

Upgrade Recycling of PET - Synthesis of Aramide from PET by Using Reaction-induced Crystallization

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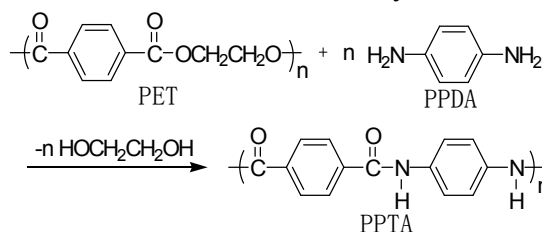
Abstract: In order to develop the upgrade recycling of poly(ethylene terephthalate) (PET), preparation of poly(1,4-phenylene terephthalamide) (PPTA) which was called Kevlar was examined by using reaction-induced crystallization during ester-amide exchange reaction between PET and 1,4-phenylenediamine (PPDA). Polymerizations were carried out in aromatic solvent at 320-350°C for 24 h at a concentration of 5 wt%. PPTA was successfully obtained as plate-like crystals under non-stoichiometric condition, of which weight-average molecular weight (M_w) was in the range of $8.4 \times 10^3 - 1.02 \times 10^4$.

Keywords: Upgrade recycling / PET / Aramide / Crystallization / Ester-amide exchange reaction

1. Introduction

Polyester resins especially PET have been widely used as beverage containers, fibers for clothing, films for wrapping and so on in our daily life, and the demand for PET resins is increasing in these days. PET can be converted to the monomers *via* hydrolysis, and therefore it has not only good mechanical recyclability but also feed-stock recyclability. In the general mechanical recycling system, collected PET is recycled by reforming the materials of which the required properties are less than those for virgin resin, called cascade recycling or downgrade recycling. However, upgrade recycling providing value-added materials is of importance to establish an effective recycling system for construction of recycling-based society.

Aromatic polyamides called aramides are well known as high-performance materials. Among them, PPTA named Kevlar is a representative and it has many applications, ranging from bicycle tires and racing sails to body armor owing to their excellent thermal stability, mechanical properties, chemical resistance and so on. PPTA is commonly synthesized by the polymerization of terephthaloyl chloride and PPDA. However, eliminated HCl is toxic and corrosive. Therefore more safe and environmental-friendly procedure is required. If PPTA will be synthesized from the collected PET resin, it will provide a novel synthesis procedure without eliminating HCl to contribute an upgrade recycling system as aforesaid. Several studies for the conversion of PPTA from PET by ester-amide exchange reaction were previously reported.^(1, 2) In these studies, the reactions were carried out in the melt phase or solution phase. When the content of 1,4-phenylene terephthalamide (PTA) moiety increased in PET, the formed poly(ester-*co*-amide) became insoluble and infusible. Therefore, the poly(ester-*co*-amide)s were precipitated in the solution or solidified in the melt, and the content of PTA moiety was limited to at most 60 %.



Scheme Preparation of PPTA from PET *via* ester-amide exchange reaction

In this study, the preparation of PPTA from PET was examined as shown in Scheme by

reaction-induced phase separation to overcome the above limitation, resulting in the establishment of the novel upgrade recycling system.

2. Experimental

Into a cylindrical vessel, PET ($M_w = 2.8 \times 10^4$, acid value = 4.11×10^{-5} mol/g) and dibenzyltoluene (Matsumura Oil Co.) were placed, and the mixture was heated up to polymerization temperature under nitrogen atmosphere. Concentration of PET was 5 wt%. When the PET was entirely dissolved, PPDA was added under stirring. Stirring was stopped when PPDA was dissolved, reaction was continued without stirring. Precipitated products were collected by filtration, and washed with *n*-hexane and acetone.

3. Results and Discussion

3.1 Polymer preparation under stoichiometric condition

Reactions were carried out at 320°C by the addition of PPDA equimolar to the ester linkage in PET ($M = [\text{Amino group of PPDA}] / [\text{Ester linkage of PET}] = 1.0$). The yield and the content of PTA moiety (χ_{PTA}) of the precipitates increased with polymerization time, and the χ_{PTA} value became 92 mol% after 12 h as shown in Fig. 1. Oligomers containing PTA moiety formed by ester-amide exchange reaction were precipitated to form the crystals owing to the decrease in the solubility. However, the χ_{PTA} value did not increase after 12 h, and it did not reach to 100 mol%, meaning that PTA could not be prepared. The χ_{PTA} value of the precipitates prepared for 0.5 h was only 22 mol%. The ester content of 78 mol% remained in the crystals during the reaction, being good agreement with 92 mol% after 12 h. This result indicates that the χ_{PTA} value of precipitated oligomers increases with the yield by the precipitation of oligomers rich in PTA and the exchange-reaction does not occur in the precipitated crystals. It is important to precipitate oligomers having higher χ_{PTA} value. Morphology of the precipitates was shown in Fig. 2. Plate-like crystals were formed at the initial stage of reaction (Fig. 2 (a)), and then they changed to the aggregates of plate-like crystals after 24 h (Fig. 2 (b)). It was expected that the higher temperature enhanced the solubility of oligomers and the reaction rate. Next, the reaction was carried out at 350°C for 24 h. The χ_{PTA} value increased slightly to 96 mol% compared with that prepared at 320°C, but it did not reach to 100 mol%.

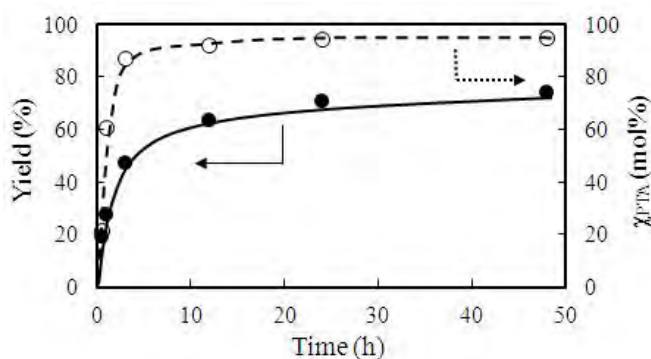


Fig. 1 Plots of yield and χ_{PTA} of polymer as a function of time in reaction at a conc. of 5 % and 320°C

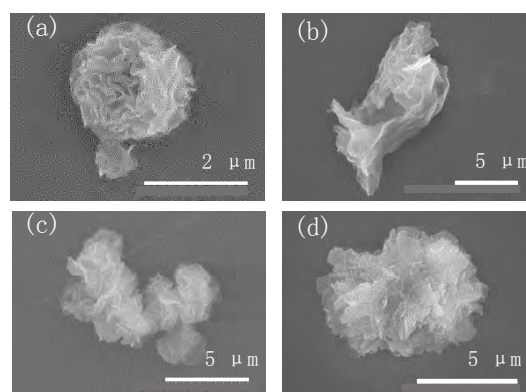


Fig. 2 Precipitates prepared at 320°C for at M of 1.0 for (a) 0.5 h, (b) 24 h, and at M of 2.0 for (c) 0.5 h, (d) 24 h

3.2 Polymer preparation under non-stoichiometric condition

In order to compensate PPTA lost by sublimation at 350°C, the reaction was carried out in the slight excess of PPDA for 24 h. PPTA was formed at 350°C at M of 1.3 and at 320°C at M of 1.7-2.0, confirmed by IR. Morphology of the PPTA precipitates prepared at 320°C at M of 2.0 was plate-like crystals as shown in Fig. 2 (c) and (d). The χ_{PPTA} value of the initial precipitates was 84 mol% in this case, which was four times higher than that prepared under stoichiometric condition. The small amount of PET moiety left in the oligomers was excluded by ester-amide exchange reaction

during crystal growth. WAXS intensity profile of the obtained PPTA precipitates was shown in Fig. 3. They possessed high crystallinity and the diffractions could be indexed according to the monoclinic (pseudo-orthorhombic) unit cell of the PPTA crystal.⁽³⁾ M_w of PPTA precipitates were estimated by solution viscosity measurements. M_w prepared at 320°C at M of 1.7 and 2.0 was 9.6×10^3 and 8.4×10^3 , and that prepared at 350°C at M of 1.3 was 1.02×10^4 . In general, it is difficult to prepare high molecular weight polymers under non-stoichiometric condition in the homogeneous polymerization system,⁽⁴⁻⁶⁾ but high molecular weight polymer can be prepared under non-stoichiometric condition by heterogeneous polymerization system as previously reported.⁽⁷⁻⁹⁾ PPDA moiety at oligomer end might be eliminated to polymerize with the crystal growth, resulting in the adjustment of the stoichiometric balance.

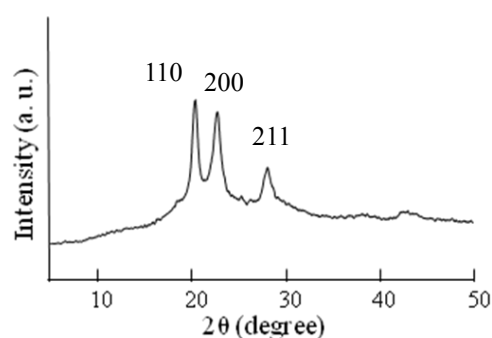


Fig. 3 WAXS intensity profile of PPTA precipitates prepared at 320°C at M of 2.0

4. Conclusions

High molecular weight PPTA was prepared from PET and PPDA by using reaction-induced crystallization of oligomers during ester-amide exchange reaction and following polymerization in the crystals. This result provides not only a new synthesis procedure of PPTA from PET but also the upgrade recycling system, which will contribute the construction of recycling-based society.

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