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THERMAL BEHAVIOR OF POLY(*p*-PHENYLENE DIACRYLIC ACID DIETHYL ESTER)

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ABSTRACT

Poly(*p*-phenylene diacrylic acid diethyl ester) was prepared by photopolymerization of *p*-phenylene diacrylic acid diethyl ester in the solid state. The resulting product was fractionated according to molecular weight by solvent extraction, and the effect of the molecular weight on the thermal behavior such as crystal-crystal transition, melting and thermal degradation was studied. The effects of reaction temperature and heat treatment on the thermal behavior of the polymer were also examined.

INTRODUCTION

Several crystalline polymers have been prepared from conjugated diolefins containing 1,4-arylene groups by the four-center type photopolymerization in the crystalline state.1) These polymers have alternating 1,3-*trans*-cyclobutane and 1,4-arylene groups in the main chain, resulting in a rigid rod-like chain structure.

In the present report, poly(*p*-phenylene diacrylic acid diethyl ester) (poly(*p*-PDAEt)) was prepared by photopolymerization in the solid state and fractionated by solvent extraction, and the effects of molecular weight, polymerization temperature and heat treatment on the thermal behavior of poly(*p*-PDAEt) was investigated.

EXPERIMENTAL

p-Phenylene diacrylic acid diethyl ester (*p*-PDAEt) crystals, finely powdered and dispersed in methanol-water mixtures with constant stirring, were irradiated with light from a 100W high pressure mercury lamp at the center of the reaction flask for 8hr at predetermined temperatures (-50, -20 and 25°C). The ratio of methanol to water was varied depending upon the polymerization temperature. After irradiation, unreacted monomer was extracted with ethanol-water mixture (1:1). Depending upon the molecular weight the resultant polymer was divided into three fractions: ethanol-soluble, ethanol-insoluble but chloroform-soluble, and chloroform-insoluble fractions. Due to its high crystallinity, the chloroform-insoluble fraction was insoluble in conventional organic solvents

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and merely soluble in strong acids such as concentrated sulfuric acid and dichloroacetic acid. A dichloroacetic acid solution of the chloroform-insoluble fraction was poured into a mixture of water and diethanolamine to regenerate amorphous poly(*p*-PDAEt). Amorphous poly(*p*-PDAEt) was soluble in chloroform, *p*-chlorophenol and 1,1,2,2-tetrachloroethane.

The DTA measurements were carried out on a Rigaku Denki Thermoflex Differential Thermal Analyzer at a heating rate of 10K/min under nitrogen.

RESULTS AND DISCUSSION

The molecular weight ($\bar{M}_v$) of chloroform-insoluble fractions were determined by viscosity measurements through use of the [η] *vs.* $\bar{M}_v$ relationship reported by Fujishige *et al.*$^{2)}$ after regenerated from dichloroacetic acid solutions. The values of $\bar{M}_v$ for polymer prepared at -50, -20 and 25°C were 2.5×10^4, 1.0×10^4 and 5.6×10^3, respectively.

GPC curves of each fractions of poly(*p*-PDAEt) and monomer *p*-PDAEt were obtained with use of chloroform as a solvent (Figure 1). The chromatogram for $CHCl_3$-insoluble fraction is characterized by a single strong peak at 16.19min. For $CHCl_3$-soluble fraction, a large peak and two small peaks are observed at 17.24min, and 16.41 and 18.11min, respectively. A large peak and a small peak appear at 18.16 and 17.27min in the GPC curve of EtOH-soluble fraction. The curve for monomer shows a large peak at 20.87min and a small peak at 18.27min.

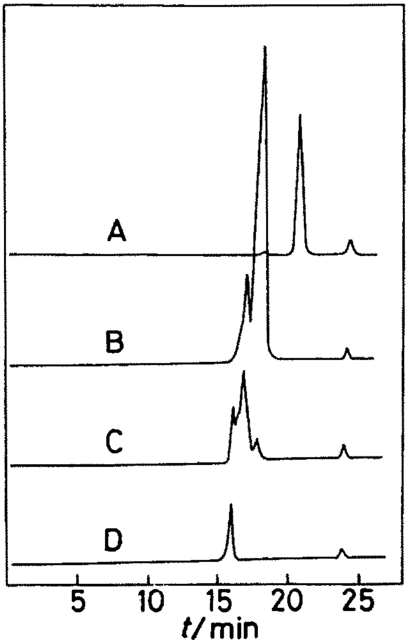

Figure 1 GPC curves of *p*-PDAEt and poly(*p*-PDAEt) fractions, (A): monomer, (B): EtOH-soluble, (C): $CHCl_3$-soluble, (D): $CHCl_3$-insoluble fractions.

In the infrared spectra of poly(*p*-PDAEt) fractions and *p*-PDAEt, the intensity of the 1640 cm^{-1}band due to C=C stretching vibration decreased in the order of monomer > EtOH-soluble > $CHCl_3$-soluble > $CHCl_3$-insoluble, No detectable absorption was observed at $1640cm^{-1}$ for $CHCl_3$-insoluble fractions.

Therefore, $CHCl_3$-insoluble fraction is assigned to the polymer, and $CHCl_3$-soluble fraction consists of mostly trimer and a small amount of oligomer. Most of EtOH-soluble fraction is dimer and contains some trimer.

DTA curves of poly(*p*-PDAEt)s prepared at 25, -25 and -50°C are shown in Figure 2. Two endothermic peaks appear at 347°C and 390 °C.

Figure 3 shows DTA curves of monomer *p*-PDAEt and poly(*p*-PDAEt) fractions. Two endothermic peaks are observed in the DTA curve of monomer. The first peak at 52°C is attributed to a crystal-crystal transition and the second one at 96°C is assigned to the melting point of monomer. The melting temperatures of trimer and dimer were determined to be 147°C and 114°C from the curve B and C in Figure 3, respectively. Two endothermic peaks occurs at 347°C and 390°C in the DTA curves of $CHCl_3$-insoluble fraction as observed in Figure 2.

In the course of irradiation, an aliquot of reaction mixture was taken out from the reaction vessel at predetermined intervals and DSC curves were recorded for each spec-

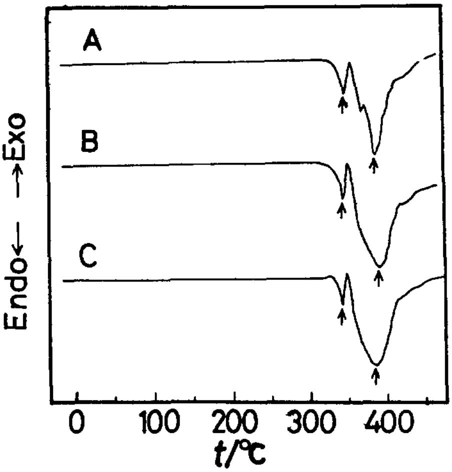

Figure 2 Effect of polymerization temperature on the DTA curves of poly(*p*-PDAEt). (A): -50°C, (B): -20°C, (C): 20°C.

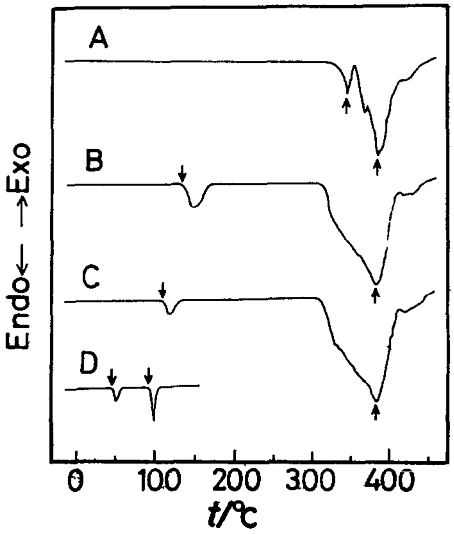

Figure 3 Effect of molecular weight on the DTA curves of *p*-PDAEt and poly(*p*-PDAEt) fractions. (A): $CHCl_3$-insoluble, (B): $CHCl_3$-soluble, (C): EtOH-soluble, (D): monomer.

imen. For an irradiation of 5 min. two endothermic peaks were observed at about 80 and 90°C. The former attributed to the melting of monomer crystals and the latter to the lowering of melting temperature of monomer due to the strain of crystal lattice induced by the polymerization. A melting peak of dimer appeared at about 110°C for 15 min of irradiation in addition to the peak at 80°C. A melting peak of trimer occurred after 30 min. The melting peak of monomer became smaller with reaction time and disappeared after 60 min. The peak at 347°C, which is observed for polymer obtained at -50°C, appeared after 120 min.

The peak at 347°C observed for polymer obtained at -50°C was further examined. After heated up to 345°C at a heating rate of 10K/min and then cooled to room temperature at the same rate, the peak becomes smaller (Figure 4). The weight loss started at about 340°C in the TG curves of polymers and lowering of molecular weight occurred. Therefore, the peak at 347°C is attributed to the degradation of polymer. An exothermic peak starting at about 300°C for regenerated polymer is attributed to the recrystallization of regenerated polymer. Broad endothermic peaks at 390°C observed for all polymers are also caused by the degradation of polymer.

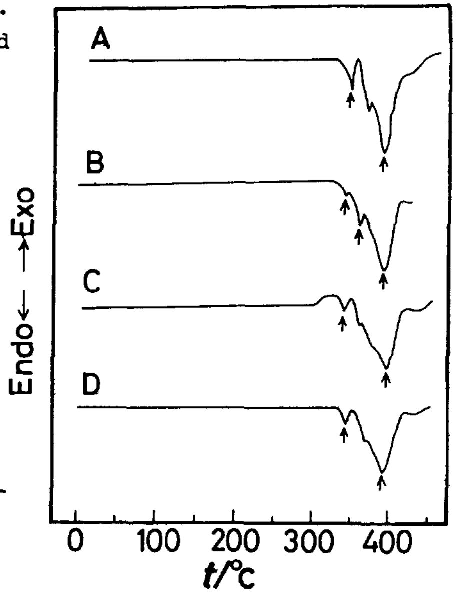

Figure 4 Effect of heat treatment on the DTA curves of poly(*p*-PDAEt). (A): polymer prepared at -50°C, (B): polymer (A) heated to 345°C and then cooled, (C): polymer (A) regenerated, (D): polymer (C) heated to 335°C, and then cooled.

REFERENCES

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