

Thermoanalytical study on anchoring effects of long-chain diynoic acids in thermal polymerization [☆]

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Received 7 June 1994; accepted 4 July 1994

Abstract

The anchoring effects of the COOH group on the surface of metals (Al, Ag and Au) in the thermal polymerization of long-chain diynoic acids (heptadeca-10,12-diynoic acid, tricosadeca-10,12-diynoic acid and nonacosadeca-10,12-diynoic acid) have been investigated by micro DSC measurements. When the mass of the sample was smaller than 0.01–0.02 mg, the molar heat of fusion estimated from the peak area in the first heating curves increased abruptly up to two or three times the normal values, although the values increased with the length of the ω -chain in diynoic acids. On the contrary, the polymerizability of diynoic acids was markedly enhanced when the mass of sample was smaller than 0.2–0.3 mg. However, in the case of gold foils which had been cleaned by a series of chemical treatments which altered the chemical property of the gold surface from hydrophilic to hydrophobic, no acceleration of the addition polymerization of diynoic acids was observed. It is concluded that these results are attributable to the anchoring of the COOH group on the metal surface by chemisorption, i.e. salt formation or hydrogen bonding.

Keywords: Anchoring; Diynoic acid; DSC; Hydrogen bond; Micro-DSC; Polymerization

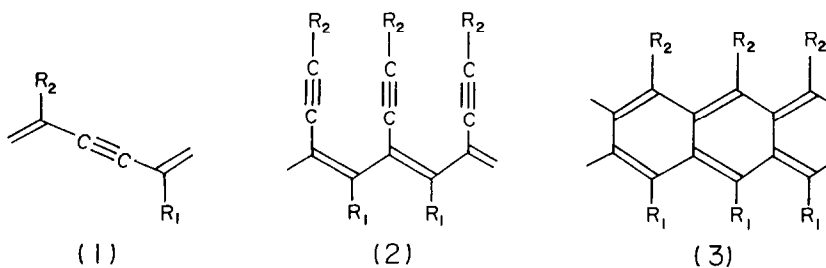
1. Introduction

Aggregation and thermal properties of amphiphilic compounds in thin solid films can be different from those of the bulk phase, because the surface-area to bulk-

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[☆] Presented at the International and III Sino–Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

volume ratio is very high and chemical interactions of polar head groups with solid surface, such as chemisorption, are expected to be fairly large. Surface effects of the aluminum sample pan were observed in micro DSC measurements of long-chain vinyl compounds [1], stearic acid [2,4] and long-chain normal paraffin [3]. We have found that thermal polymerizations of *N*-octadecyl acrylamide [4,6] and heptadeca-2,4-diyonic acid [5,6] were strongly suppressed, because in both cases functional groups for polymerization were connected directly to polar head groups. On the contrary, polymerizability of tricoso-10,12-diyonic acid, containing a flexible methylene chain inserted between COOH and C=C–C≡C groups, was enhanced owing to the anchoring of polar groups on the metal surface and the regular arrangement of diacetylene groups [5]. As discussed previously by Baughman and Yee [7], polymerizability of diacetylene derivatives depends on the state of arrangement and extent of freedom of local thermal motion (i.e. slide and rotation) of the diacetylene group. Therefore, the condition of molecular arrangement and the thermal properties of the long-chain derivatives of diacetylene in the solid films are of interest in connection with their polymerizabilities, irrespective of the structure of the resultant polydiacetylene which is an acetylene type (1) made by the usual 1,4-addition [8], or a polyene type (2) made by 1,2-addition, and a further polyacene type (3) with a ladder structure [9,10].



In this work, the anchoring effects of the COOH group on the surface of various metals (gold, silver and aluminum) in the thermal polymerization of three types of long-chain diynoic acids with ω -alkyl chains of different length have been investigated by micro DSC measurements. Moreover, we have examined a special effect of the pure surface of gold which has been cleaned by a series of chemical treatments.

2. Experimental

Heptadeca-10,12-diyonic acid $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$ (m.p. 38.7–41.3°C, abbreviated as 4-8 DA), tricoso-10,12-diyonic acid $\text{CH}_3(\text{CH}_2)_9\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$ (m.p. 58.8–59.0°C, abbreviated as 10-8 DA, and nonacososa-10,12-diyonic acid $\text{CH}_3(\text{CH}_2)_{15}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$ (m.p. 74.1–74.9°C, abbreviated as 16-8 DA) were purchased from Tokyo Kasei Kogyo and used as received.

Thermal analysis was performed using a Seiko Instruments Model DSC20 differential scanning calorimeter at scanning rates of 2–5 K min⁻¹. For normal DSC measurements, powdered samples were sealed in the aluminum pans of 50 μ l volume. For the examination of surface effects of other metals, the samples held between the gold or silver foils of 15 μ m thickness and size 4 mm \times 4 mm were sealed in the aluminum pans.

The aluminum pans and the silver and gold foils were washed using acetone and benzene under ultrasonic vibration for 15 min at room temperature. Moreover, the gold foils were cleaned by the following chemical treatments under ultrasonic vibration for 15 min in each step: (1) washing in methylisobutyl ketone at room temperature; (2) dipping in 20% nitric acid at 50–60°C; (3) dipping in 20% hydrochloric acid at 50–60°C; (4) washing in water; (5) washing in methanol.

3. Results and discussion

DSC curves for these amphiphilic monomers were measured between 20 and 200°C, because it had been found previously by TG and TG/FTIR measurements that long-chain diynoic acids were degraded immediately after thermal polymerization [5]. With every sample DSC was carried out from run 1 to run 5, and as an example, DSC curves for 10-8 DA are shown in Fig. 1. No appreciable

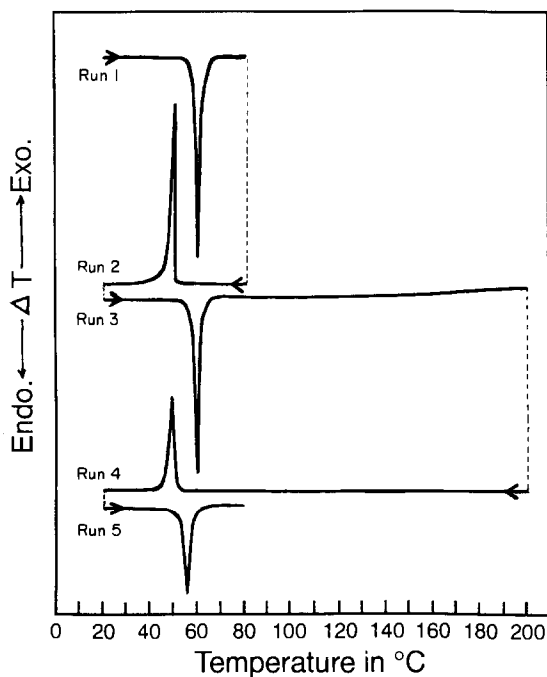


Fig. 1. DSC curves for 0.45 mg 18-8 DA; aluminum pan, 5 K min⁻¹.

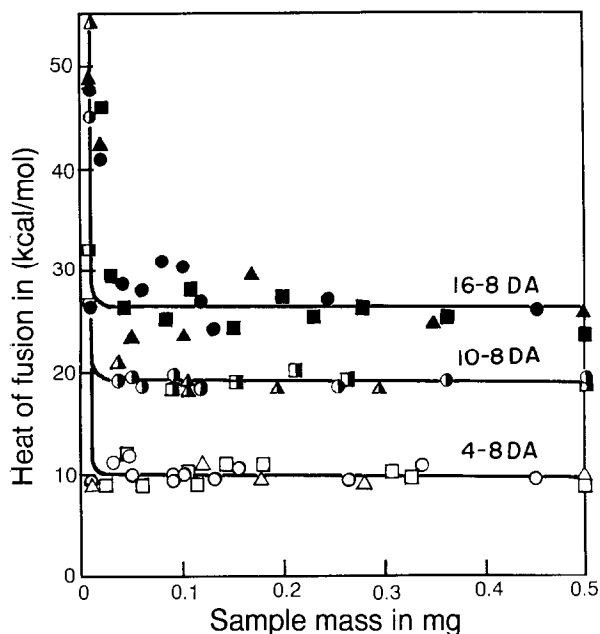


Fig. 2. Effect of sample mass on the molar heat of fusion ΔH_{fus} for 4-8 DA, 10-8 DA and 16-8 DA measured in an aluminum pan (○, ○, ●), between silver foils (△, ▲, ▲) and between gold foils (□, ■); 5 K min^{-1} (1 kcal = 4.1868 kJ).

exothermic peak for the thermal polymerization could be observed in the DSC curves of runs 3 and 5 under the experimental conditions used, but the melting peak for unreacted monomer molecules in run 5 decreased markedly after scanning up to 200°C (run 3). Therefore, percentage conversions were calculated from the relation $100(\Delta H_3 - \Delta H_5)/\Delta H_3$, where ΔH_3 and ΔH_5 are the heats of fusion for monomer molecules in runs 3 and 5, respectively. The molar heats of fusion ΔH_{fus} observed for 4-8 DA, 10-8 DA and 16-8 DA were almost constant and independent of the sample mass, although the values of $\Delta_{\text{fus}}H$ increased with the length of the ω -chain, as shown in Fig. 2. In the case of extremely small sample masses of less than 0.01–0.02 mg, however, the values of ΔH_{fus} obtained in runs 1 and 3 increased abruptly. This result resembles that for stearic acid [4]. On the contrary, endothermic peaks in run 5 became much smaller than those in run 3 with the decrease of sample mass, indicating that thermal polymerization can be enhanced by the surface effect of metals. As shown in Fig. 3, the relationships between conversion and sample mass for 4-8 DA indicate that thermal polymerization was markedly enhanced with the decrease of sample mass, especially when it was less than 0.2–0.3 mg. The enhancement of polymerizability is attributable to the anchoring effect of the COOH group on the surfaces of aluminum and silver by chemisorption or salt formation. This discrepancy between the critical sample mass for the anchoring effects on the melting behavior and on the polymerizability can be explained as follows. The value of $\Delta_{\text{fus}}H$ may be affected only by the molecules adsorbed directly

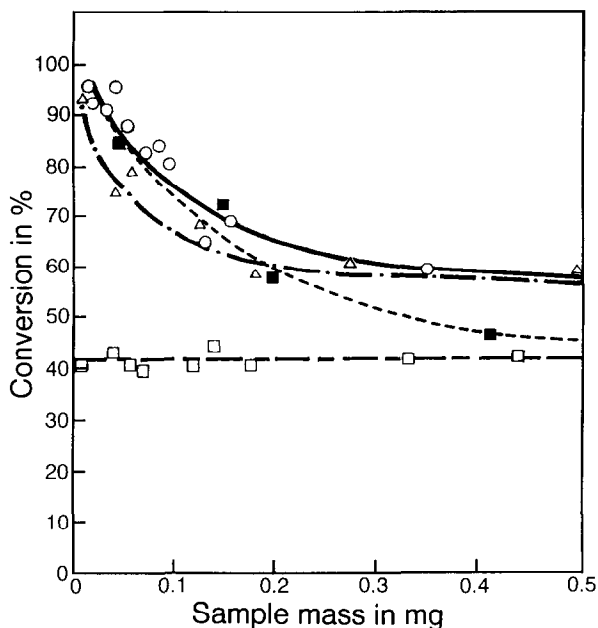


Fig. 3. Effect of sample mass on the polymerization of 4-8 DA measured in an aluminum pan (○), between silver foils (△), between gold foils cleaned by chemical treatments (□) and between gold foils washed in acetone and benzene (■); 5 K min^{-1} .

on the metal surface. On the contrary, in the addition polymerization of diynoic acid, the initiation reaction is followed by the propagation reaction in which numerous monomer molecules (up to several hundreds) may react; as mentioned in a previous paper [6], the initiation reaction is mainly influenced by the anchoring of the COOH group on the metal surface, although the propagation reaction can be influenced a little by an epitaxial effect on the arrangement of monomer molecules. Therefore, we can observe the anchoring effect of the COOH group on the metal surface with a sensitivity 10–100 times higher than that for the usual phase transition, through the addition polymerization of long-chain diynoic acid.

However, in the case of gold foil cleaned by the chemical treatments mentioned above, the acceleration of thermal polymerization by anchoring effects cannot be observed. This result can be attributed to the fact that chemisorption of the COOH group hardly occurs on the clean surface of gold, which is hydrophobic and chemically stable. However, in the case of gold foils which had been washed by acetone and benzene under ultrasonic vibration, an anchoring effect occurs which is similar to those observed with aluminum and silver, as shown in Fig. 3. These results can be ascribed to the change of chemical property of the gold surface from hydrophilic to hydrophobic occurring upon cleaning. In other words, anchoring of the COOH group on the surface of gold foil which has been cleaned sufficiently cannot occur, and then the thermal polymerization of long-chain diynoic acid between the gold foils proceeds in a similar manner to those in bulk phase.

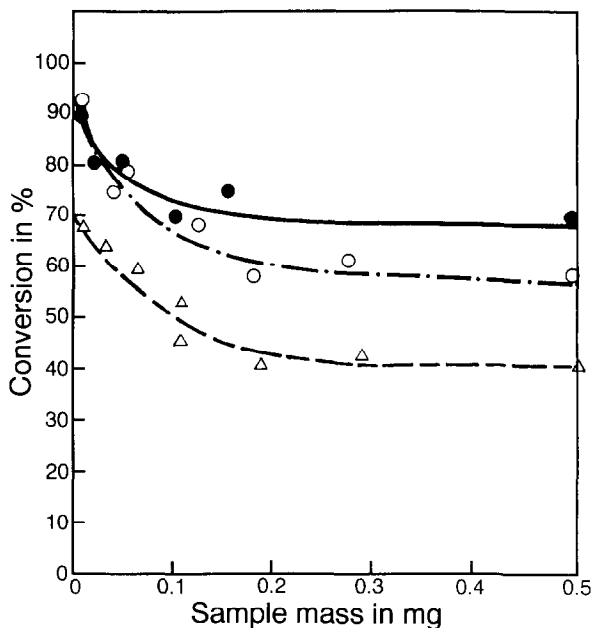


Fig. 4. Effect of the length of ω -chain in diynoic acids (16-8 DA (●), 10-8 DA (Δ) and 4-8 DA (○)) measured between silver foils; 5 K min^{-1} .

Effects of ω -alkyl chain length on thermal polymerization were examined using the three long-chain diynoic acids. As a typical example for the anchoring effect, the results obtained using the silver foils are shown in Fig. 4. In the cases of 4-8 DA, 10-8 DA and 16-8 DA, the acceleration of the thermal polymerization by the anchoring effect was very similar in each case, whereas the polymerizability of 10-8 DA was less than those of 4-8 DA and 16-8 DA. This difference may be attributed to the lack of purity of the 10-8 DA sample. As shown in Fig. 5, effects of ω -alkyl chain length were also observed in the case of gold foils which had been cleaned by chemical treatments. Conversions for 4-8 DA, 10-8 DA and 16-8 DA are almost constant regardless of the reduction in sample mass because of the lack of a sufficient anchoring effect of the carboxyl end group. The extent of conversion in the thermal polymerization may reflect the polymerizability of these monomers, and it depends mainly on the ability of the regular arrangement of $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ groups owing to the long ω -alkyl chain, and also on the purity of the sample. It could be expected that the order of polymerizability for these diynoic acids under the conditions mentioned above would correspond to the order of length of the ω -chain, if it were possible to use a highly purified 10-8 DA sample.

As a consequence of these results, two explanations for the enhancement of the thermal polymerization of n -alkyl-10,12-diynoic acids are postulated here, accord-

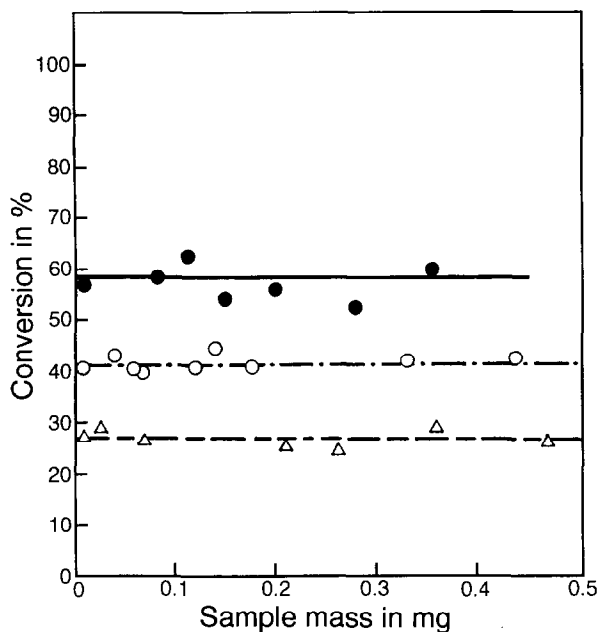


Fig. 5. Effect of the length of the ω -chain in diynoic acids (16-8 DA (●), 10-8 DA (Δ) and 4-8 DA (○)) measured between gold foils cleaned by chemical treatments; 5 K min^{-1} .

ing to the schematic representations for the bulk state (A) and the adsorbed state on the metal surface (B), as shown in Fig. 6. Firstly, at temperatures above the melting point, the anchoring of COOH groups on the metal surfaces by chemisorption leads to a favorable aggregation state for polymerization in which diacetylene groups are arranged regularly with sufficient conformational freedom, owing to flexible methylene chains inserted between COOH and $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ groups. Secondly, long ω -alkyl chains linked to $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ groups facilitate the regular arrangement of these groups by the coagulation force of linear long hydrocarbon chains, even though in the bulk phase the long-chain diynoic acid dimers and the two dimensional network structure due to hydrogen bonds are easily broken at elevated temperatures.

4. Concluding remarks

It is clarified that the acceleration of thermal polymerization of long-chain diynoic acids is caused by the anchoring of COOH groups on metal surfaces. Furthermore, chemical properties of solid surfaces, for example the difference between the usual surface and the especially cleaned surface of gold, can be examined with high sensitivity by measuring the anchoring effects of amphiphilic monomer molecules in thermal polymerization using the micro DSC technique.

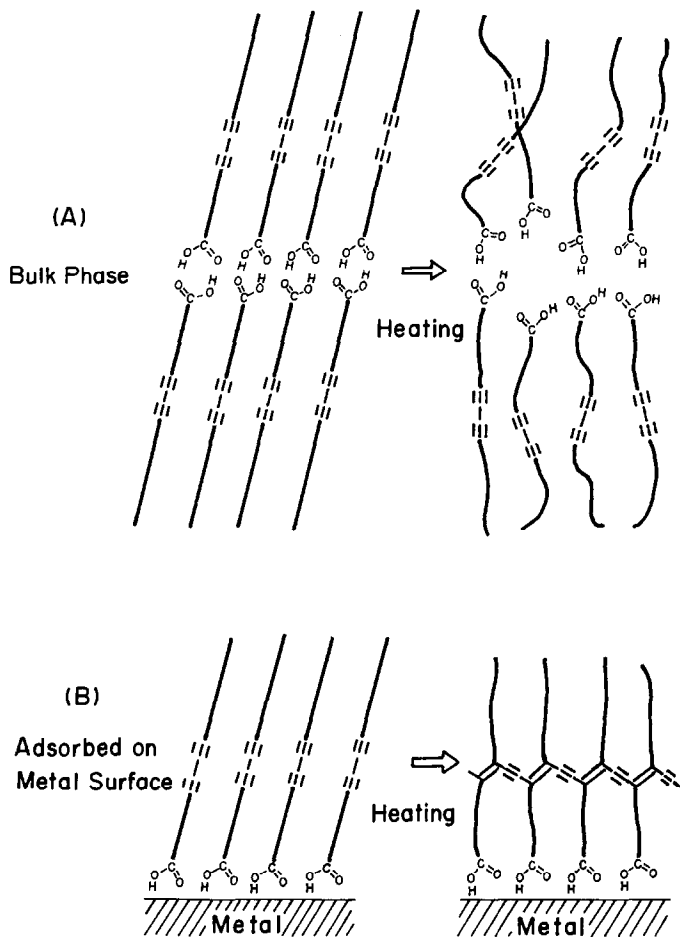


Fig. 6. Schematic representation of the acceleration of thermal polymerization of long-chain diynoic acids: (A) dimerization by hydrogen bonding and two dimensional network formation in bulk phase; (B) anchoring of COOH groups on the metal surface and addition polymerization.

References

- [1] Y. Shibasaki and K. Fukuda, *Thermochim. Acta*, 123 (1988) 191.
- [2] Y. Shibasaki, *Netsu Sokutei*, 15(4) (1988) 163.
- [3] K. Takamizawa and Y. Urabe, *Chem. Lett.*, (1990) 63.
- [4] Y. Shibasaki and K. Fukuda, *Thermochim. Acta*, 183 (1991) 199.
- [5] Y. Shibasaki, K. Fukuda and Y. Nishimoto, *J. Therm. Anal.*, 40 (1993) 491.
- [6] Y. Shibasaki, *Netsu Sokutei*, 20(2) (1993) 61.
- [7] R.H. Baughman and K.C. Yee, *J. Polym. Sci. Macromol. Rev.*, 13 (1978) 219.
- [8] B. Tieke, G. Lieser and G. Wegner, *J. Polym. Sci. Polym. Chem. Ed.*, 17 (1979) 1631.
- [9] A. Berlin, M. Cherkasin, M. Chauser and R. Shifrina, *Polym. Sci. USSR*, 9(10) (1967) 2510.
- [10] A.W. Olsen and Z.H. Kafafi, *J. Am. Chem. Soc.*, 113 (1991) 7758.