Conversion of Polyester into Heat-Resistant Polyamide by Reacting with Aromatic Diamine Compound

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ABSTRACT: The ester–amide exchange reaction between poly(ethylene terephthalate) and *p*-phenylenediamine in *n*-dodecylbenzene as a solvent in the absence of catalyst was carried out to obtain heat-resistant polyamide. The observation of the amide group generated in the reaction product was made by FTIR analysis and the relative extent of reaction was estimated by the amidation ratio from FTIR and the nitrogen content determined from elemental analysis. The effect of chemical structure in the homologous series of aliphatic and aromatic diamines on the reactivity of ester–amide exchange reaction was studied. How reaction variables such as time, temperature, and the amount of diamine used affected the extent of reaction and the heat-resistant property of polyamide obtained was thoroughly studied. Finally, a search for an efficient catalyst among metal acetates was attempted. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2502–2512, 2004

Key words: polyesters; polyamides; thermogravimetric analysis (TGA); ester–amide exchange reaction; catalysts

INTRODUCTION

Poly(ethylene terephthalate) (PET) resin exhibits high strength, low specific gravity, low CO_2-gas permeability, and relatively high transparency; furthermore, it is known to be harmless to the human body. PET is one of the fastest growing polymers with a variety of application areas such as home electronic appliances, automobiles, and beverage bottles. With the increased demand for PET usage, PET resin places a substantial burden on disposal of used plastics. Therefore, the development of novel recycling technology of waste PET resin is to be addressed and studied.

Simionescu et al.[1] reported that PET could be converted into polyamide by reacting ethylenediamine with functional end groups [–COOH, –CH=CH$_2$, –(CH$_2$)$_2$OH] generated in PET by mechanical means or by using ^{60}Co γ-ray. Based on this interesting process, Nakano[2] claimed that a variety of polyamides could be obtained from the conversion reaction processes, which consist of batch and semibatch reaction processes, by reacting polyester with aliphatic or aromatic diamines in the presence of organic solvent. Nakano and Kato[3] proposed a novel process for producing high-performance poly(hexamethylene terephthalamide) (polyamide-6T) from PET by reacting PET with hexamethylenediamine in solvent. The conversion reaction of PET into polyamide shows a possibility that PET resin can be converted into a high-performance aromatic polyamide if an aromatic diamine [e.g., *p*-phenylenediamine (PDA)] as diamine compound is used in the reaction process. The feasibility of the conversion of PET into an aromatic polyamide is to be studied implying that a polymer (I) could be converted into another value-added polymer (II) and it also could be applied for one of the recycling technologies of waste PET resin; however, any experimental study on the conversion reaction using PDA has never been reported except a short statement described in the patent literature by Nakano.[2] It was claimed in the patent that the conversion reaction of PET into polyamide needs to be carried out for more than 10 h (at least 7 h) in the batch reactor.[2] The relatively long reaction time needs to be shortened to develop an economically feasible process by searching for an effective reaction catalyst in the conversion reaction of PET into polyamide. According to a Japanese patent,[4] it has been claimed that a complex salt compound of metal acetate as a reaction catalyst was used to obtain a heat-resistant fibrous product by reacting PET resin with an excess amount of diamine. However, any explanation on how effective the reaction catalyst is in the minimization of reaction time was not made in the patent.[4]

In the present study, we carry out a conversion reaction of PET into polyamides by reacting PET with various diamines in the presence of solvent and further we sought to obtain poly(*p*-phenylene terephthalamide) from PET by reacting with *p*-phenylenediamine in *n*-dodecylbenzene. Finally, we attempted to
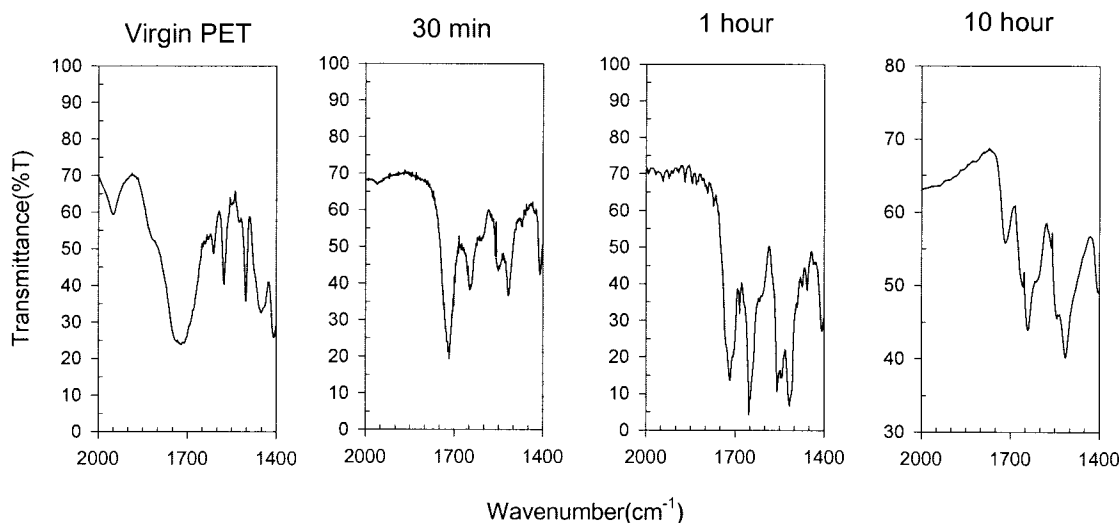
Figure 1 Variation of IR spectrum with time for polyamide obtained by reacting PET with *p*-phenylenediamine. Reaction conditions: 210°C, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.

search for a catalyst that is effective with respect to the reduction of reaction time in the conversion reaction.

EXPERIMENTAL

Materials

PET of commercial homopolymer resin (Grade A7045; Saehan Co., Korea) having an intrinsic viscosity ($[\eta]$) of 0.635 was used after drying in a convection oven before the reaction experiment. Aliphatic and aromatic diamines purchased from Aldrich Chemical Co. (Milwaukee, WI) were used to react with PET without further purification: 4,4'-diaminodiphenylmethane (DADPM), 4,4'-diaminodiphenylethane (DADPE), 1,8-octanediamine (ODA), 1,4-butanediamine (BDA), hexamethylenediamine (HMD), 4,4'-diaminodiphenylether (DADPEt), 4,4'-diaminodiphenylsulfide (DADPS), *p*-phenylenediamine (PDA), *p*-xylenediamine (XDA), 1,2-diaminocyclohexane (DACH). Magnesium acetate tetrahydrate, calcium acetate monohydrate, calcium acetate hydrate, barium acetate, cobalt(II) acetate tetrahydrate, aluminum acetate, lithium acetate dihydrate, sodium acetate, lead(IV) acetate, manganese(II) acetate, tin(II) acetate, and zinc acetate dihydrate were used as reaction catalysts without further purification and purchased from Aldrich Chemical Co. *N*-Dodecylbenzene (NDDB) and *o*-dichlorobenzene were used as solvents in the conversion reaction of PET into polyamide and purchased from Kanto Chemical Co. (Japan).

Conversion reaction of PET into polyamide

The conversion reaction of PET into polyamide was carried out in a batch reactor pressurized using nitrogen gas (about 7 kg/cm^2) and reaction conditions such as reaction time, temperature, and mole ratio of PDA to PET were varied. NDDB was added in the reaction mixture as a solvent as much as ten times by weight of the amount of diamine used. After a batch reaction process was completed, the reaction mixture was precipitated with an excess amount of methanol, and the solid product was recovered by filtering. The recovered solid reaction product was dried in vacuum for 24 h at 120°C and then used for the analysis.
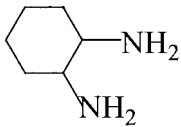
Analysis of polyamide

Amidation ratio (AR) was used as a relative indicator of the reaction progress and estimated from the FTIR spectrum as follows:

$$AR = \frac{\lambda_{1510}}{\lambda_{1510} + \lambda_{1710}}$$

Here λ_{1510} and λ_{1710} are the IR absorbencies of characteristic peaks at 1510 cm^{-1} (–CO—NH– group) and 1710 cm^{-1} (–COO– group), respectively. The nitrogen content (wt %) of reaction product was also estimated using the elemental analysis method with CHNS-mode and used as the barometer of the relative extent of reaction along with the AR value. The heat-resistant property of polyamide was analyzed using thermogravimetric analysis (TGA) method and compared with T_{50} value, which is the temperature at which 50% weight loss has occurred. Measurement errors for amidation ratio, nitrogen content, and T_{50} in TGA are AR $\pm$ 0.005, N $\pm$ 0.4%, and T_{50} $\pm$ 5°C, respectively.

TABLE I
Properties of Polyamides Obtained by Reacting PET with Aliphatic Diamines[a]

Diamine	Chemical structure	AR	Nitrogen (wt %)	T_{50} (°C)
BDA	$H_2N—(CH_2)_4—NH_2$	0.752	11.21	463
HMD	$H_2N—(CH_2)_6—NH_2$	0.663	10.47	460
ODA	$H_2N—(CH_2)_8—NH_2$	0.655	10.28	442
DACH	(cyclohexane with two NH₂ groups)	0.580	9.45	419

[a] Reaction conditions: 180°C, 10 h, diamine/PET (mole ratio) = 1.0. Solvent: o-dichlorobenzene.

RESULTS AND DISCUSSION

FTIR analysis to observe amide group generated in reaction product

The reaction mechanism for the conversion of PET into polyamide was proposed by Nakano and Kato[3] and it consists of an ester–amide exchange reaction. An attack of diamine on PET supersedes the ester group with the amide group and generates ethylene glycol as a reaction byproduct. Also it suggests that the polymeric chain length is not shortened but extended by the intermolecular and intramolecular reactions.[3] According to the reaction mechanism from PET to polyamide proposed by Nakano and Kato,[3] a reaction route toward aromatic polyamide [i.e., poly(p-phenylene terephthalamide)] by reacting PET with aromatic diamine (i.e., PDA) is described as follows:
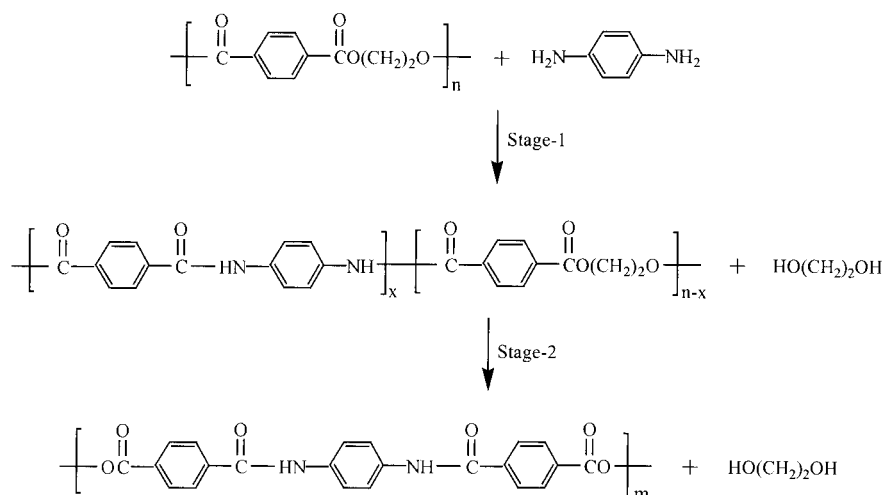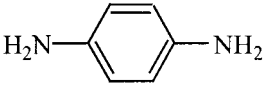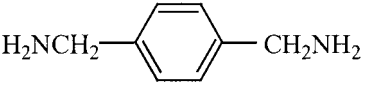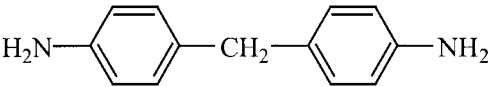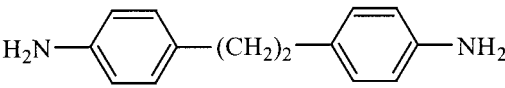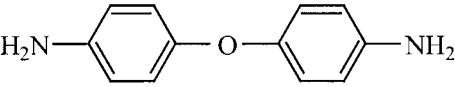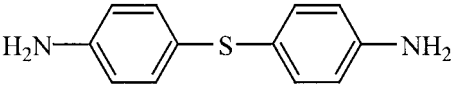

The initial reaction product from the conversion reaction is a sort of polyester–polyamide copolymer whose ester group is partially converted into an amide group. The final reaction product to be obtained by allowing the reaction to proceed to completion is poly(p-phenylene terephthalamide), which is known as Kevlar (DuPont, Wilmington, DE). Figure 1 shows that PET is progressively converted into polyamide with reaction time and thus the ester group peak at 1710 cm^{-1} continues to disappear and the amide group peak at 1510 cm^{-1} becomes observable with progress of the reaction.

Effect of chemical structure of diamine on the reactivity of ester–amide exchange reaction

The effect of chemical structure of diamine on the extent of reaction (amidation ratio and nitrogen content) and the heat-resistant property (T_{50}) of polyamide was investigated. Homologous series of aliphatic (Table I) and aromatic (Table II) diamines were used in the conversion reaction of PET into polyamide and the properties of polyamides were compared under the constant reaction conditions, which revealed that aliphatic diamine is relatively easy to react with PET, indicating higher values of AR and nitrogen content compared with aromatic diamines. However, polyamides obtained from aromatic diamines show higher heat-resistant property compared with that of polyamides from aliphatic diamines. The reactivity differences (i.e., AR and nitrogen content) among the homologs are explained by steric hindrance resulting from the bulkiness of diamine compound and the molecular mobility of the substituent group in diamines.

TABLE II
Properties of Polyamides Obtained by Reacting PET with Aromatic Diamines[a]

Diamine	Chemical structure	AR	Nitrogen (wt %)	T_{50} (°C)
Group (I)				
PDA	H_2N—⟨benzene⟩—NH_2	0.589	9.78	633
XDA	H_2NCH_2—⟨benzene⟩—CH_2NH_2	0.515	7.61	405
Group (II)				
DADPM	H_2N—⟨benzene⟩—CH_2—⟨benzene⟩—NH_2	0.568	7.42	708
DADPE	H_2N—⟨benzene⟩—$(CH_2)_2$—⟨benzene⟩—NH_2	0.525	6.64	561
DADPEt	H_2N—⟨benzene⟩—O—⟨benzene⟩—NH_2	0.628	7.56	715
DADPS	H_2N—⟨benzene⟩—S—⟨benzene⟩—NH_2	0.556	6.80	664

[a] Reaction conditions: 210°C, 10 h, diamine/PET (mole ratio) = 1.0. Solvent: n-dodecylbenzene.

Effect of reaction variables (time, temperature, mole ratio of diamine to PET) on the extent of reaction and the heat-resistant property of the product in the ester–amide exchange reaction

We selected PDA from among the aromatic diamines to study an ester–amide exchange reaction between PET and PDA in n-dodecylbenzene. The ester–amide exchange reaction between PET and PDA finally produced poly(p-phenylene terephthalamide) in the complete conversion and a reaction product obtained in the midstage of the reaction progress was a polyester–polyamide copolymer with high heat-resistant property. Figure 2 shows the amidation ratio and nitrogen content increase with reaction time, which
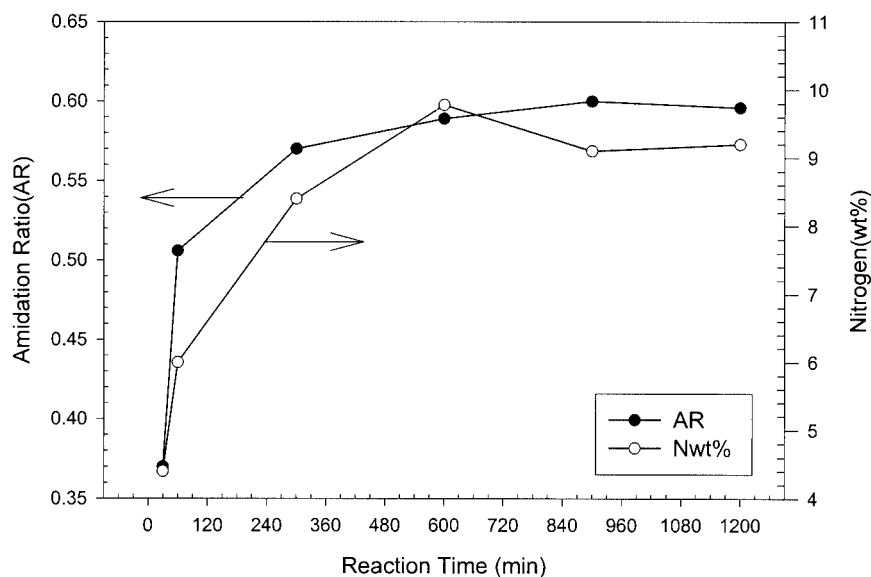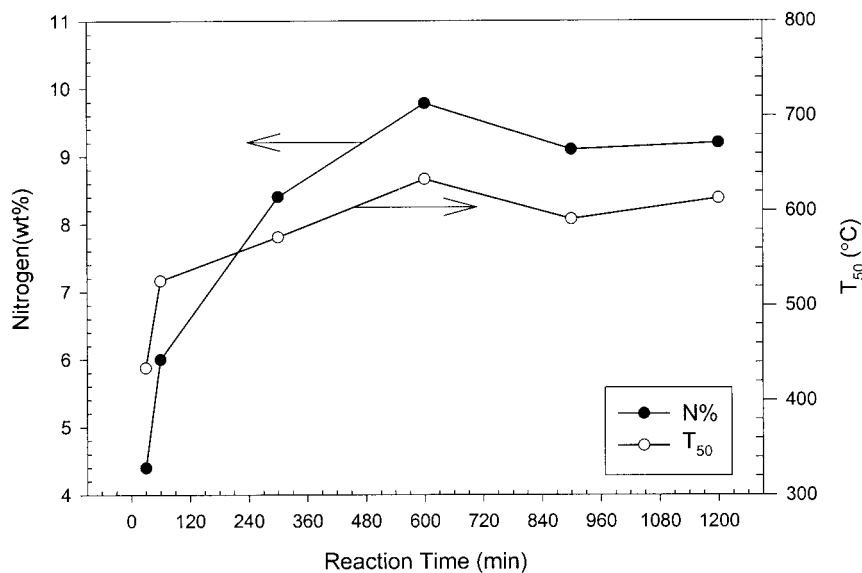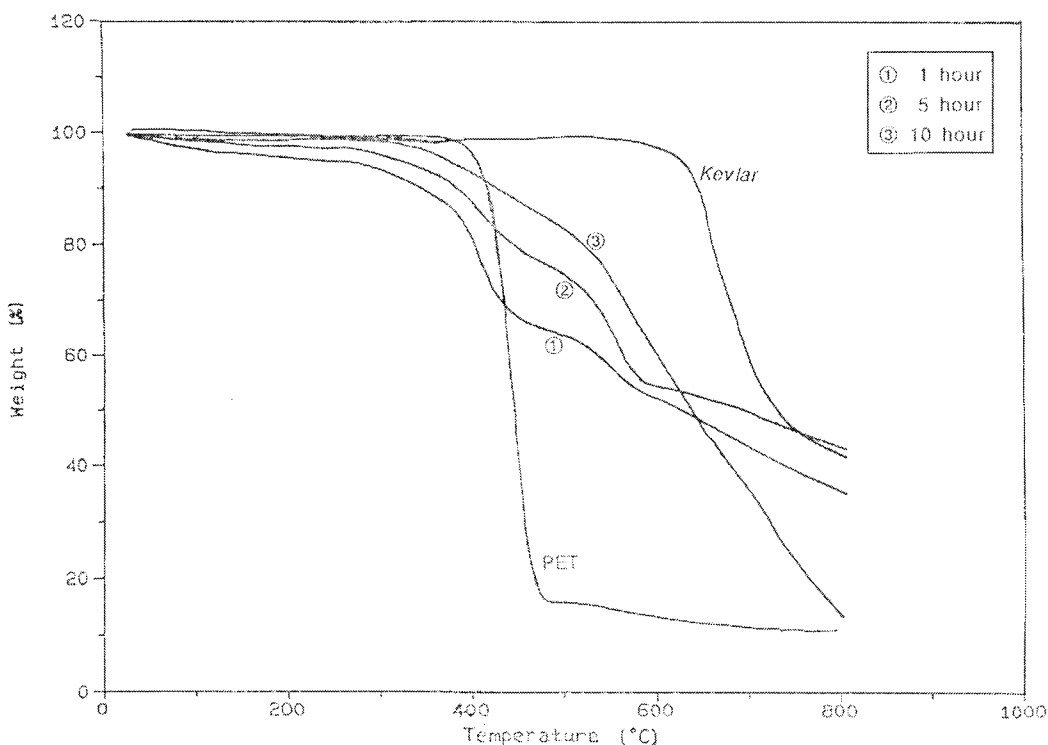

Figure 2 Progress of reaction with time for the ester–amide exchange reaction of PET using p-phenylenediamine. Reaction conditions: 210°C, PDA/PET (mole ratio) = 1.0. Solvent: n-dodecylbenzene.

Figure 3 Variation of heat resistance with time for polyamide obtained by reacting PET with *p*-phenylenediamine. Reaction conditions: 210°C, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.

finally reaches a reaction equilibrium beyond 10 h with constant value of AR (0.595) and nitrogen content (9.4%) under the specified reaction conditions [210°C, PDA/PET (mole ratio) = 1.0]. The profile of nitrogen content with reaction time is similar to that of amidation ratio estimated from the FTIR analysis. It shows that both amidation ratio and nitrogen content are indicators of the extent of reaction with high reliability. Figure 3 shows that the heat-resistant property of reaction product becomes conspicuous with increase of nitrogen content and at reaction equilibrium it reaches a constant T_{50} value (i.e., $\sim$ 600°C), which is much higher than that of virgin PET (448°C). The heat-resistant behavior of polyamide was estimated

Figure 4 TGA curves for polyamides obtained by reacting PET with *p*-phenylenediamine and varied with reaction time. Reaction conditions: 210°C, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.
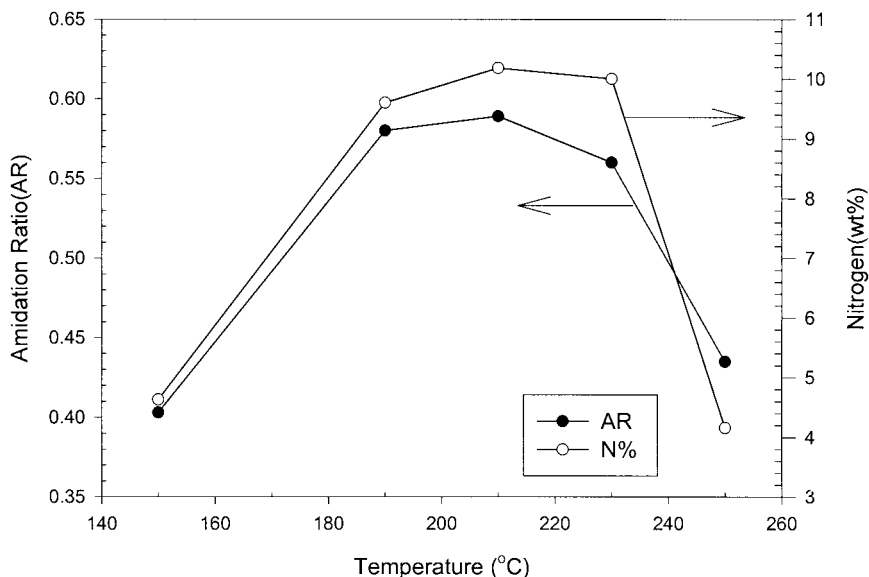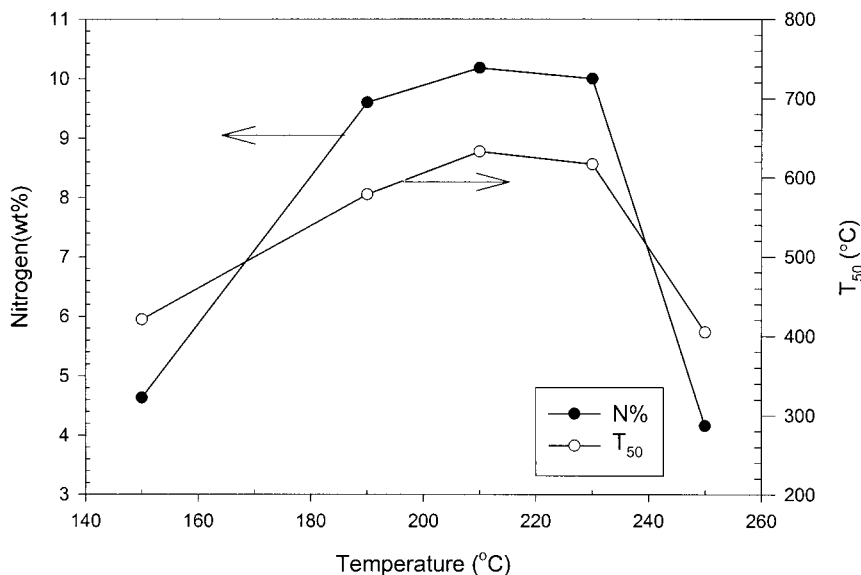
Figure 5 Variation of reaction progress with temperature for the ester–amide exchange reaction of PET using *p*-phenylenediamine. Reaction conditions: 10 h, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.

by TGA and compared with that of the virgin PET and the commercial poly(*p*-phenylene terephthalamide) resin (Kevlar). Figure 4 shows the thermogravimetric behavior of polyamides depending on the variation of reaction time. It clearly shows that the heat-resistant property of polyamide continues to increase with reaction time up to 10 h and it is higher than that of virgin PET.

Figures 5 and 6 show how reaction temperature affects the extent of reaction in the ester–amide exchange reaction and heat-resistant property of the product, respectively. The amidation ratio and nitrogen content show maxima in a certain reaction tem-

perature range (200–220°C) under the specified reaction conditions [10 h, PDA/PET (mole ratio) = 1.0]. Variation of T_{50} depending on reaction temperature shows a peak behavior in the same temperature range and such behavior is coincident with the profile of nitrogen content. Figure 7 shows how reaction temperature affects the thermogravimetric behavior of polyamide and indicates that an optimum reaction temperature needs to be applied to obtain an excellent heat-resistant polyamide. The heat-resistant property of polyamide obtained is highly improved compared with that of virgin PET but still lower than that of Kevlar resin.
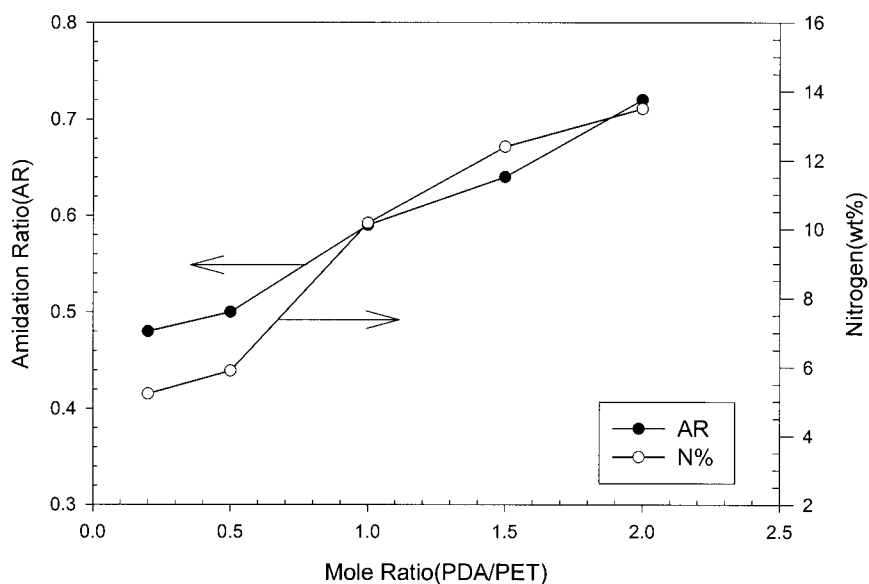

Figure 6 Variation of heat resistance with temperature for polyamide obtained by reacting PET with *p*-phenylenediamine. Reaction conditions: 10 h, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.
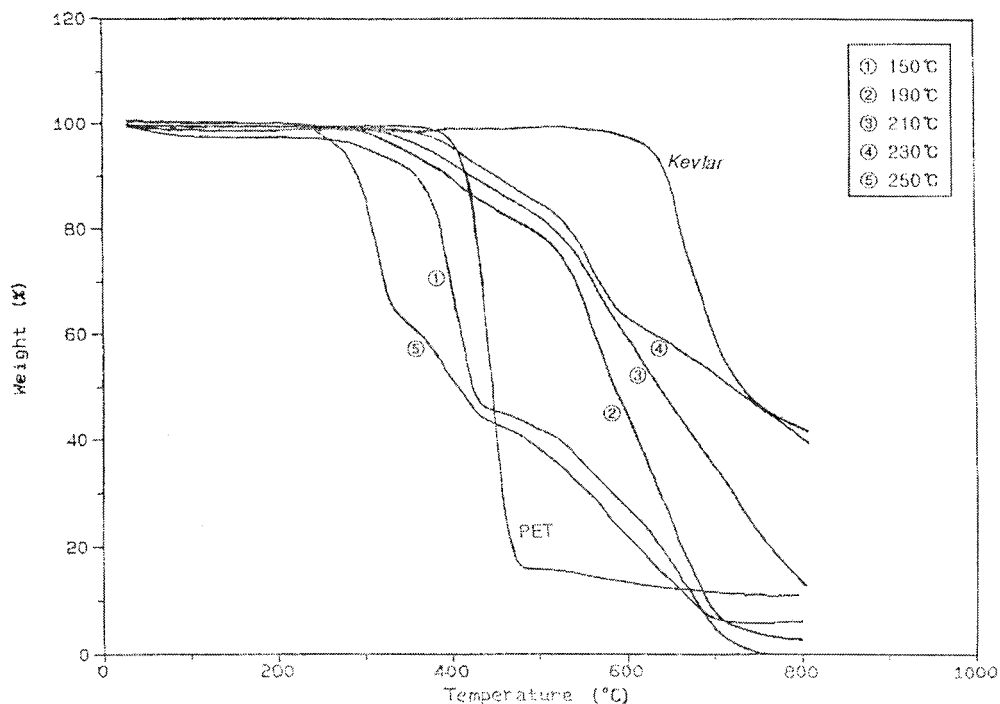
Figure 7 TGA curves for polyamides obtained by reacting PET with *p*-phenylenediamine and varied with reaction temperature. Reaction conditions: 10 h, PDA/PET (mole ratio) = 1.0. Solvent: *n*-dodecylbenzene.

The amount of PDA added in the ester–amide exchange reaction is another critical operation variable with respect to the control of polyamide property. It is highly possible that the excess amount of diamine added in the reaction causes a breakage of polymer main chain and degrades PET. The aminolysis[5] of PET in which primary aliphatic amine adds more than 70 times the number of moles as

that of PET causes a reduction in polymer weight and thus causes a degradation of polymer. Nakano[2] claimed that it needs the stoichiometric balance of PET and HMD in the conversion of PET into polyamide-6T to obtain the highest molecular weight of polyamide. We investigated how the amount of PDA added in the ester–amide exchange reaction affects the reaction progress and the heat-resistant


Figure 8 Variation of reaction progress with mole ratio for the ester–amide exchange reaction of PET using *p*-phenylenediamine. Reaction conditions: 210°C, 10 h. Solvent: *n*-dodecylbenzene.
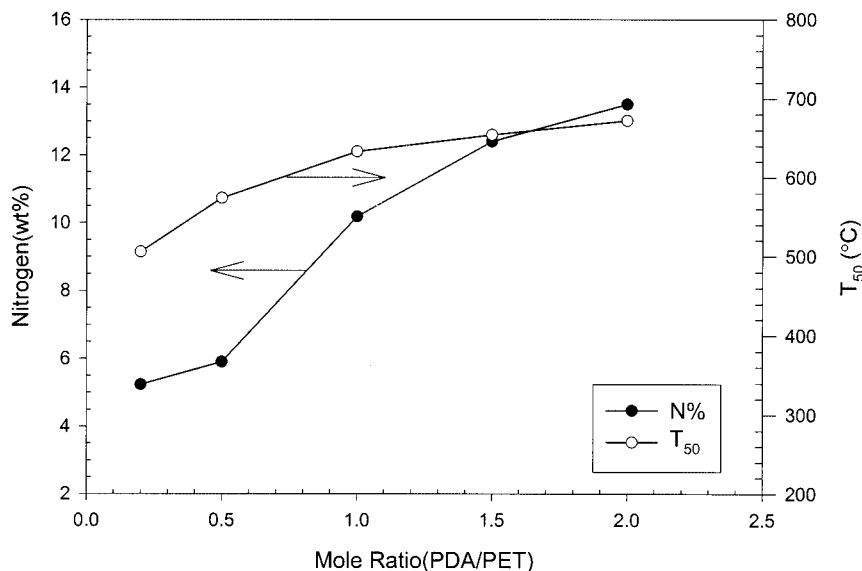
Figure 9 Variation of heat resistance with mole ratio for polyamide obtained by reacting PET with *p*-phenylenediamine. Reaction conditions: 210°C, 10 h. Solvent: *n*-dodecylbenzene.

property of polyamide obtained. Figure 8 shows the extent of reaction gradually increases with the addition of PDA; however, the heat-resistant property of polyamide (T_{50}) shows a plateau behavior ($\sim$ 650°C of T_{50}) over 1.0 of mole ratio of PDA to PET, as shown in Figure 9. The use of stoichiometric balance of PET and PDA in the ester–amide exchange reaction is required and the excess addition

of PDA is redundant under the specified reaction conditions (210°C, 10 h). The thermogravimetric behavior depending on the mole ratio of PDA to PET is shown in Figure 10. The weight loss behavior of reaction product is highly improved by increasing the amount of PDA added in the ester–amide exchange reaction, reaching an upper limit over 1.0 of mole ratio of PDA to PET.
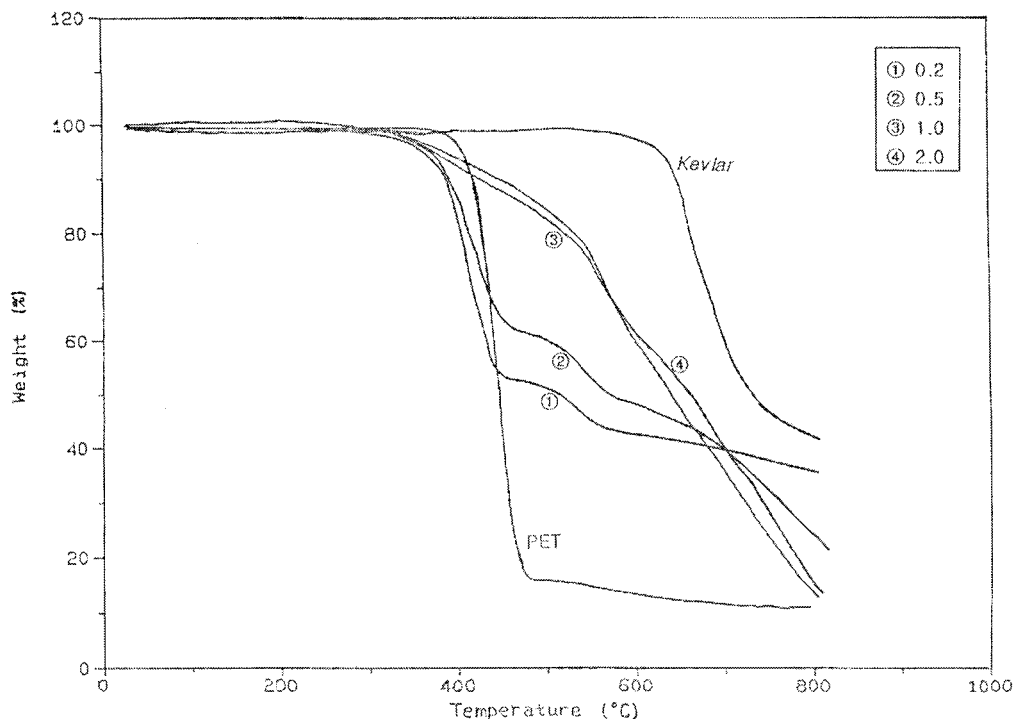
Figure 10 TGA curves for polyamides obtained by reacting PET with *p*-phenylenediamine and varied with mole ratio of PDA/PET. Reaction conditions: 210°C, 10 h. Solvent: *n*-dodecylbenzene.

TABLE III
Properties of Polyamides Obtained by Reacting PET with *p*-phenylenediamine
with the Addition of Metal Acetates as Catalyst at 210°C[a]

Reaction no.	Catalyst type	AR	Nitrogen (wt %)	T_{50} (°C)
C1	Magnesium acetate tetrahydrate	0.511	5.62	467
C2	Calcium acetate monohydrate	0.516	5.43	477
C3	Calcium acetate hydrate	0.559	7.23	610
C4	Brium acetate	0.525	6.79	562
C5	Cobalt(II) acetate tetrahydrate	0.536	7.19	548
C6	Aluminium acetate	0.517	6.32	521
C7	Lithium acetate dihydrate	0.573	7.62	661
C8	Sodium acetate	0.564	6.79	598
C9	Lead(IV) acetate	0.587	9.56	685
C10	Manganese(II) acetate	0.522	5.88	497
C11	Zirconium acetate	0.527	5.83	567
C12	Tin(II) acetate	0.502	4.97	452
C13	Zinc acetate dihydrate	0.541	7.02	550
REF	Uncatalyzed reaction	0.589	9.78	633

[a] Catalyzed reaction (C1–C13): 1 h, catalyst/PET (mole ratio) = 0.015. Reference reaction (REF): 10 h, uncatalyzed reaction. Common reaction conditions: 210°C, PDA/PET (mole ratio) = 1.0, *n*-dodecylbenzene (solvent).

## Effect of the addition of metal acetate as a catalyst on the progress of reaction

The reaction route[3] toward polyamide-6T through the ester–amide exchange reaction between PET and HMD in the absence of catalyst showed many similarities to the transesterification reaction mechanism between dimethylterephthalate (DMT) and ethylene glycol (EG) for the synthesis of PET. Transesterification catalysis for the reaction between DMT and EG was extensively studied[6,7] and the reaction mechanism was also proposed by Fontana[8] and Otton et al.[9] Metal acetates have attained commercial acceptance because of their high catalytic effect on the transesterification reaction. Also without detailed explanation, a Japanese patent[4] claimed that metal acetate can be used as catalyst in the conversion reaction of PET into polyamide. In this study metal acetates were selected and used in the conversion reaction of PET into polyamide to study the effectiveness of catalysts with respect to the shortening of reaction time without losing heat-resistant property.

We carried out 13 different batch reactions by reacting PET with PDA with the addition of metal acetate as a catalyst with the variation of metal component. Table III shows amidation ratio, nitrogen content, and T_{50} value of polyamides obtained from the batch reactions. The catalyzed ester–amide exchange reaction was maintained at 210°C, PDA/PET (mole ratio) = 1.0, catalyst/PET (mole ratio) = 0.015, and it was allowed to proceed for 1 h in the presence of *n*-dodecylbenzene as solvent. The extent of reaction (AR and nitrogen content) and T_{50} value for polyamide obtained from the catalyzed reaction were compared with those of the polyamide produced by the uncatalyzed reaction that proceeded for 10 h unde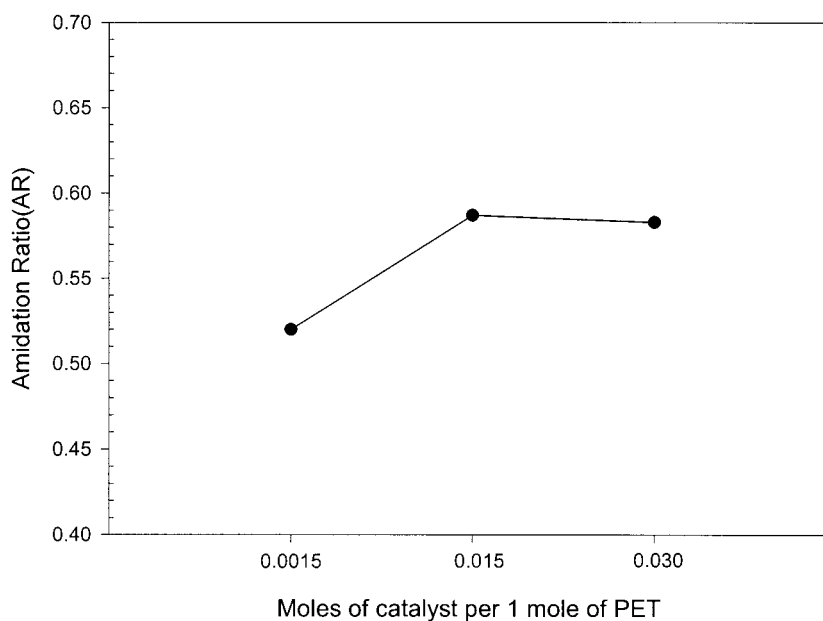r common reaction conditions [210°C, PDA/PET (mole ratio) = 1.0, *n*-dodecylbenzene]. Figure 11 reveals that the extent of reaction and the heat-resistant property varied with the type of metal component and the relative efficiency of these catalysts appears to change according to the order lead(IV) acetate > lithium acetate dehydrate > calcium acetate hydrate. The reason that the efficiency of catalysts varied with the type of metal component is not clear and the explanation for this phenomenon is not possible within the context of this study; further investigation will be needed. However, note that the extent of reaction (AR = 0.587) of the catalyzed reaction proceeded for only 1 h reached to the level (AR = 0.589) of that of the uncatalyzed reaction carried out for 10 h without losing heat-resistant property at all. Figure 12 shows the effect of the amount of lead(IV) acetate added on the extent of reaction for the ester–amide exchange reaction of PET using PDA. The optimum amount of lead(IV) acetate to be added is 0.015 mol per 1 mol of PET under the specified reaction conditions [210°C, 1 h, PDA/PET (mole ratio) = 1.0].

CONCLUSIONS

The ester–amide exchange reaction between poly(ethylene terephthalate) and *p*-phenylenediamine in *n*-dodecylbenzene as solvent occurred and with progress of reaction there was a gradual disappearance of the ester group peak at 1710 cm^{-1} and apparent appearance of amide group peak at 1510 cm^{-1} in the FTIR spectrum. The differences of amidation ratio and nitrogen content among the homologous series of aliphatic and aromatic diamines are explained by steric hindrance resulting from the bulkiness of the diamine compound and the molecular mobility of the substituent group in diamines. The conversion reaction of
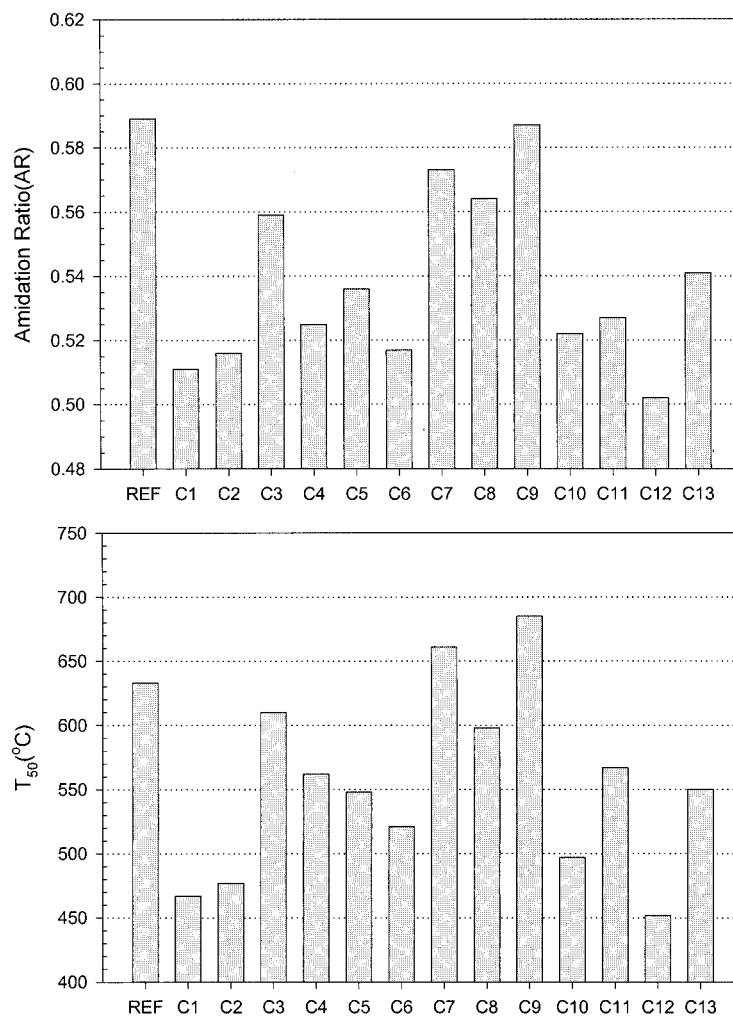
Figure 11 Variation of reaction progress and heat resistance with the type of catalyst used for the ester–amide exchange reaction of PET using *p*-phenylenediamine at 210°C. Catalyzed reaction: 1 h, catalyst/PET (mole ratio) = 0.015; reference reaction: 10 h, uncatalyzed reaction; common condition: 210°C, PDA/PET (mole ratio) = 1.0, *n*-dodecylbenzene (solvent).

Figure 12 Variation of reaction progress with the addition of catalyst for the ester–amide exchange reaction of PET using *p*-phenylenediamine at 210°C. Reaction conditions: 1 h, PDA/PET (mole ratio) = 1.0. Catalyst: lead(IV) acetate. Solvent: *n*-dodecylbenzene.

poly(ethylene terephthalate) into polyamide by using *p*-phenylenediamine showed a reaction equilibrium over 10 h of reaction time at 210°C and PDA/PET (mole ratio) = 1.0. The heat-resistant property of polyamides, which is estimated from the T_{50} value of thermogravimetric analysis, continuously increased with reaction time up to 10 h but plateaued beyond that. The amidation ratio and nitrogen content of polyamides obtained from the ester–amide exchange reaction showed maxima in the range of 200–220°C of reaction temperature at 10 h and PDA/PET (mole ratio) = 1.0. The heat-resistant property of polyamides was increased to the greatest extent in the same range of reaction temperature. Addition of a stoichiometric amount of *p*-phenylenediamine in the ester–amide exchange reaction at 210°C and 10 h is necessary to obtain a desirable polyamide. The efficiency of catalyst is different according to the type of metal component in metal acetates. With respect to the shortening of reaction time without losing heat-resistant property, lead(IV) acetate is most effective catalyst among metal acetates at 210°C, 1 h, and PDA/PET (mole ratio) = 1.0. Polyamides obtained from the ester–amide exchange reaction between poly(ethylene terephthalate) and *p*-phenylenediamine showed highly improved heat-resistant property compared with that of virgin poly(ethylene terephthalate).

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