

Free-Radical Attachment of Nadic Anhydride onto Poly(alkylene terephthalate)s

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ABSTRACT: There has been little research on poly(alkylene terephthalate) modification by graft copolymerization with vinyl monomers. There is no reported information on graft polymerization in the molten state. In this study, nadic anhydride was grafted onto poly(butylene terephthalate) and poly(trimethylene terephthalate) with a free-radical initiator in an internal mixer. The influence of the monomer

and initiator concentrations on the degree of grafting was investigated. The degradation of these polymers was investigated and characterized with their complex melt viscosity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1839–1845, 2003

Key words: modification; graft copolymers; polyesters; degradation

INTRODUCTION

There has been great interest since the 1960s in making graft copolymers of polyolefins with vinyl carboxylic acids and anhydrides.^{1–11} There has, however, been more limited interest in carrying out similar melt grafting of other families of polymers. Our intention in this article is grafting acidic and anhydride units onto the backbone of poly(alkylene terephthalate)s [Fig. 1(a)].

Uchida and coworkers^{12–15} grafted various ionic vinyl monomers onto poly(ethylene terephthalate) (PET) film by ultraviolet (UV) radiation. In their study, PET film was immersed in an aqueous solution containing monomers. Subsequently, UV was irradiated to start the graft polymerization. In this study, only the surface of the PET film could be modified. For acrylic acid, the degree of grafting reached a level of approximately 30 $\mu\text{g}/\text{cm}^2$ after 3 h of polymerization.

Polycarbonate (PC) has been grafted with various vinyl monomers with a free-radical initiator.¹⁶ Both styrene and acrylonitrile have been grafted onto a PC backbone. However, the mechanism has not been addressed.

Although there seems to be limited literature on grafting onto poly(alkylene terephthalate)s, there is considerable interest in their degradation in the molten state and in the presence of air, oxygen, nitrogen, or water.^{17–25} The random ester scission mechanism for the degradation of PET has been known since the 1950s. Because poly(butylene terephthalate) (PBT) was not produced commercially until the 1970s, its degra-

ration received little attention until then. The primary mechanism for degradation found for PET and PBT is hydrolysis of the ester linkage, which leads to random scission. For PBT, $-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ is then formed, which can be degraded into tetrahydrofuran or butadiene.¹⁹ The mechanism for PET has been proposed to be similar.^{18,25}

The purpose of this study was to graft carboxylic groups and anhydrides onto molten poly(alkylene terephthalate)s, particularly PBT and poly(trimethylene terephthalate) (PTT), in an internal mixer. We attempted to accomplish this with nadic anhydride (NA) as the grafting monomer.

EXPERIMENTAL

Materials

Commercial PBT (N1100; melting point = 223°C) was supplied by Mitsubishi Rayon. Commercial PTT (Corterra CP509201; melting point = 226°C) was supplied by Shell Chemical. Both polymers were crystalline. These polymers were used (1) as received and (2) after drying in a vacuum oven. We used NA [Fig. 1(b)] as a monomer to be grafted onto PBT and PTT and α,α -dimethylbenzyl hydroperoxide [DMBHP; Fig. 1(c); 70%, water solution] as an initiator. The monomer and initiator were purchased from Aldrich Chemical. Solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol, chloroform, and acetone which we used to remove unreacted NA, were also purchased from this company.

PBT and PTT modification by the graft polymerization of NA

PBT and PTT were grafted with NA in a Brabender Plasticorder laboratory internal mixer. At first, the

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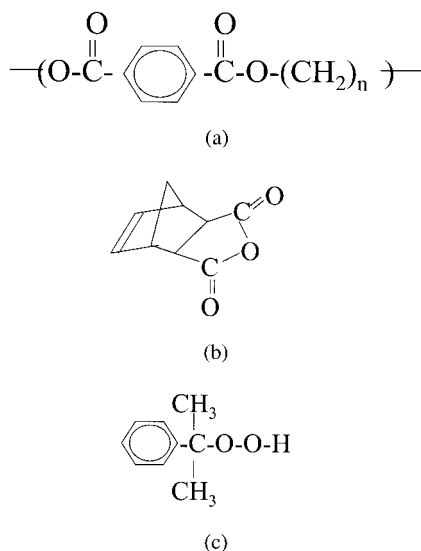


Figure 1 (a) Poly(alkylene terephthalate), (b) NA, and (c) DMBHP.

polymer was loaded into the mixer, which was kept at 250°C. NA and DMBHP were then added. The reaction time was 10 min. The monomer concentration and initiator concentration ranged from 1 to 3 wt % and from 0 to 3 wt % on the basis of 100 wt % polymer, respectively. Unreacted NA was extracted by precipitation. The samples were dissolved in a mixed solvent of 1,1,1,3,3,3-hexafluoro-2-propanol (50 wt %) and chloroform (50 wt %) to make a 10 wt % polymer solution. The solution was precipitated in 10 times as much acetone as the polymer solution (by volume), and the residual solvents were removed in a vacuum oven.

Determination of the NA incorporation onto PBT and PTT

The degree of NA grafting onto PBT and PTT was determined by Fourier Transform Infrared (FTIR) spectroscopy. The correlation curves used to determine the degree of grafting were made in the following way. PBT or PTT and NA were mixed in various ratios in an internal mixer at 230°C for PBT and at 235°C for PTT. Then, thin films were made by compression molding, and their FTIR spectra were measured. Here, the absorbance at 1780 cm^{-1} (A_{1780}), which corresponded to anhydride, was chosen for the evaluation of the degree of grafting. A_{1780} was calculated by the subtraction of the absorbance of the original PBT or PTT at 1780 cm^{-1} from that of PBT or PTT, which contained NA. The absorbance peak at 1578 cm^{-1} (A_{1578}), which corresponded to the aromatic ring in these polymers, was chosen as an internal standard. A_{1578} was calculated by the subtraction of the baseline

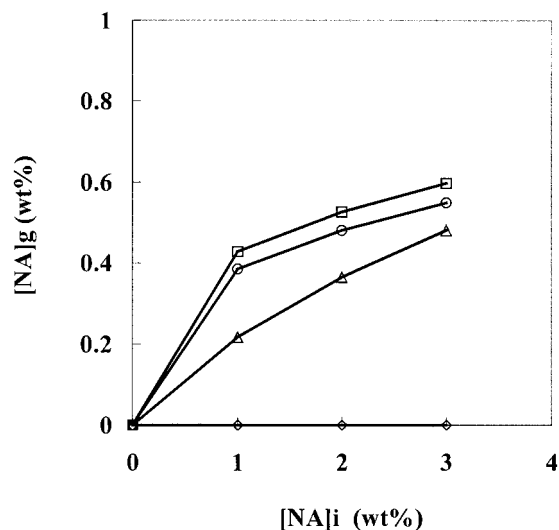


Figure 2 Effect of the initial NA concentration ($[\text{NA}]_i$) on the grafting NA concentration ($[\text{NA}]_g$) for PBT in an internal mixer (60 rpm, 250°C, and 10 min): (□) 3.0, (○) 2.0, (△) 1.0, and (◇) 0.0 wt %.

from the absorbance of the original PBT or PTT at 1578 cm^{-1} .

Complex viscosity (η^*) of grafted PBT and PTT

$\eta^*(\omega)$ (where ω is the frequency) of grafted PBT and PTT was measured at 240°C under nitrogen in a parallel-plate mode (Rheometric Scientific). The unreacted monomer was removed by precipitation, and the samples were dried in a vacuum oven at 120°C for 15 h before being characterized.

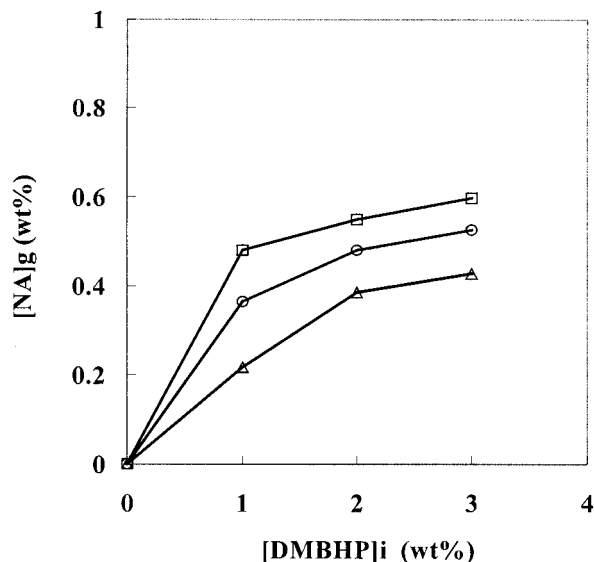


Figure 3 Effect of the initial DMBHP concentration ($[\text{DMBHP}]_i$) on the grafting NA concentration ($[\text{NA}]_g$) for PBT in an internal mixer (60 rpm, 250°C, and 10 min): (□) 3.0, (○) 2.0, and (△) 1.0 wt %.

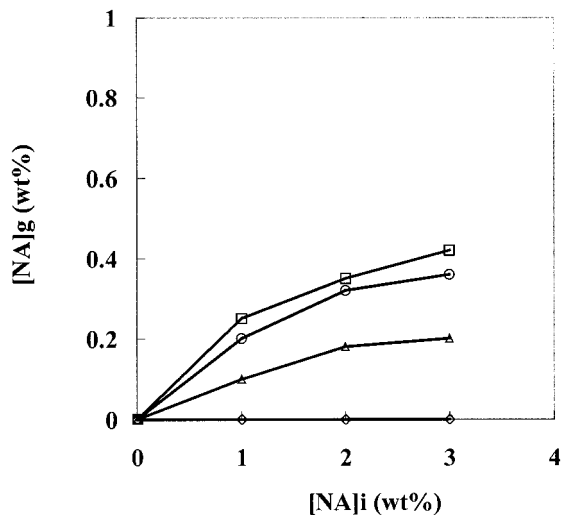


Figure 4 Effect of the initial NA concentration ($[NA]_i$) on the grafting NA concentration ($[NA]_g$) for PTT in an internal mixer (60 rpm, 250°C, and 10 min): (□) 3.0, (○) 2.0, (△) 1.0, and (◇) 0.0 wt %.

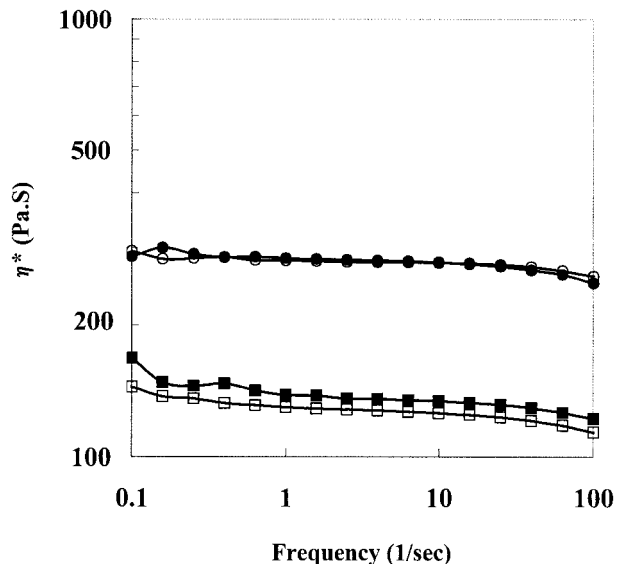


Figure 6 Effect of the frequency on η^* (at 240°C) of (○) original PBT, (●) original PTT, (□) grafted PBT, and (■) grafted PTT.

Mastication of poly(alkylene terephthalate)s under air and nitrogen

For further insight, the molecular weight change of PBT and PTT by mastication was investigated.

PBT and PTT were masticated in a Brabender Plasticorder laboratory internal mixer in air and dry nitrogen for 10 min. The temperatures were 230, 250, and 270°C for PBT and 235, 250, and 270°C for PTT. In this experiment, we used these polymers (1) as received and (2) after being dried in a vacuum oven at 120°C for 15 h.

Treatments of poly(alkylene terephthalate)s with water and peroxide

For further insight, the molecular weight change of PBT and PTT by water and peroxide treatments was investigated.

At first, the dried polymer was loaded and kneaded in the mixer under air. Water or peroxide was subsequently added to the molten polymer. The amount of the water or peroxide was 2 wt %. The temperatures were 230, 250, and 270°C for PBT and 235, 250, and 270°C for PTT.

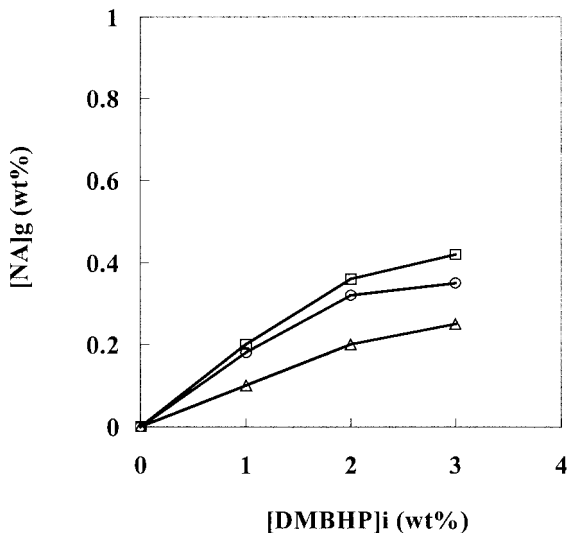


Figure 5 Effect of the initial DMBHP concentration ($[DMBHP]_i$) on the grafting NA concentration ($[NA]_g$) for PTT in an internal mixer (60 rpm, 250°C, and 10 min): (□) 3.0, (○) 2.0, and (△) 1.0 wt %.

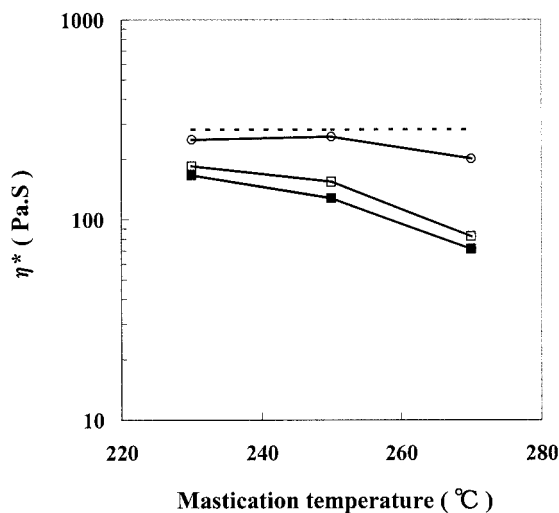


Figure 7 Effect of the mastication temperature on η^* (at 240°C and 1 rad/s) of (○) masticated PBT (dried) under nitrogen, (□) masticated PBT (dried) under air, (■) masticated PBT (as received) under air, and (—) original PBT.

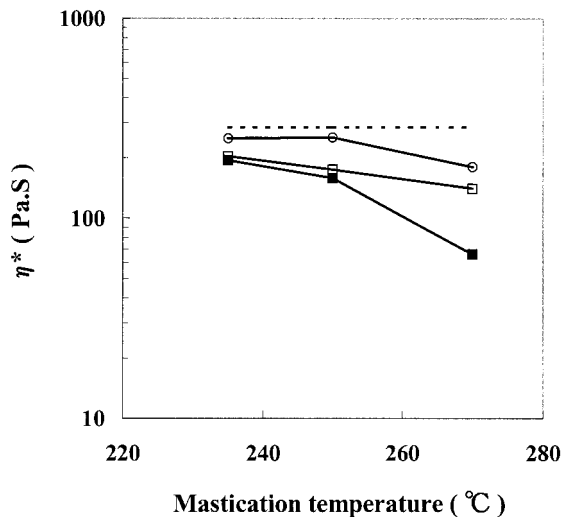


Figure 8 Effect of the mastication temperature on η^* (at 240°C and 1 rad/s) of (○) masticated PTT (dried) under nitrogen, (□) masticated PTT (dried) under air, (■) masticated PTT (as received) under air, and (—) original PTT.

Characterization of masticated and treated poly(alkylene terephthalate)s

The various masticated and otherwise treated polymers were dried in a vacuum oven at 120°C for 15 h before being characterized. $\eta^*(\omega)$ was measured at 240°C under nitrogen in a parallel-plate mode.

RESULTS

PBT modification by NA

Figure 2 shows the influence of the initial NA concentration on the degree of grafting. The reaction was

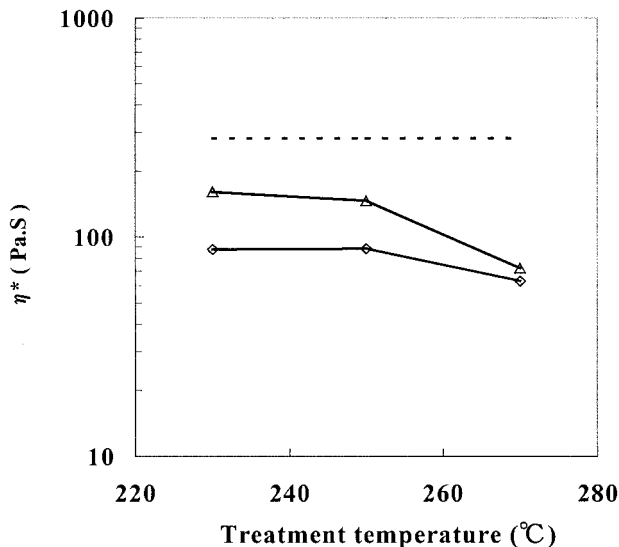


Figure 9 Effect of the treatment temperature on η^* (at 240°C and 1 rad/s) of treated PBT: (△) water-treated PBT, (◇) peroxide-treated PBT, and (—) original PBT.

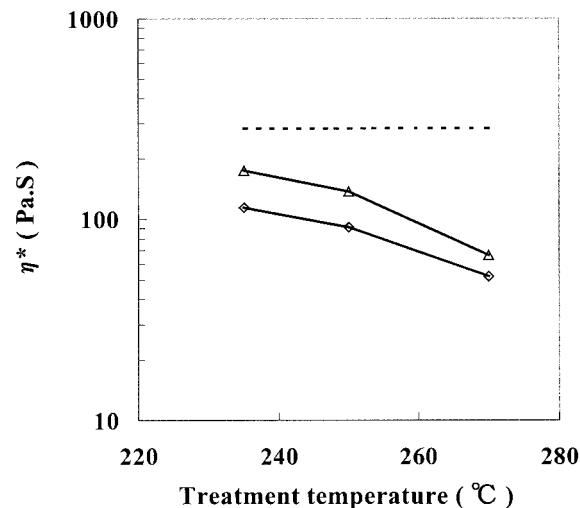


Figure 10 Effect of the treatment temperature on η^* (at 240°C and 1 rad/s) of treated PTT: (△) water-treated PTT, (◇) peroxide-treated PTT, and (—) original PTT.

conducted in the internal mixer at 250°C for 10 min. With an increase in the initial monomer concentration, the grafting degree increased. It showed a tendency of leveling off at high NA concentrations. At all nadic anhydride concentrations, this monomer was not polymerized without DMBHP. This indicated that this grafting took place through a free-radical mechanism. Figure 3 shows the influence of the initial DMBHP concentration on the degree of grafting. With an increase in the initiator concentration, the grafting degree increased, but it showed a tendency of leveling off. The maximum degree of grafting, which was approximately 0.6 wt %, was obtained at an NA concentration of 3 wt % and a DMBHP concentration of 3 wt %.

We also sought to identify pure polymerized poly(nadic anhydride). None was found. Apparently, all the reacting NA was incorporated into PBT, even though the possibility existed that an oligomer of NA was formed, which was dissolved in the acetone extract.

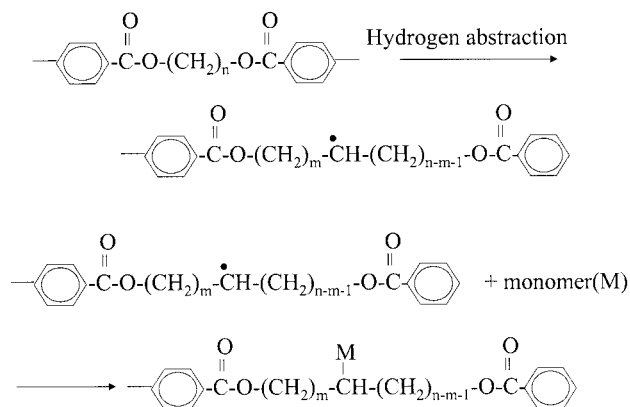


Figure 11 Grafting of poly(alkylene terephthalate).

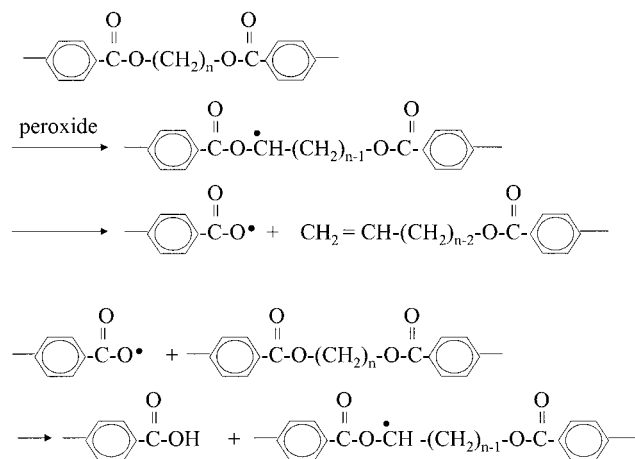


Figure 12 Peroxide-induced degradation of poly(alkylene terephthalate).

PTT modification by NA

PTT modification by NA was carried out with the same procedure used for PBT modification. Figure 4 shows the influence of the initial NA concentration on the grafting degree. Figure 5 shows the influence of the initial DMBHP concentration. In this case, NA was not consumed without the presence of DMBHP. The behavior of the NA and DMBHP concentrations was similar to that observed for PBT. The maximum degree of grafting, which was approximately 0.4 wt %, was obtained at an NA concentration of 3 wt % and a DMBHP concentration of 3 wt %. Again, we found no poly(nadic anhydride), even though oligomeric NA, which could be dissolved in acetone, might have been formed.

η^* of the original PBT and PTT and grafted PBT and PTT

Figure 6 shows the frequency dependence of η^* for the original PBT and PTT. The frequency effect on η^* of PBT and PTT was very small. η^* of the original PBT was 281 Pa S at $\omega = 1$ rad/s. η^* of the original PTT was 284 Pa S at this frequency.

Figure 6 also shows the effect of frequency on η^* at 240°C of grafted PBT and PTT. These polymers were grafted by NA at 250°C for 10 min in the mixer with 2 wt % NA and 2 wt % DMBHP. $\eta^*(\omega = 1)$ of grafted PBT was 130 Pa S, which was 46% of that of the

original PBT. $\eta^*(\omega = 1)$ of grafted PTT was 138 Pa S, which was 49% of that of the original PTT.

Mastication of PBT and PTT under air and nitrogen

We attempted to discover the mechanism of viscosity (molecular weight reduction) during the grafting reaction.

Figure 7 shows the influence of the mastication temperature on η^* of masticated PBT. In this figure, the value of η^* is that at $\omega = 1$ rad/s. η^* of the original PBT was 281 Pa S at this frequency. For as-received PBT under air, η^* decreased to 25–59% of that of the original PBT. With an increasing mastication temperature, η^* decreased more. For dried PBT under air, η^* decreased to 29–65% of that of the original PBT. The same temperature effect was observed as for an as-received sample. When dried PBT was masticated under nitrogen, η^* decreased to 71–92% of that of the original PBT.

Figure 8 shows the influence of the mastication temperature on η^* of masticated PTT. η^* of the original PTT was 284 Pa S at this frequency. For as-received PTT under air, η^* decreased to 23–68% of that of the original PTT. With increasing temperature, η^* decreased more. For dried PTT under air, η^* decreased to 49–71% of that of the original PTT. The same temperature effect was observed for as-received sample. When dried PTT was masticated under nitrogen, η^* decreased to 63–89% of that of the original PTT.

Water and peroxide treatments of PBT and PTT

Figure 9 shows the influence of the treatment temperature on η^* of PBT treated with water and peroxide. Both water and peroxide enhanced the reduction of η^* . In the water-treatment case, η^* decreased to 26–57% of that of the original PBT. With the peroxide treatment, η^* decreased to 22–31%.

Figure 10 shows the influence of the treatment temperature on η^* of PTT treated with water and peroxide. Both water and peroxide enhanced the reduction of η^* . In the water-treatment case, η^* decreased to 23–61% of that of the original PTT. With the peroxide treatment, η^* decreased to 18–40%.

TABLE I
Complex Viscosity Reduction of PBT [η^*/η^* (Original)]

	Mastication (dried) under nitrogen	Mastication (dried) under air	Mastication (as received) under air	Water treatment	Peroxide treatment
230°C	0.89	0.65	0.59	0.57	0.31
250°C	0.92	0.55	0.45	0.52	0.31
270°C	0.71	0.29	0.25	0.26	0.22

TABLE II
Molecular Weight Reduction of PBT [M_w/M_w (Original)]

	Mastication (dried) under nitrogen	Mastication (dried) under air	Mastication (as received) under air	Water treatment	Peroxide treatment
230°C	0.97	0.89	0.86	0.85	0.72
250°C	0.98	0.84	0.80	0.83	0.72
270°C	0.91	0.70	0.67	0.68	0.65

DISCUSSION

Comparison to earlier work and mechanism of anhydride incorporation

It is well known that polyolefins, such as polyethylene and polypropylene, can be grafted with various vinyl monomers. The radical abstracts hydrogen from the backbone of the polyolefin, and monomer molecules are attached to it. Because of the polyolefin grafting mechanism, radicals derived from the peroxide presumably attack butylene in PBT and trimethylene in PTT to abstract hydrogen. NA is presumably grafted on this radical site. This mechanism is shown in Figure 11.

This mechanism is similar to that of polyethylene and should lead to crosslinking.

Degradation of masticated and treated PBT and PTT

As-received PBT and PTT contain moisture and oxygen. For this reason, as-received PBT and PTT degrade more than dried materials through hydrolysis and oxidative degradation. Dried PBT and PTT contain less moisture and oxygen than as-received polymers. In this sense, dried PBT and PTT degrade through established thermal degradation mechanisms. However, during melt mixing in an internal mixer under air, oxygen and moisture go into the molten polymers. This should cause enhanced degradation of dried PBT and PTT. By the introduction of dry nitrogen into the mixer, the trapping of oxygen and moisture can be avoided somewhat. This agrees with our experimental results showing that the molecular weight reduction was suppressed under nitrogen in comparison with air.

In the water treatment of PBT and PTT, most water added to the molten polymer evaporated instantly, but a very small portion might have been trapped in

the molten polymers. For both PBT and PTT, η^* of the water-treated polymers was lower than that for the dried polymers. This means that water trapped in the polymers degraded them more.

In the peroxide treatment, in comparison with the water treatment, the degradation of PBT and PTT was enhanced. The peroxide that we used contained 30 wt % water. However, the water treatment did not degrade PBT and PTT as much as this peroxide treatment. Therefore, peroxide itself played an important role in the chain scission of PBT and PTT. The peroxide-induced degradation of these polymers could take place as shown in Figure 12.

The carbon radical next to an ester group presumably destabilizes the ester group, and $-\text{COO}\cdot$ might be formed at the end of a polymer chain. This may be a reason that PBT and PTT degraded instead of crosslinking, as observed for polyethylene. The radical at the end of a polymer chain is transferred to another polymer chain to abstract hydrogen subsequently. Through this mechanism, the degradation of PBT and PTT is enhanced in the presence of peroxide to yield lower molecular weight polymers.

The molecular weight can be estimated by the melt viscosity. The melt viscosity of PBT was reportedly proportional to $M_w^{3.5}$,²⁶ where M_w is the weight-average molecular weight. We assumed that this could be applied to PTT. Tables I and II summarize the viscosity and molecular weight reduction of PBT, respectively. Tables III and IV summarize the viscosity and molecular weight reduction of PTT, respectively. The molecular weight reduction was calculated under the aforementioned assumption. As shown in these tables, the drying of these polymers before use could suppress the molecular weight reduction. Also, nitrogen suppressed the reduction in comparison with air. M_w of masticated and dried PBT and PTT under nitrogen was 91–98% of M_w of the original PBT and 88–97% of

TABLE III
Complex Viscosity Reduction of PTT [η^*/η^* (Original)]

	Mastication (dried) under nitrogen	Mastication (dried) under air	Mastication (as received) under air	Water treatment	Peroxide treatment
235°C	0.88	0.71	0.68	0.61	0.40
250°C	0.89	0.61	0.56	0.48	0.32
270°C	0.63	0.49	0.23	0.23	0.18

TABLE IV
Molecular Weight Reduction of PTT [M_w/M_w (Original)]

	Mastication (dried) under nitrogen	Mastication (dried) under air	Mastication (as received) under air	Water treatment	Peroxide treatment
235°C	0.96	0.91	0.90	0.87	0.77
250°C	0.97	0.87	0.85	0.81	0.72
270°C	0.88	0.82	0.66	0.66	0.62

M_w of the original PTT, respectively. The water and peroxide treatments enhanced M_w reduction for both PBT and PTT. M_w of water-treated and peroxide-treated PBT decreased to as little as 68 and 65% of M_w of the original PBT, respectively. M_w of water-treated and peroxide-treated PTT decreased to as little low as 66 and 62% of M_w of the original PTT, respectively.

Degradation during the grafting reaction

During the grafting reaction, both graft polymerization and degradation took place. However, as clearly shown in our experimental results, the η^* values of grafted PBT and PTT were larger than those of peroxide-treated PBT and PTT. In this sense, degradation was suppressed somewhat during the grafting reaction in comparison with the peroxide treatment of these polymers.

CONCLUSIONS

PBT and PTT were successfully grafted by NA in the molten state. The degrees of grafting for PBT and PTT were up to 0.6 and 0.4 wt %, respectively. With higher concentrations of the monomer and initiator, the degree of grafting was observed to increase.

The degradation of dried and as-received PBT and PTT was conducted under air and nitrogen. For as-received and dried PBT under air, η^* decreased to as little as 25 and 29% of that of the original material, respectively. For as-received and dried PTT under air, it decreased to as little as 23 and 49%. In both cases, the as-received material had a lower η^* value than the dried material, and this clearly showed that moisture and oxygen in PBT and PTT enhanced the degradation. When we applied nitrogen to the mixer, the degradation of these dried polymers was suppressed. When water and peroxide treatments were carried out in the molten state, these treatments enhanced the degradation. In water and peroxide treatments of PBT, the viscosity decreased to as little as 26 and 22%, respectively. In water and peroxide treatments of PTT,

the viscosity decreased to as little as 23 and 18%, respectively. In each case, at a higher temperature, a lower viscosity was obtained.

During the grafting reaction, both graft polymerization and degradation took place, and degradation was suppressed in comparison with the peroxide treatment.

References

- Nowak, R. M. U.S. Pat. 3,270,090 (1966).
- Kasei, A. Br. Pat. 1,217,231 (1970).
- McConnell, R. L. U.S. Pat. 3,658,948 (1972).
- Bartz, K. W.; Higgins, J. J.; Berejka, A. J.; DiCresce, A. J. U.S. Pat. 3,868,433 (1975).
- Caywood, S. W. U.S. Pat. 3,884,882 (1975).
- Yamamoto, N.; Isoi, M.; Yoda, M.; Wada, S. U.S. Pat. 4,146,529 (1979).
- Chen, P. N.; Glick, M. M.; Jaffe, M. M.; Forschirm, A. U.S. Pat. 5,173,541 (1992).
- Martinez, J. M. G.; Taranco, J.; Laguna, O.; Collar, E. P. Int Polym Process 1994, 9, 246.
- Kim, B. J.; White, J. L. Int Polym Process 1995, 10, 213.
- Hojabr, S.; Baker, W. E.; Russell, K. E.; McLellan, P. J.; Huneault, M. A. Int Polym Process 1998, 13, 118.
- Cha, J.; White, J. L. Polym Eng Sci 2001, 41, 1227.
- Uchida, E.; Uyama, Y.; Ikada, Y. J Polym Sci Part A: Polym Chem 1989, 27, 527.
- Uchida, E.; Uyama, Y.; Ikada, Y. J Appl Polym Sci 1990, 41, 677.
- Uchida, E.; Uyama, Y.; Iwata, H.; Ikada, Y. J Polym Sci Part A: Polym Chem 1990, 28, 2837.
- Uchida, E.; Uyama, Y.; Ikada, Y. J Appl Polym Sci 1993, 47, 417.
- Cantrill, J. E. U.S. Pat. 3,462,515 (1969).
- Ravens, D. A. S.; Sisley, J. E. In Chemical Reactions of Polymers; Fettes, E. M., Ed.; Interscience: New York, 1964; p 551.
- Nealy, D. L.; Adams, L. J. J Polym Sci Part A-1: Polym Chem 1971, 9, 2063.
- Lum, R. M. J Polym Sci Polym Chem Ed 1979, 17, 203.
- Zimmerman, H.; Kim, N. T. Polym Eng Sci 1980, 20, 680.
- Jabarin, S. A.; Lofgren, E. A. Polym Eng Sci 1984, 24, 1056.
- Edge, M.; Allen, N. S.; Wiles, R.; McDonald, W.; Mortlock, S. V. Polymer 1995, 36, 227.
- Duvall, D. E. Polym Plast Technol Eng 1995, 34, 227.
- Dzieciol, M.; Trzeszczynski, J. J Appl Polym Sci 1998, 69, 2377.
- Botelho, G.; Queiros, A.; Liberal, S.; Gijsman, P. Polym Degrad Stab 2001, 74, 39.
- Borman, W. F. H.; Kramer, M. Am Chem Soc Coat Plast Prepr 1974, 34, 77.