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Thermoanalytical studies on the comb-like polymers containing diamino-*s*-triazine groups[1]

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Abstract

Thermal properties and thermal degradation mechanisms at higher temperatures for a homopolymer of 6-vinyl-2,4-diamino-*s*-triazine (VT) and copolymers with octadecylacrylate (OA) having various compositions were investigated by DSC and TG/FTIR measurements. The melting temperatures of poly (VT-*co*-OA)'s were higher than that of the OA homopolymer and increased slightly with the VT content. The thermal stability of the homopolymer of VT was rather low and that of poly (VT-*co*-OA) increased with the OA content, probably because NH_2 groups in the VT unit actively reacted with ester groups in the OA unit and others at temperatures higher than 200°C.

Keywords: Comb-like polymer; DSC; TG/FTIR; Thermal analysis; *s*-Triazine

1. Introduction

Thin solid films of comb-like polymers containing 2,4-diamino-*s*-triazine group seem to have special functions, such as the selective capture of ions. However, the thermal properties of comb-like polymers are influenced by the rigidity of the main chain and the length of the side-chain [1–8]. In this work, the thermal properties and thermal degradation mechanisms at higher temperatures for a homopolymer of 6-vinyl-2,4-diamino-*s*-triazine and its copolymers with octadecylacrylate having various compositions were investigated by DSC and TG/FTIR measurements.

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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2. Experimental

6-Vinyl-2,4-diamino-*s*-triazine (m.p. not determined, abbreviated as VT) was supplied from Shikoku Kasei Kogyo and used as received. Octadecylacrylate (m.p. 32.5–33.0°C, abbreviated as OA) was bought from Tokyo Kasei Kogyo and purified by recrystallization from the methanol solution. Saturated solutions of VT in DMSO and solutions of VT–OA mixtures of various compositions in an equivolume mixed solvent of DMSO and THF were sealed in Pyrex tubes (i.d., 10 mm) under nitrogen atmosphere. The solutions were solidified by rapid cooling in liquid nitrogen. After irradiation by ^{60}CO γ-rays of 774 Ckg^{-1} (3 Mrad total does) at -196°C, post-polymerization at 30°C was allowed to proceed for 24 h. A polymerization scheme for poly (VT-*co*-OA) is shown in Fig. 1. Copolymers of VT and OA with various compositions (VT : OA = 2 : 1, 1 : 1, 1 : 2 mol ratios) were synthesized, and their compositions were determined using relative intensities of characteristic bands in the IR spectra. The thermal properties and thermal degradation behavior of polymers were measured using a differential scanning calorimeter type DSC20 and a thermobalance type TG/DTA320 (Seiko Instruments), and IR spectra were measured by a JASCO Model VALOR III Fourier-transfer IR spectrophotometer.

3. Results and discussion

As shown in Fig. 2, the melting peaks for *n*-octadecyl groups in the copolymers of VT and OA were rather higher than that for the homopolymer of OA (POA), and also that the melting temperatures increased slightly with VT content. From these results it can be assumed that each monomer unit of VT and OA is arranged alternatively in a statistical sense in the copolymers of VT and OA, and that the melting temperature increases with the probability of finding the short sequences of OA units interposed between the VT units in the copolymer chains. In addition, at a higher temperature of about 220°C, an exothermic peak was observed.

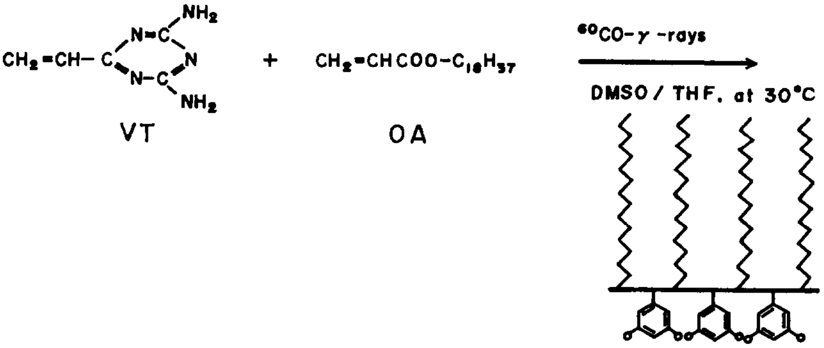

Fig. 1. A polymerization scheme for poly (VT-*co*-OA) by γ-ray-irradiated post-polymerization.

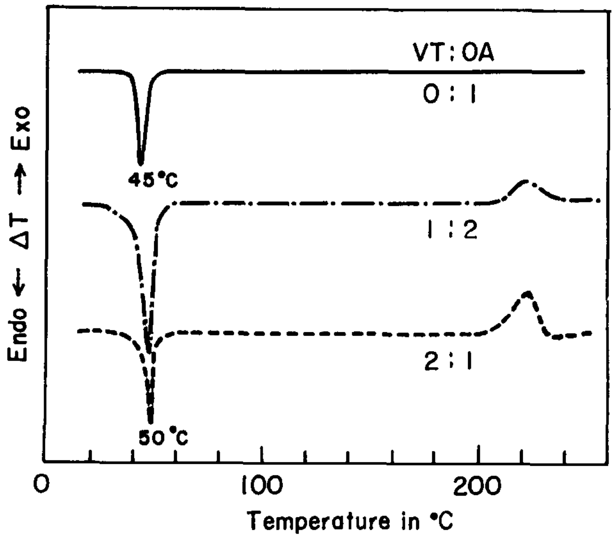

Fig. 2. DSC curves for copolymers of VT and OA with various compositions and of OA homopolymer; aluminum pan, 5 K min^{-1}, insufficiently purged by N_2 gas.

Next, to elucidate the exothermic reaction in the copolymers of VT and OA, the TG/DTA measurements were carried out under nitrogen atmosphere after a rough nitrogen gas purge. As an example, TG and DTA curves for a copolymer of VT and OA (2:1) are shown in Fig. 3. In the DTA curve measured at a heating rate of 10°C min^{-1}, two exothermic peaks appeared at 280 and 415°C. From the TG curve, it was clarified that an abrupt decrease of sample mass of about 5% occurred in a temperature region from 200 to 220°C and a remarkable decrease of mass was observed in the higher temperature region of 350–450°C. As shown in Fig. 4, when the atmosphere was sufficiently replaced with N_2, no exothermic reaction occurred in the DSC curves for copolymers with various compositions. From the examination of the residues of the poly (VT-*co*-OA)'s by IR spectra after TG/DTA measurements upto 500°C and the results mentioned above, we can assume the following mechanisms. In the case of insufficient N_2 gas purge, the reaction between NH_2 groups and ester groups with formation of intra- and intermolecular amide groups and the release of octadecanol, as shown in Fig. 5, was accelerated by a minute amount of oxygen remaining in the polymer sample. However, in the absence of any oxygen, thermal degradation proceeded without any side reaction.

With the homopolymer of VT (PVT), four endothermic peaks were observed (Fig. 4, top curve). These peaks correspond well to the loss of mass as shown in Fig. 6 (solid line). Furthermore, the IR spectra of the evolved compounds for PVT were examined by TG/FTIR measurement. In a relatively low temperature region, the bands due to diamino-*s*-triazine group (δ (NH_2), 1605 cm^{-1}; ν (–C=N–) , 1562 cm^{-1} and 1427 cm^{-1}) were observed, and then at higher temperature above 350°C, four bands at 991, 953, 841 and 764 cm^{-1}, which may be assigned to the *s*-triazine ring, obviously

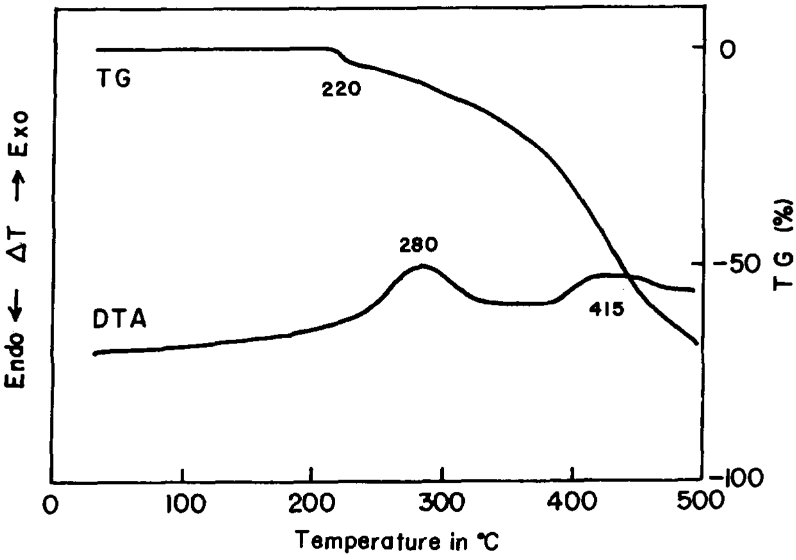

Fig. 3. TG/DTA curves for poly (VT-*co*-OA) (2:1); aluminum pan, 10 K min^{-1}, insufficiently purged by N_2 gas.

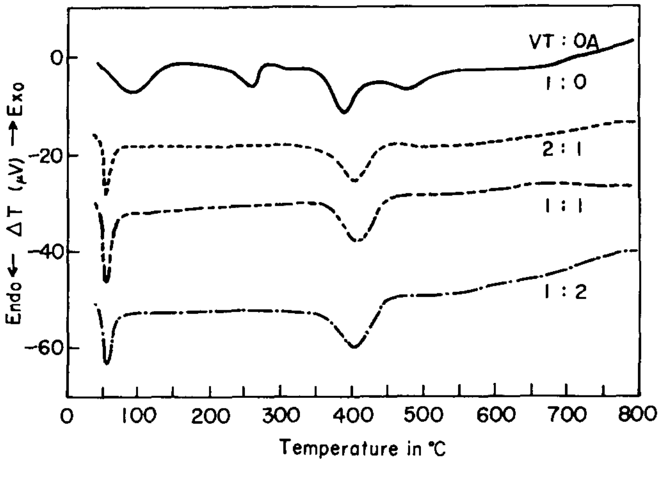

Fig. 4. DTA curves for the homopolymer of VT and copolymers of VT and OA with various compositions; aluminum pan, 10 K min^{-1}, sufficiently purged by N_2 gas.

appeared. From these results, it can be considered that the lowest is caused by evaporation of adsorbed water and the higher three peaks at about 250, 380 and 470°C seem to correspond to the thermal degradations; bond rupture, reconstruction, release of small molecules, and to other chemical reactions combined with endothermic change

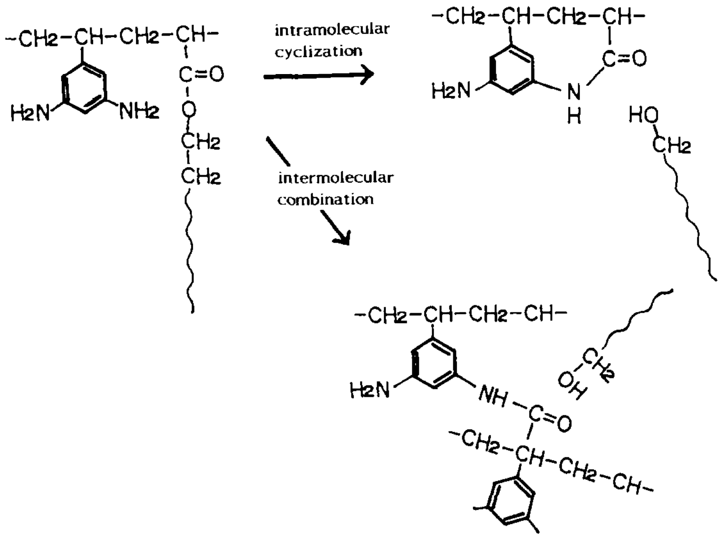

Fig. 5. Schematic representation of the intramolecular cyclization and intermolecular combination reactions between NH_2 groups and ester groups on heating under an atmosphere containing a minute amount of oxygen.

and mass loss. The thermal instability exhibited by PVT was entirely unexpected. It was found from the results of TG and DTA (Figs. 4 and 6) that the thermal stability of copolymers with OA increased with the OA content. In particular, this tendency is clear in the TG curves in the temperature range from 200 to 350°C. Large endothermic peaks

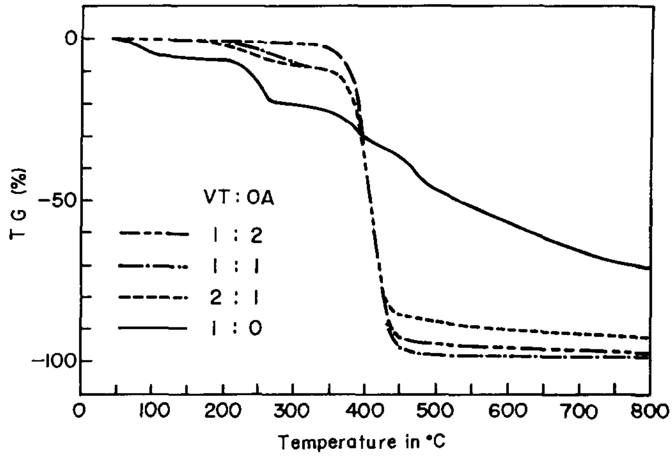

Fig. 6. TG curves for the homopolymer of VT and copolymers of VT and OA with various compositions, corresponding to the DTA curves in Fig. 4; aluminum pan, 10 K min^{-1}, sufficiently purged by N_2 gas.

in the DSC curves at about 400°C correspond exactly to the abrupt decrease of mass in the TG curves. These results indicate that depolymerization of the copolymer caused by scission of the C–C bond in the main chain chiefly occurs at this temperature.

In addition, to clarify the relationship between copolymer composition and thermal degradation mechanism, the degradation products evolved from the TG measurement were introduced directly into the FTIR sample cell at regular intervals (10 min) and the IR spectra of the evolved products were observed. The change in the IR spectra for poly (VT-*co*-OA) (2:1) is shown in Fig. 7, as an example. The abscissa is wavenumber (cm^{-1}), the height is the intensity of the absorbance, and the IR spectra are drawn with displacement of the time interval (10 min). The IR spectra changed with increasing temperature. The absorption bands assigned to the diamino-*s*-triazine group $\delta(NH_2)$, 1601 cm^{-1}; and ν(–C=N–), 1458 cm^{-1}) were increased and followed by an increase in the absorption bands due to OA ($\nu(CH_2)$, 2932 cm^{-1} and 2836 cm^{-1}; ν(C=O, 1747 cm^{-1}). The FTIR results for the copolymers correspond well to the change in the TG curve (Fig. 6). Therefore, it was clarified that the character of the thermal degradation of poly (VT-*co*-OA) is as follows. On heating, the thermal degradation of VT residue begins at about 200°C, and at higher temperatures, the OA residue decomposes.

4. Concluding remarks

It was found that on heating poly (VT-*co*-OA)'s containing chemically active amino groups, the thermal degradation was influenced by the atmosphere. When a minute amount of oxygen remained in the system, the structure of the polymers changed, accompanied by exothermic reactions in the temperature region 200–300°C. In

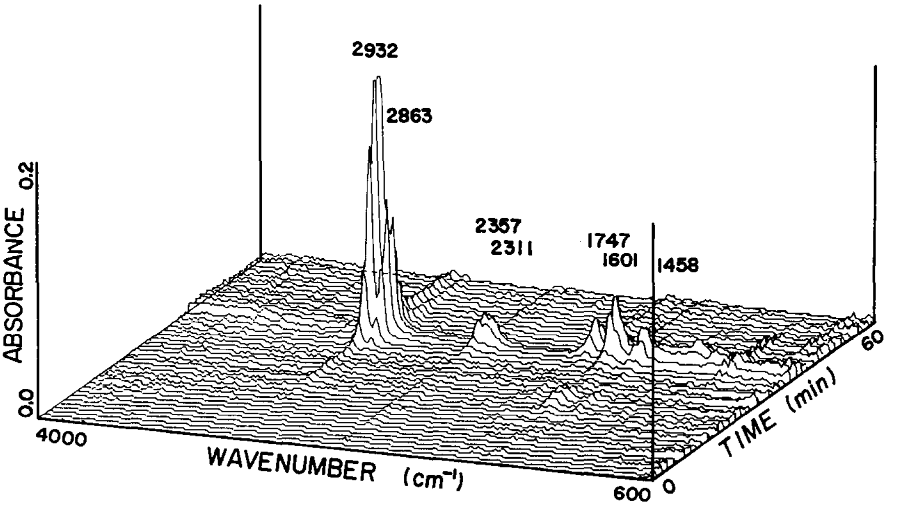

Fig. 7. IR spectra of the evolved products from the TG measurement of poly (VT-*co*-OA) (2:1); 10 K min^{-1}, sufficiently purged by N_2 gas.

contrast, after a sufficient nitrogen gas purge, the copolymers were stable in this temperature range and decomposed with violence in the higher temperature region of 350–450°C, releasing *n*-octadecanol and OA monomer. Combining the measurements of DSC, DTA and TG with FTIR measurement of the evolved compounds is quite effective in the study of the thermal degradation of macromolecules. By analysis of IR spectra, the chemical structure of the evolved gases can easily be estimated. The evolved gas analysis can compensate for a lack of accurate information in the investigation of the chemical structure of the deeply colored polymer residue using the usual IR absorbance technique.

References

[1] E.F. Jordan, Jr., D.W. Feldeisen and A.N. Wrigley, J. Polym. Sci. A-1, 9 (1971) 1835.
[2] H.W.S. Hsieh, B. Post and H. Morawetz, J. Polym. Sci., Polym. Chem. Ed., 14 (1976) 1241.
[3] Y. Shibasaki and K. Fukuda, J. Polym. Sci., Polym. Chem. Ed., 18 (1980) 2437.
[4] Y. Shibasaki and K. Fukuda, Thermal Analysis (Proc. 7th Int. Conf. Thermal Analysis), Vol. II, John Wiley and Sons, New York, 1982, pp. 1517–1523.
[5] T. Hirabayashi, T. Kikuta, K. Kasabou and K. Yokota, Polym. J., 20 (1988) 693.
[6] T. Hirabayashi, K. Kasabou and K. Yokota, Polym. J., 20 (1988) 911.
[7] H. Kunisada, Y. Yuki, S. Kondo, J. Miyatake and C. Maeda, Polym. J., 22 (1990) 559.
[8] C.-J. Hsieh, S.-H. Wu, G.-H. Hsiue and C.S. Hsu, J. Polym. Sci.: Part A: Polym. Chem., 32 (1994) 1077.