C–C≡C–COOH, HD-2,4-DA, mp 58.8°–59.0°C and
tricosa-10,12-diynoic acid:
$CH_3(CH_2)_9$–C≡C–C≡C–$(CH_2)_8$COOH, TC-10,12-DA, mp 57.0°–57.2°C
was purchased from Tokyo Kasei Kogyo and used as received.

Thermal analyses were performed using Seiko Denshi Kogyo Models DSC20 and DSC100 differential scanning calorimeters and a Seiko Denshi Kogyo Model TG/DTA300 thermobalance. The linearity of sensitivity of the DSC apparatus was checked using indium as a standard. Scanning rates of 1–10 deg·min^{-1} were used and sample weights were varied in the range of 0.1–3 mg. For DSC measurement, powdered samples were sealed tightly in Al pans (50 μl). In other cases, the samples holded between the Au or Ag foils of 15 μm thick and 4 mm x 4 mm size were sealed in the Al pans. The sample weights were measured by a Mettler micro-balance AE163 and a Sartorius ultra microbalance 4504MP8. A newly developed TG/FT-IR apparatus of Seiko Densi Kogyo was used also.

Results and discussion

Thermal behaviors of long-chain diynoic acids

Thermal behavior of long-chain diynoic acids as a whole, including melting, polymerization and thermal decomposition, have been investigated by the simultaneous TG/DTA measurements. Figure 1 shows DTA and TG curves obtained for these monomers of 3.5 mg under a condition of 10 deg·min^{-1}, in nitrogen flow. In the DTA curve of HD-2,4-DA (Fig. 1(A)), a sharp melting peak at 57.0°C and a broad exothermic peak corresponding to a thermal polymerization at a temperature range of 100°–200°C were appeared. On further elevation of temperature a small exothermic peak due to thermal decomposition was observed at about 444°C. The thermal polymerization was accompanied with a weight loss of 8.8% as shown in the TG curve. When the heating rate was lowered to 1 deg·min^{-1}, thermal polymerization occurred at a lower temperature region of 90°–160°C and the weight loss was slightly increased to 9.6%. This weight loss may correspond to the thermal decomposition of carboxyl groups in HD-2,4-DA monomers of about 53%. According to examination of the IR spectra of the residual products of HD-2,4-DA heated up to 200°C, it was found that the absorption band at 2230 cm^{-1} due to a stretching vibration of C≡C–C≡C group remarkably decreased and $\nu_{C=O}$ (acid) at 1700 cm^{-1} almost disappeared, while $\nu_{C=O}$ (acid anhydride) at about 1780 cm^{-1} newly appeared. In addition, TG/FT-IR spectra measured under N_2 flow (not shown) have confirmed the decarboxylation of this monomer by the liberation of CO_2 gas. The 1,4-addition of diacetylene groups, in either linear type [4] or ladder type [5], may introduce a strong steric hindrance in the resultant polymer chain, which may lead to acceleration of the decarboxylation. On the other hand, with TC-10,12-DA monomer (Fig. 1 (B)) any peak for polymerization

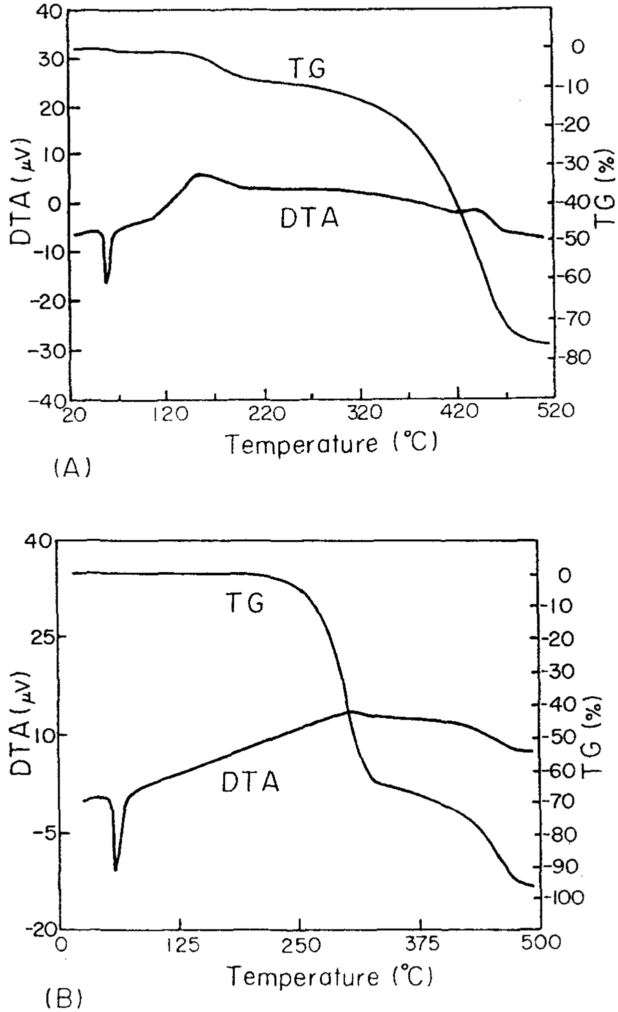

Fig. 1 TG and DTA curves of long-chain diynoic acids: (A) HD-2,4-DA (3.321 mg); (B) TC-10,12-DA (3.345 mg); TG/DTA 300, Al pan, 10 deg·min^{-1}, N_2 gas flow

could not be observed, but a remarkable weight loss occurred at a temperature range of 250°–315°C. In the case of a slower heating rate of 1 deg·min^{-1}, however, the thermal polymerization of TC-10,12-DA was observed as a very weak and broad peak in the temperature range of 90°–200°C, and followed by a drastic thermal decomposition.

Effects of metal surface on melting and polymerization

Influence of surface of Al, Ag and Au on the melting and the polymerization of diynoic acids have been investigated. DSC curves of HD-2,4-DA with different sample weights (0.100–1.030 mg) measured in Al pans are shown in Fig. 2.

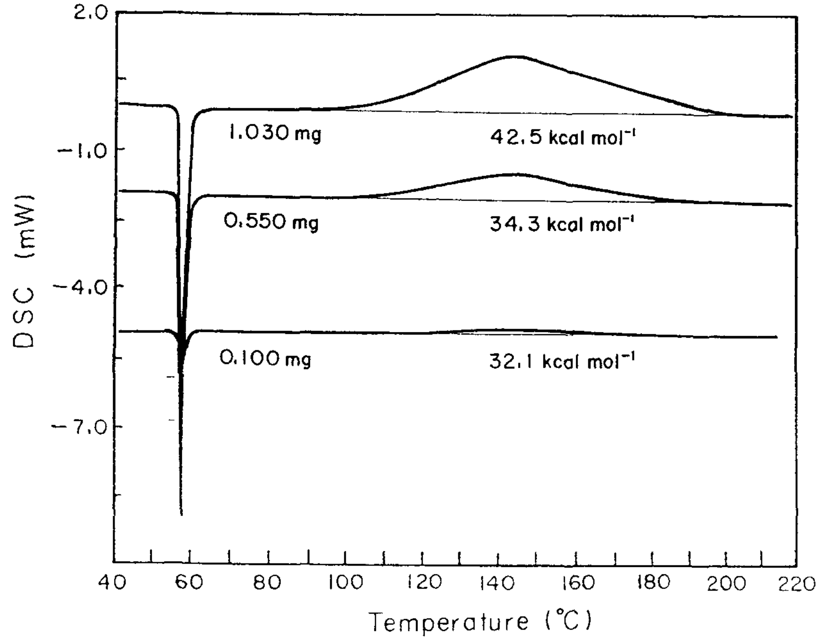

Fig. 2 DSC curves for HD-2,4-DA of various weights. DSC 100, Al pan 5 deg·min^{-1}, N_2 gas flow

The molar heat of polymerization ΔH_p decreased from 42.5 to 32.1 kcal·mol^{-1} with the decrease of sample weight from 1.030 to 0.100 mg, although melting point was kept almost constant. On the other hand, when the sample weight was less than about 0.2 mg, the molar heat of fusion ΔH_f for first run increased with the decreasing of sample weight, while that for second heating decreased. With TC-10,12-DA, similar effect of sample weight on the melting behavior was observed. These surface effects on melting and polymerization can be attributed to the strong interaction of polar head group with the surface of the pan, in analogy with those for stearic acid and N-octadecyl acrylamide [2]. Figure 3 shows the effects of Ag surface on the melting and crystallization behaviors of HD-2,4-DA and TC-10,12-DA. In the case of HD-2,4-DA (Fig. 3 (A)), melting peak become broader and heats of fusion and crystallization decreased after thermal treatment. Especially, the crystallizing peak split into two peaks. With TC-10,12-DA (Fig. 3 (B)), similar thermal behaviors were observed. The surface effects mentioned above, however, were not observed in micro DSC measurements using Au foils and Al pans. These results indicate that the chemical interaction of carboxyl group with Ag surface is due to the salt formation [6] which is much stronger than those of Al and Au.

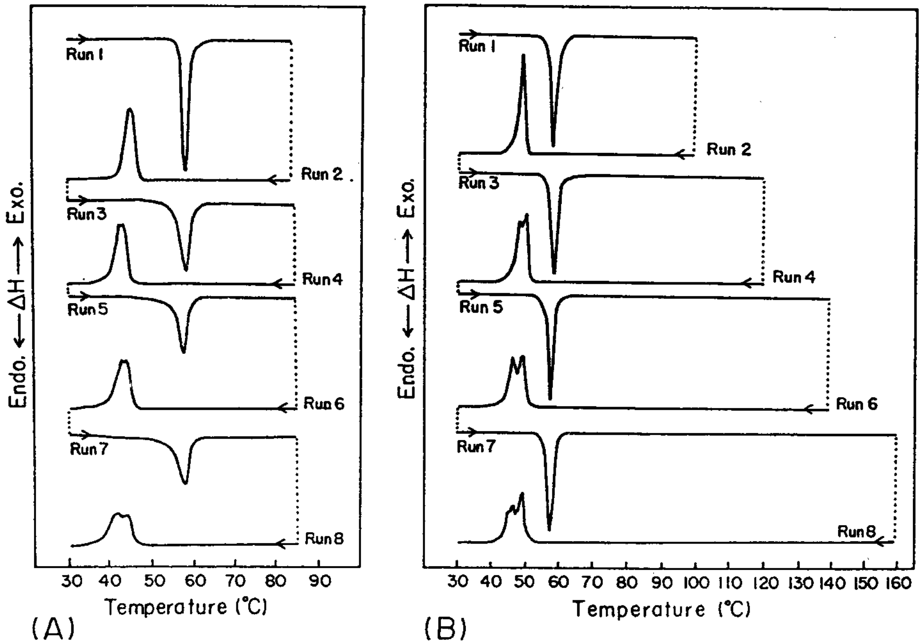

Fig. 3 DSC curves of long-chain diynoic acids holded between Ag foils: (A) HD-2,4-DA; (B) TC-10,12-DA; DSC 20, 5 deg·min^{-1}, 1 mg

Effects of sample weight on the ΔH_f (for second heating) and ΔH_p of HD-2,4-DA are shown in Fig. 4. When the sample weight was diminished below a critical value of about 0.2 mg, ΔH_f decreased in the cases of Ag and Al except for Au (Fig. 4 (A)), reflecting the degree of chemical interaction with metal surfaces. On the other hand, the ΔH_p for milligram order samples greatly varied depending on nature of metals, and the values of ΔH_p for Ag, Al and Au were 56, 45 and 34 kcal·mol^{-1}, respectively. Further, with the minute sample less than about 0.4 mg, ΔH_p decreased markedly. For such a small sample, the fraction of monomer molecules adsorbed strongly on the metal surface through the chemical interaction with carboxyl group should be increased. It is considered that the conformational freedom of the adsorbed molecules is lowered and hence polymerization is suppressed. This is the reason why the heat of polymerization decreased remarkably with the decrease of sample weight in the micro DSC measurement using metal pan.

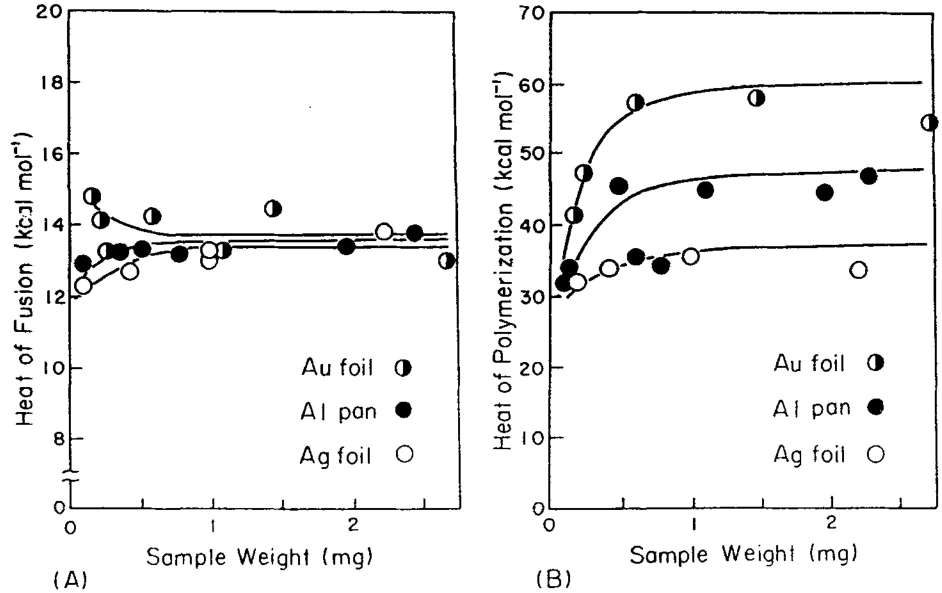

Fig. 4 Effects of metal surfaces on the molar heats of fusion ΔH_f (A) and polymerization ΔH_p (B) of HD-2,4-DA; DSC 20, 5 deg·min^{-1}

The values of ΔH_f (for first heating) and ΔH_p for TC-10,12-DA measured between Ag foils using a heating rate of 2 deg·min^{-1} increased remarkably with the decreasing of sample weight less than 0.2 mg (not shown). For TC-10,12-DA, flexible methylene chains inserted between COOH and C≡C–C≡C groups can act like as ropes mooring regularly many boats at the pier. At temperatures above the melting point, anchoring of carboxyl groups on metal surfaces by chemisorption leads to a favorable aggregation state for polymerization in which diacetylene groups are arranged regularly. Therefore, polymerization can occur at a lower temperature region free from the thermal degradation.

Concluding remarks

The surface effects of metals are enhanced in the order of Au, Al and Ag, reflecting the strength of chemical interaction between metal surfaces and carboxyl group. Therefore, the influences of metal surface on the melting behavior and thermal polymerization of HD-2,4-DA and TC-10,12-DA are attributable to the anchoring of carboxyl groups on the metal surface by chemisorption or salt formation. Fixing of carboxyl groups on a solid surface suppress the polymerization of HD-2,4-DA having diacetylene group connecting directly to carboxyl group, whereas it is rather favorable for the polymerization of TC-10,12-DA with diacetylene group separated by methylene chain from carboxyl group.

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Zusammenfassung — Mittels DSC, TG und anderen Methoden wurde der Einfluß von Metalloberflächen, wie z.B. Aluminium, Silber und Gold auf das Schmelzverhalten und die thermische Polymerisation von langkettigen Diincarbonsäuren mit einer Diacethylengruppe in verschiedener Position untersucht. Die Oberflächeneffekte der Metalle liegen der Größe nach in der Reihenfolge Ag, Al und Au. Diese Effekte können der Haftung der Carboxylgruppen an der Metalloberfläche durch Chemisorption zugeschrieben werden, was zu ungünstigen Bedingungen für die Polymerisation von Heptadeka-2,4-diincarbonsäure führt. Im Falle von Trikosa-10,12-diincarbonsäure, welche eine flexible Methylengruppe zwischen den COOH und C≡C–C≡C Gruppen enthält, verursacht das Haften von COOH an der Metalloberfläche eher zu günstigen Effekten für die Polymerisation.