Synthesis and Properties of Thermally Reversible Polyesters

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Summary: Thermally reversible polyesters were obtained by the ester formation reaction of thermoplastic polyesters with hydroxyl end groups and the diacid anhydride of tetra carboxylic acid as a thermally reversible chain extender. Typical example of the thermally reversible polyesters was obtained by the reaction of PBT (polybutylene terephthalate) and PMA (pyromellitic dianhydride). This material having twice as large molecular weight as the original PBT exhibited almost the same melt viscosity as the original. Also that thermally reversible chain extension reaction occurred without unfavorable side reaction such as cross-linking. This material shows both good processability and superior mechanical properties due to its thermally reversible characters.

Keywords: chain extension, polybutylene terephthalate, polyester, thermally reversible, viscosity

Introduction

Thermoplastic polyesters are of great importance due to their excellent balance of thermal and mechanical properties and processability in practical use. Same as other thermoplastics, properties of thermoplastic polyesters are much affected by their molecular weight. For instance, increasing the molecular weight of the polymer is one of the good solutions to realize superior toughness and impact strength. However, it is not so easy to increase the molecular weight of the polyesters polymerized by melt polycondensation process, and the processability of polyesters with high molecular weight is reduced due to high melt viscosity. In order to solve the conflict between high molecular weight and excellent processability, so called thermally reversible polymers have been proposed.[1] In the thermally reversible polymers, thermally reversible chain extension-fission manner is generally used, which should realize a polymeric material with low molecular weight at the elevated temperature during processing, and with high molecular weight at the ambient temperature for practical usage. Though many approaches to the polymers have been investigated by introducing thermally reversible

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covalent linkage to polymers, there were few successful examples in practical sense. In most cases, chain extension or crosslinking reactions are possible, but thermally reversible chain dissociation reactions are difficult because of side reactions and thermally decomposition. One example of the trials of thermally reversible polyester[2] shows the difficulty of thermally reversible dissociation crosslinking due to the slow reaction and thermal decomposition of polyesters.

Strategy

Fig. 1 shows the strategy for the main chain type thermally reversible polymers, which is consisting of low molecular weight polymer and thermally reversible chain extender. Both components react with each other and form covalent chemical bond that dissociate at the elevated temperature. As the result of the thermally reversible covalent bond, it behaves like low molecular weight polymer at the elevated temperature and high molecular weight polymer at the ambient temperature. By the above-mentioned mechanism, it may exhibit both excellent mechanical properties due to high molecular weight and excellent processability due to low molecular weight. That character of thermally reversible polymers is suitable for the application of large structural parts and the matrices resins of fiber reinforced composite, and it also has good recyclability.

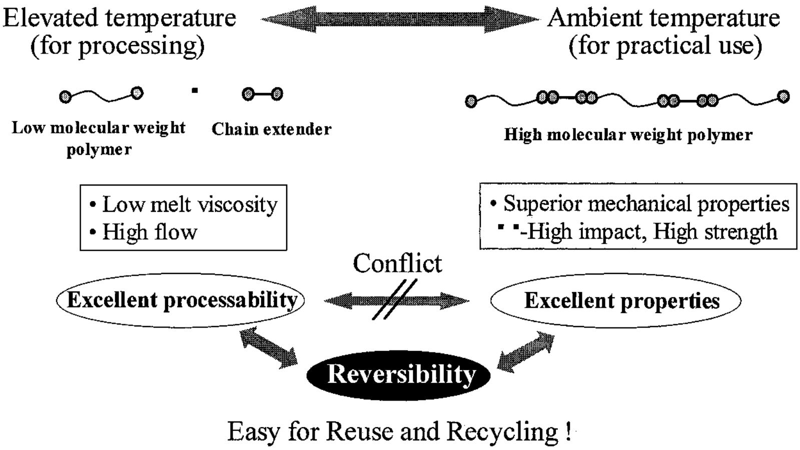


Fig. 1. Strategy of thermally reversible polymers.

We focused on the introduction of thermally reversible bond into the chain ends of polyester. We selected the reaction of diacid anhydride of tetracarboxylic acid and hydroxyl group as a thermally reversible reaction. It is very convenient to introduce hydroxyl groups to the chain ends of polyesters especially in case of polymers with low molecular weight.

Synthesis

First, we selected polybutylene terephthalate (PBT) as a basic polyester with hydroxyl end groups. And the thermally reversible PBT was obtained by melt mixing of the low molecular weight PBT with hydroxyl end groups and a diacid anhydride compound as a chain extender at 280 °C for 10 minutes followed by slow cooling. The molecular weight of the obtained thermally reversible PBT was determined by gel permeation chromatography (GPC).

The relation between the structure of chain extender and molecular weight increment after the reaction with low molecular weight PBT is shown in Fig. 2. All the chain extenders tried in this study exhibited a function of chain extender. Among these compounds, pyromellitic dianhydride was most effective.

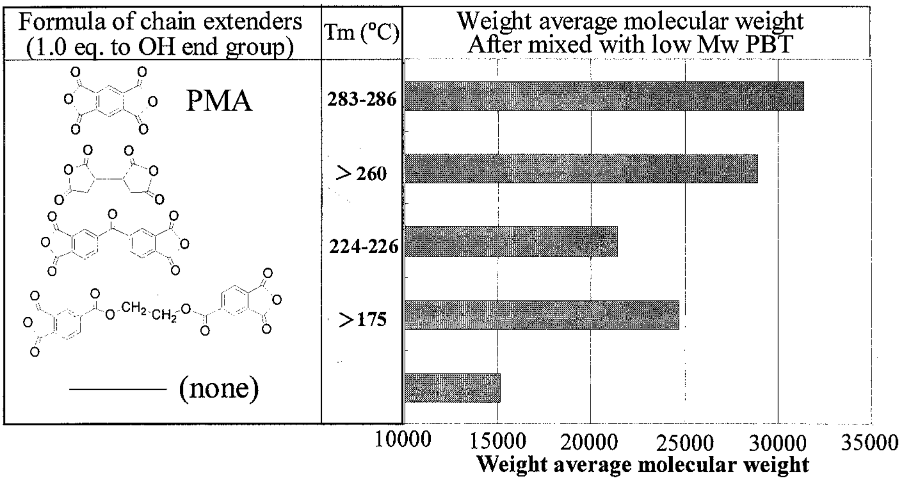


Fig. 2. Weight average molecular weight of polymers obtained by mixing of low Mw PBT and tetracarboxylic acid dianhydride compounds.

Thermally Reversible Phenomena

Fig. 3 shows the relation between melt viscosity measured at 280 °C and weight average molecular weight. This shows that the ordinary PBT has good correlation between melt viscosity and molecular weight. On the other hand, high molecular weight PBT obtained by the reaction of low molecular weight PBT having OH end groups and PMA exhibited as low melt viscosity as that of the low molecular weight PBT itself. This phenomenon explains that high molecular weight PBT changes its molecular weight at the elevated temperature. This phenomenon also means that this thermally reversible PBT may realize both high molecular weight and low viscosity.

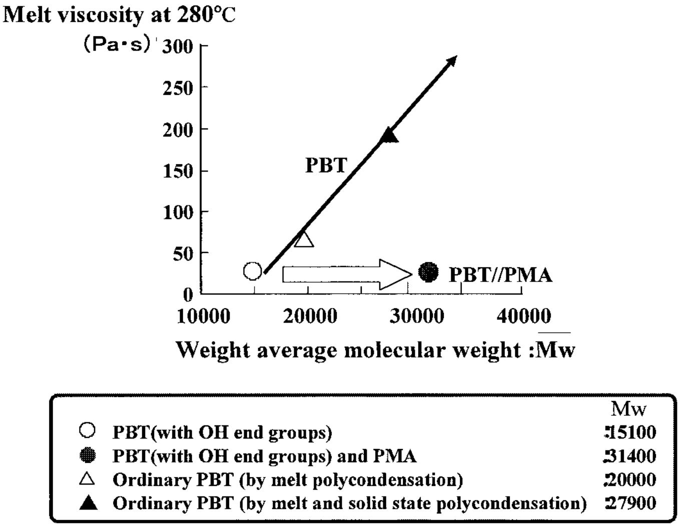
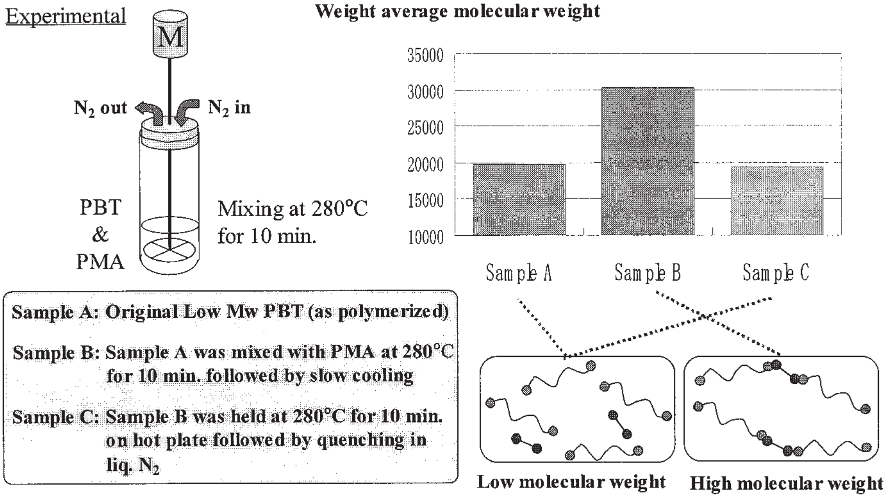


Fig. 3. Relation between melt viscosity and weight average molecular weight; Melt viscosity was determined by capillary-type rheometer.

Thermally Reversible Temperature

In order to determine the thermally reversible temperature, especially the temperature that the ester bonds dissociate, we proceeded following experiment. Low molecular weight PBT having OH end groups (Sample A) and PMA were charged in the test tube in the nitrogen atmosphere and heated up to 280 °C, then kept the temperature for 10 minutes followed by slow cooling. By this procedure, high molecular weight PBT with the weight average molecular weight of more than 30,000 (Sample B) was formed. The obtained Sample B was set on the hot plate and heated up to 280 °C followed by rapid quenching in liquid nitrogen to form Sample C. The molecular weight of Sample C was almost the same as Sample A. This means that the thermally reversible bond formed by the reaction OH end group and acid anhydride group was completely dissociated at 280 °C (Fig. 4). This method can be applied to determine the reversible temperature by changing the resident temperature on the hot plate.



Sample A: Original Low Mw PBT (as polymerized)

Sample B: Sample A was mixed with PMA at 280°C for 10 min. followed by slow cooling

Sample C: Sample B was held at 280°C for 10 min. on hot plate followed by quenching in liq. N_2

Fig. 4. Experiment for the determination of the thermally reversible temperature.

The result of the detection of reversible temperature is shown in Fig. 5. It was certain that the thermally reversible ester bond was completely dissociated above 240 °C. But a little amount of reversible ester bond was dissociated less than 230 °C.

The next step of the experiment is to determine the formation temperature of thermally reversible ester bond. We used the Sample C obtained by rapid quenching in liquid nitrogen from 280 °C as the starting material. Sample C was held at the varied resident temperature on the hot plate for 10 minutes followed by rapid quenching in liquid nitrogen, and then the molecular weight was measured by GPC. The result of the experiment was described in Fig. 6. The increment of the molecular weight was determined even in 180 °C, and the formation of thermally reversible ester bond was occurred less than 230 °C.

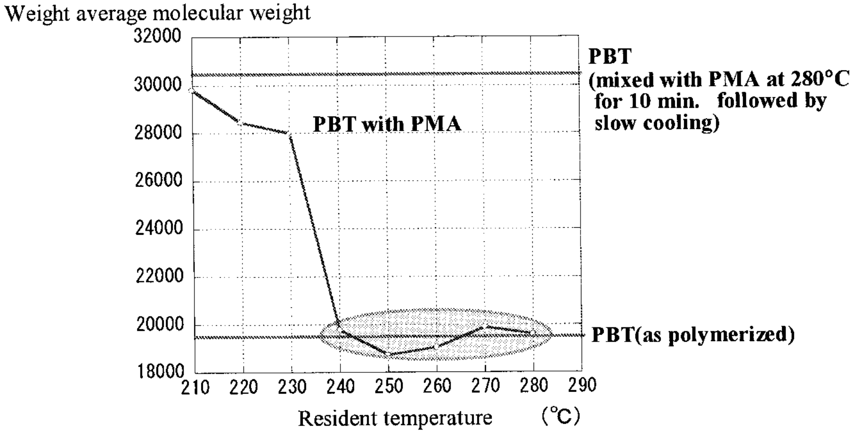


Fig. 5. Dissociation temperature of thermally reversible ester bond; Low Mw PBT and PMA were mixed at 280°C for 10 min followed by slow cooling, then held at the resident temperature on the hot plate for 10 minutes followed by rapid quenching in liquid nitrogen. Mw was measured by GPC.

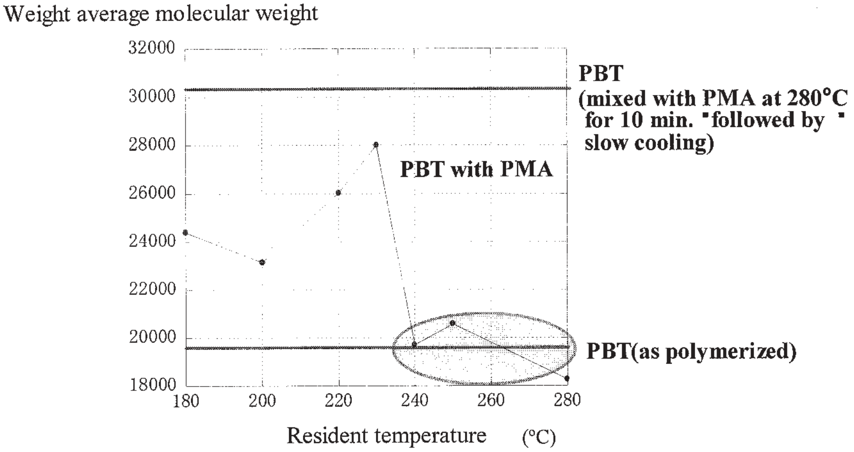


Fig. 6. Formation temperature of thermally reversible ester bond; Low Mw PBT and PMA were mixed at 280°C for 10 min followed by rapid quenching in liquid nitrogen, then held at the resident temperature on the hot plate for 10 minutes followed by rapid quenching in liquid nitrogen. Mw was measured by GPC.

Properties of Thermally Reversible PBT

We tried to clarify the structure of the thermally reversible PBT obtained by the reaction of low molecular weight PBT and PMA as a thermally reversible chain extender compared to a copolymer consisting of PBT and pyromellitic acid. We synthesized a copolymer of PBT and pyromellitic acid by ordinary method. We investigated the correlation between concentration and reduced viscosity. The result is shown in Fig. 7. It is clear that the ordinary PBT and the thermally reversible PBT using thermally reversible chain extender are the similar correlation, on the other hand, copolymer of PBT and pyromellitic acid exhibit steeper correlation compared to former two polymers.

This result seems to suggest that the thermally reversible PBT has linear structure and the copolymer of PBT and pyromellitic acid has branched structure. The pyromellitic acid acts as a branch generator when condensed with PBT. These two polymers have totally different structure.

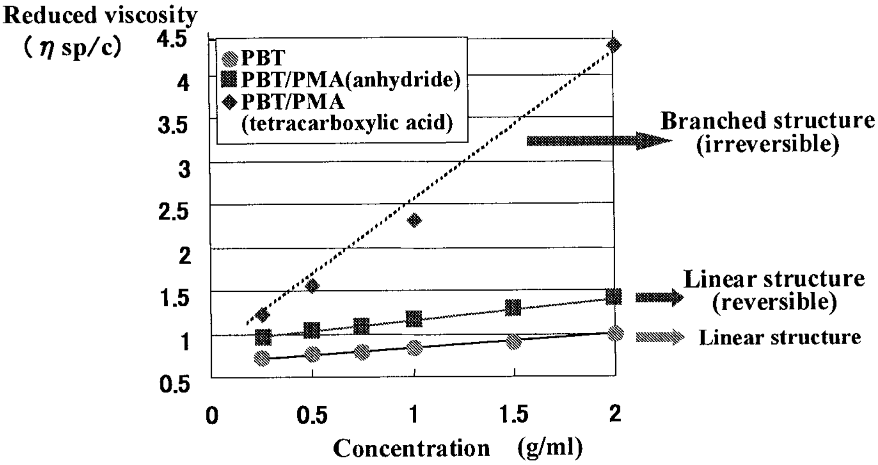


Fig. 7. Correlation between concentration and reduced viscosity (o-chlorophenol at 25 °C).

Thermal Properties

The DSC analysis of the thermally reversible PBT was shown in Table 1 compared to the ordinary PBT, which exhibits that the thermally reversible PBT has smaller heat of fusion and smaller heat of crystallization than those of the ordinary PBT without PMA, even it has almost the same melting point and crystallization point as the ordinary PBT. The results show the thermally reversible PBT has low crystallinity due to the introduction of PMA molecules in the main chain of PBT.

Table 1. Thermal properties of thermally reversible PBT.

sample	Thermal properties			
	Tm2(℃)	⊿Hm2(J/g)	Tc2(℃)	⊿Hc2(J/g)
PBT	224.6	48.5	183.8	58.4
PBT/PMA	223.5	33.2	182.0	48.0

Mechanical Properties

Mechanical properties of injection molded articles of the thermally reversible PBT are shown in Table 2 compared to the ordinary PBT and the low molecular weight PBT with OH end groups before mixing with PMA. The thermally reversible PBT has excellent toughness due to high molecular weight at the ambient temperature. Though the reason for the high modulus of it has not been clear, one possibility is the formation of pseudo-crosslinking structure by the interaction of between carboxyl groups formed by the reaction of OH end groups of PBT and PMA.

Table 2. Mechanical properties of thermally reversible PBT.

	Ordinary PBT (Mn:20000)	PBT with OH end group (Mn:15100)	PBT with OH end group and PMA(Mn:31400)
Notched Izod impact strength (J/m)	53.8	49.2	54.2
Flexural modulus (GPa)	2.40	2.40	2.53
Flexural strength (MPa)	77.6	77.8	82.7
Tensile strength (MPa)	56.3	54.1	57.8
Elongation at break (%)	15.1	8.2	52.4

Conclusion

Thermally reversible polyesters were obtained by the reaction of polyesters with OH end group and dianhydrides of tetracarboxylic acid. Obtained thermally reversible linear polyesters show unique properties such as,

-Low molecular weight and low melt viscosity at high temperature

-High molecular weight at ambient temperature

-Excellent mechanical properties due to high molecular weight

Thermally reversible reaction proceeded without annoying side reaction such as crosslinking or decomposition. A variety of molecular structure can be applied as the need arises.

[1] L. P. Engle and K. B. Wagener, *J. M. S.-Rev. Macromol. Chem.Phys.*, **1993,** *C33 (3)*, 239.
[2] J. R. Jones et al., *Macromolecules*, **1999**, *32*, 5786.