# Synthesis and Characterization of Poly(ethylene-*co*-trimethylene terephthalate)s

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**ABSTRACT:** Taking advantage of a melt polycondensation process, a series of copolyesters composed of pure terephthalate acid (PTA), ethylene glycol (EG), and 1,3-propanediol (1,3-PDO) were synthesized. The component, molecular weight, molecular weight distribution, and thermal properties of the copolymers were characterized. The results show that the contents of trimethylene terephthalate (TT) units in the resulting copolyesters are higher than PDO compositions in original diol. Oligomer content in the copolyesters varies with the compositions and attains a minimum value when the TT ingredient is 49.52 mol %. The glass transition temperature ($T_g$) of the copolyesters varies from 78.5°C for PET (polyethylene terephthalate) to 43.5°C for PTT (polytrimethylene terephthalate) and decreases monotonically with the components. The copolyesters are amorphous copolymers when TT content is in the range of 32.4–40.8 mol %, as calculated from the melting enthalpy ($\Delta H_m$) measured via differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1511–1521, 2006

**Key words:** melt polycondensation; copolyester; esterification; composition

## INTRODUCTION

Both polyethylene terephthalate (PET) and polytrimethylene terephthalate (PTT) are important polyesters in industry and have wide applications in fibers, films, and engineering plastics.[1–5] In recent years, many researches have been carried out by blending two polyesters or by copolymerization of their monomers to enhance the crystallization rate of PET or improve the mechanical and thermal properties of PTT.[6–9] But all the reports about the copolyester polymerization follow dimethyl terephthalate (DMT) synthesis route, and pure terephthalate acid (PTA) method has not been revealed.[10–13] In this study, a series of poly(ethylene-*co*-trimethylene terephthalate)s (PETTs) of PET and PTT through PTA method were synthesized and characterized by viscometry, ^{1}H NMR spectra, and differential scanning calorimetry.

## EXPERIMENTAL

### Materials

Monomers pure terephthalate acid (PTA), ethylene glycol (EG), and 1,3-propanediol (PDO) were supplied by Yizheng Chemical Fibers Co., Ltd. (China), Yangzi Pet-rochemical Co. Ltd. (Nanjing, China), and Shell Corp., respectively. Poly(ethylene-*co*-trimethylene terephthalate)s (PETTs) have been prepared by polycondensation of PTA, EG, and PDO in the presence of tetrabutyl titanate (TBT), antimony triacetate, and tribenzene phosphate (TBP), which were used as received.

### Synthesis of copolymer

As can be seen from Figure 1, PETT copolyesters can be synthesized through two steps. First, the esterification reaction was performed as follows: 60 mol mixed diol (EG and 1,3-PDO), 30 mol PTA, and 0.0075 mol antimony triacetate were put into a 20-L reactor vessel. Before the esterification period, the reactor vessel was replaced by 0.1 MPa nitrogen at least three times to make sure that there is no residual oxygen inside the reactor. The reactor was pressurized by nitrogen up to 0.1 MPa. The stirrer was turned on at a stirring speed of 80 rpm. The temperature and pressure in the reactor were set at 220–235°C and 0.25 ± 0.01 MPa, respectively. The esterification reaction was finished when about 60 mol of water as its by-product was discharged.

Next, the catalyst TBT and the thermal stabilizer TBP were added to the esterification product before condensation reaction. When the pressure in the reactor decreased gradually to 100 Pa and the temperature was up to 270°C within 45 min, the condensation reaction began with the stirring rate of 80 rpm. The
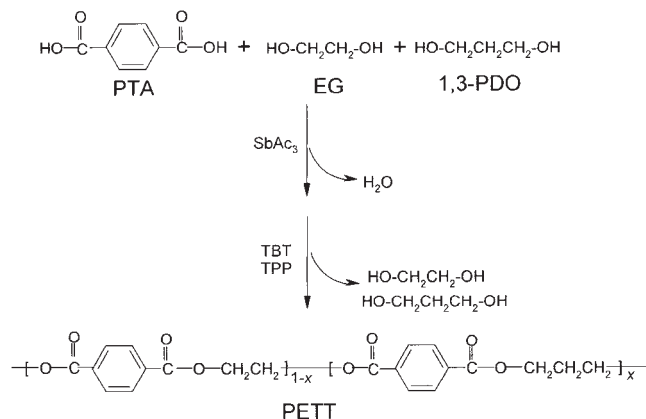
**Figure 1** Synthetic scheme of poly(ethylene-*co*-trimethylene terephthalate)s.

stirring rate was thereafter adjusted to 40 rpm when the stirring torque boosted up to 60 rpm, and the temperature and pressure in the reactor were kept stable. The copolyesters were obtained at last when the stirring torque was 100 rpm. Table I gives the feed ratio of these copolyester samples.

## Characterization

### Determination of intrinsic viscosity and molecular weight

The intrinsic viscosity of the copolymers was measured at 25°C in an Ostwald viscometer using a solution of 125.0–145.0 mg copolyester chip in 25 mL phenol/carbon tetrachloride (3 : 2, w/w) as a mixing solvent.

The molecular weight (MW) and molecular weight distribution (MWD) of the copolymers were determined on a Waters Alliance GPC V2000. Polystyrenes with narrow MWD were used as the standard reference samples. About 15 mg copolyesters dissolved in 1 mL ortho-chlorophenol and 9 mL chloroform as a dilution agent were used as the measuring solution for GPC.

### Determination of chemical composition

$^1$H NMR spectra of the copolyesters were recorded on a Bruker ASPECT 300 Hz spectrometer at 60°C. Each of the copolyesters was dissolved in a mixture solution of $CF_3COOD/CDCl_3$ (3 : 1, v/v). Tetramethylsilane was used as the standard reference material for $^1$H NMR spectra. The chemical composition of the copolyesters was calculated from the data obtained from these spectra.

### Thermal analysis

Thermal analysis of the copolyesters was conducted using a PerkinElmer DSC-7 instrument under nitrogen atmosphere. Temperature and heat calibrations were carried out using pure samples of In and Sn. Differential scanning calorimetry (DSC) experiments have been performed as follows: the copolyesters were heated to 280°C at a rate of 10°C/min and maintained for 10 min at 280°C until no residual crystals existed in the melt. Then the samples were quickly cooled to room temperature and were allowed to stand for 2 min at room temperature and heated again to 280°C at a rate of 10°C/min. The glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting point ($T_m$), crystallization enthalpy ($\Delta H_c$), and melting enthalpy ($\Delta H_m$) were obtained from the DSC curves of the heating process. In addition, the cooling crystallization temperature ($T_{mc}$) and cooling crystallization enthalpy ($\Delta H_{mc}$) could also be obtained from the DSC curves of the cooling process.

## RESULTS AND DISCUSSION

### Esterification and polymerization

The amount of water (by-product) expelled is basically linear with the esterification time during the esterification reaction. Table II indicates the relation of total expelled water and average expelled water rate (calculated by linear fitting) when the diols were esterified with PTA.

**TABLE I**
**Feed Ratio of 1,3-PDO, EG, and PTA for Copolycondensation**

| No. | Polymer | 1,3-PDO | | EG | | PTA | |
|---|---|---|---|---|---|---|---|
| | | g | mol | g | mol | g | Mol |
| 1 | PET | 0 | 0 | 3720 | 60 | 4980 | 30 |
| 2 | PETT10 | 456 | 6 | 3348 | 54 | 4980 | 30 |
| 3 | PETT20 | 912 | 12 | 2976 | 48 | 4980 | 30 |
| 4 | PETT30 | 1368 | 18 | 2604 | 42 | 4980 | 30 |
| 5 | PETT40 | 1824 | 24 | 2232 | 36 | 4980 | 30 |
| 6 | PETT50 | 2280 | 30 | 1860 | 30 | 4980 | 30 |
| 7 | PETT60 | 2736 | 36 | 1488 | 24 | 4980 | 30 |
| 8 | PETT70 | 3192 | 42 | 1116 | 18 | 4980 | 30 |
| 9 | PETT80 | 3648 | 48 | 744 | 12 | 4980 | 30 |
| 10 | PETT90 | 4104 | 54 | 372 | 6 | 4980 | 30 |
| 11 | PTT | 4560 | 60 | 0 | 0 | 4980 | 30 |

**TABLE II**
**The Relation of Total Expelled Water and Average Expelled Water Rate**

| No. | Polymer | 1,3-PDO (mol %) | Total esterification time (min) | Total expelled water (mL) | Average expelled water Rate (mL/min) | $r^{2a}$ |
|---|---|---|---|---|---|---|
| 1 | PETT10 | 10 | 125 | 1050 | 8.71 | 0.995 |
| 2 | PETT20 | 20 | 125 | 1010 | 8.96 | 0.993 |
| 3 | PETT30 | 30 | 120 | 1020 | 9.08 | 0.994 |
| 4 | PETT40 | 40 | 125 | 1050 | 9.00 | 0.988 |
| 5 | PETT50 | 50 | 125 | 1010 | 9.05 | 0.945 |
| 6 | PETT60 | 60 | 110 | 1050 | 10.17 | 0.994 |
| 7 | PETT70 | 70 | 110 | 1050 | 10.11 | 0.985 |
| 8 | PETT80 | 80 | 110 | 1070 | 10.23 | 0.990 |
| 9 | PETT90 | 90 | 115 | 1050 | 10.33 | 0.965 |
| 10 | PTT | 100 | 105 | 1050 | 10.58 | 0.960 |

[a] Relative coefficient in linear fitting.

From Table II, it can be seen that the expelled water rate increases with the augment of 1,3-PDO content in the feed ratio during esterification.

One reason for the expelled water rate is greater during esterification reaction of 1,3-PDO and PTA than during esterification of EG and PTA is that the number of methylenes capable of donating electrons in PDO is more than in EG. Consequently, the electronegativity of oxygen atom in PDO is stronger than that of oxygen atom in EG. As can be seen from the process of esterification reaction between PTA and fatty diols,[14] the carboxylic acid in PTA may itself cause catalytical effect. Thus, the first step in the process of esterification is the reaction between two of the carboxylic acids:
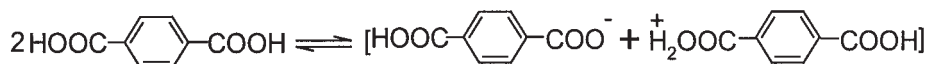


Scheme 1

that is, the hydrion ($H^+$) in the carboxylic acid supplies an empty orbit to a lone pair electron of carbonylic group oxygen in another carboxylic acid. This is also called a practicing coordination:
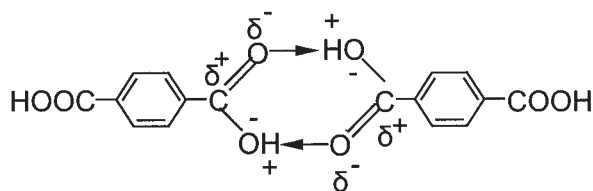


Scheme 2

Thereof, the electronpositivity of carbon atom of carbonylic group is strengthened, and the esterification reaction has been completed after the carbon of carbonylic group is linked with oxygen atom of diols:

**TABLE III**
**Copolycondensation Preprocessing Parameters**

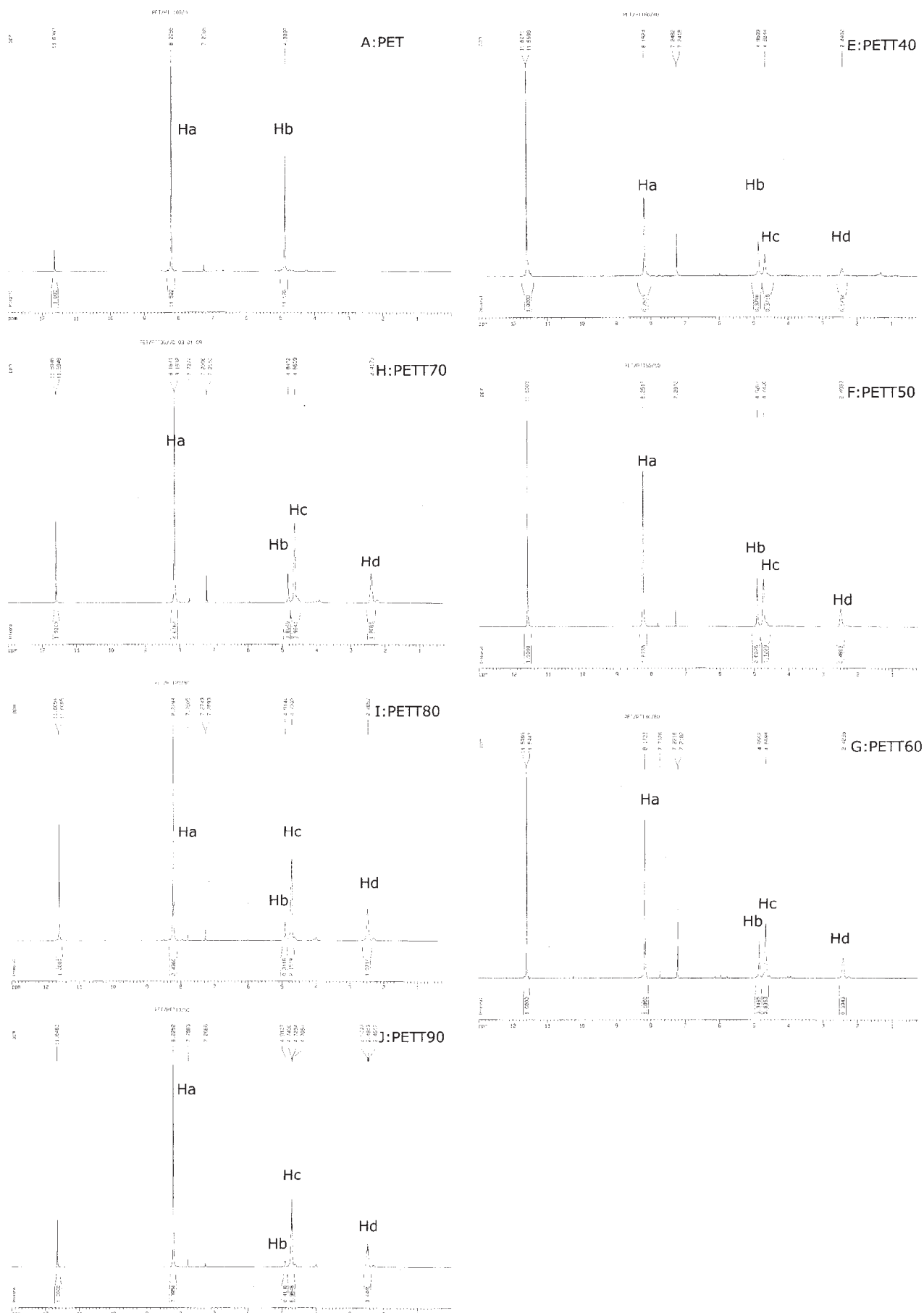| No. | PETTn | Polymerization temperature (°C) | Pressure (Pa) | Polymerization time (min) | Stirring power added ($\Delta w$) |
|---|---|---|---|---|---|
| 1 | PETT10 | 270 | 100 | 130 | 100 |
| 2 | PETT20 | 270 | 100 | 142 | 100 |
| 3 | PETT30 | 270 | 100 | 147 | 100 |
| 4 | PETT40 | 270 | 100 | 165 | 100 |
| 5 | PETT50 | 270 | 100 | 165 | 100 |
| 6 | PETT60 | 270 | 100 | 186 | 100 |
| 7 | PETT70 | 270 | 100 | 201 | 99 |
| 8 | PETT80 | 270 | 100 | 170 | 78 |
| 9 | PETT90 | 270 | 100 | 180 | 75 |
| 10 | PTT | 270 | 100 | 190 | 68 |

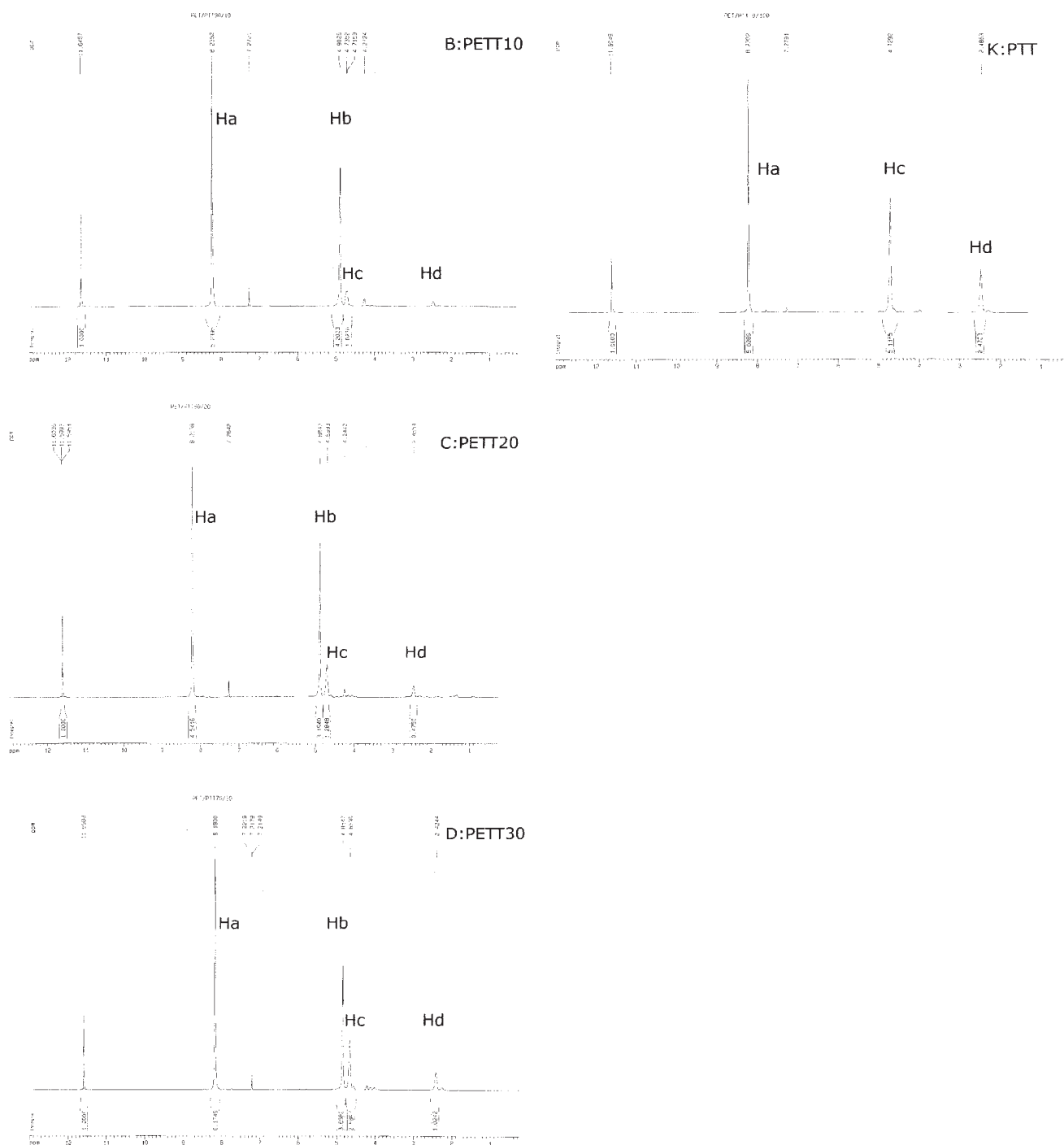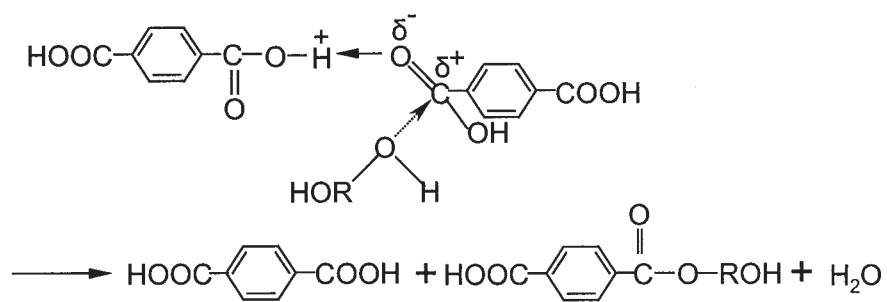**Figure 2**   <sup>1</sup>H NMR spectra of PETT copolyester.

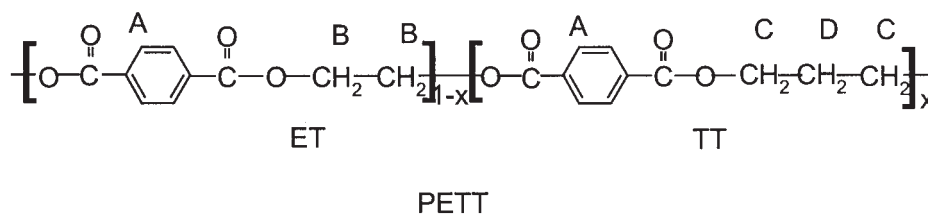**Figure 2** (*Continued from the previous page*)



Scheme 3

**TABLE IV**
**Composition of the Prepared PETT*n* Varies with the Feed Ratio of Diol Monomers**

| PETT*n* | 1,3-PDO (mol %) | TT (mol %) in copolymer |
|---|---|---|
| PET | 0 | 0 |
| PETT10 | 10 | 19.58 |
| PETT20 | 20 | 28.69 |
| PETT30 | 30 | 41.45 |
| PETT40 | 40 | 49.52 |
| PETT50 | 50 | 65.04 |
| PETT60 | 60 | 70.58 |
| PETT70 | 70 | 82.09 |
| PETT80 | 80 | 87.37 |
| PETT90 | 90 | 94.42 |
| PTT | 100 | 100 |

The oxygen atom in PDO connects easily to the electronpositive carbon of carbonylic group because the electronegativity of the oxygen atom in PDO is greater than that of the oxygen atom in EG, which benefits the esterification reaction.

Second, the electronegativity of the oxygen atom in PDO is greater than that of the oxygen atom in EG; thus the 1,3-PDO molecule dehydrates easily, constructs an allyl alcohol, and finally becomes a stable acrolein. As mentioned earlier, we can see why the expelled water rate increases with the increase in 1,3-PDO content in the esterification of the mixing diols and PTA. However, there is only a little difference between the two esterification rates when the esterification reaction of 1,3-PDO and PTA is compared with that of EG and PTA.

With the continuation of polymerization, the stirring torque increases after the MW of copolyester approaches to a certain value because the dynamic viscosity of the copolyester melt increases with the increase in MW. The copolycondensation preprocessing parameters are given in Table III.

As shown in Table III, with an increase of 1,3-PDO in copolycondensation reaction (No. 1–6), the polymerization time, under the stirring torque 100 reached at last, will be extended. From No. 7–10, when the 1,3-PDO content is increased further, the stirring torque cannot reach 100 ultimately even if the polymerization time is extended. The reasons are as follows. On one hand, the boiling point of 1,3-PDO is 214°C, which is 7°C higher than that of EG, resulting in lower volatility of 1,3-PDO when compared with that of EG. Therefore, it gets difficult for 1,3-PDO to diffuse in the melt when the melt viscosity reaches to a certain value. On the other hand, 1,3-PDO changes to an allyl structure easily because of bigger electronegativity on its oxygen atom, and its ester bond is easily ruptured, which leads to a decline of its stability. The thermal degradation reaction is also accompanied with the polycondensation reaction.

### Copolyester composition characterization

The copolyester PETT structure can be expressed as follows:



Scheme 4

There are four peaks in the $^1$H NMR spectra (A, B, C, and D; see Fig. 2) except the solvent peak. Chemical shifts of these peaks are 8.2, 4.9, 4.7, and 2.5ppm respectively. If the etherification reaction and the influence of end group are ignored, the mole percentage of trimethylene terephthalate chain segment units (TT mol %) can be calculated from $S_C/(S_B + S_C)$. The results can be observed in Table IV and Figure 3.

It can be seen from Table IV and Figure 3, as for all the copolyesters, that the content of TT chain segment in copolyesters is more than 1,3-PDO content in the feed ratio of diols without exception. In the same way, this result can be explained from two aspects. First, as mentioned earlier, the electronegativity of the oxygen atom in 1,3-PDO is stronger than that of the oxygen atom in EG because the methylene number of 1,3-PDO is more than that of EG. Thereby, the esterification reaction occurs between 1,3-PDO and PTA easily. On this ground, the TT unit content (TT mol %) is heightened in the copolyester. Second, it is also due to the higher boiling point of 1,3-PDO, whose volatility is lower than that of EG. In other words, the EG composition will be easily volatilized during polycondensation reaction, which results in an increase in TT content (mol %) in the copolymer. This finding is similar to that of Lee's study,[11] where polytrimethylene terephthalate (PTT) was synthesized by DMT synthesis method. There is only a little difference in that the TT chain segment units in PTT prepared by PTA direct
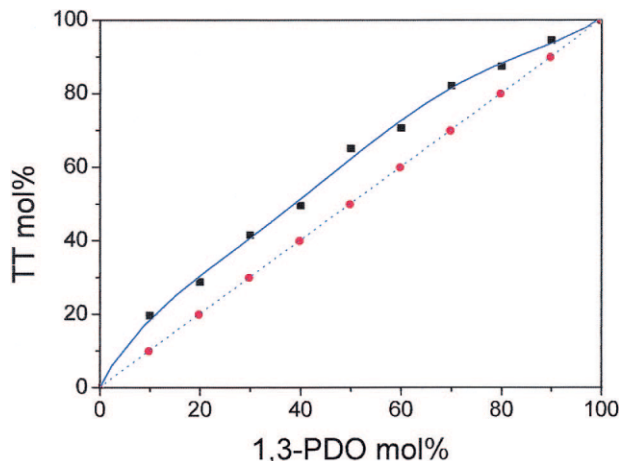
**Figure 3** Composition of PETT$n$ as a function of feed ratio of diols. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polycondensation are larger than those prepared by DMT method.

The MWD curves for polyethylene terephthalate (PET), PETT50, and PTT are shown in Figure 4, and those for the others can be observed in Table V in which $M_p$ is the peak value of MW in MWD curve.

Table V illustrates that the variability of the MW coincides with that of the intrinsic viscosity for the copolyesters whose indexes of MWD ($M_w/M_n$) are all around 2, but the oligomer content alters with composition of the copolyesters (see Fig. 5).

With increased TT content, the oligomer content in the copolyesters decreases first, gains minimum point at ~50 mol % of TT, and then increases (Fig. 5). The results in previous studies[15–18] denote that the oligomer is more often than not a cyclized oligomer, such as the cyclic trimer for PET and the cyclic dimer for PTT [see Scheme 5].
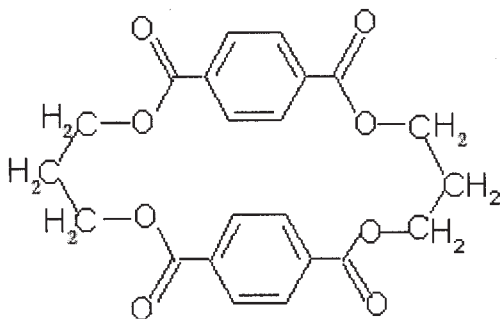


Scheme 5

The cyclized oligomer is formed under the looping mechanism of end groups of a macromolecule. [19]That is to say, formation of cyclized structure takes place only if there are end groups with same composition. The cyclic possibility will be declined if there is a

copolymerization component. Hence, when the TT content is low, the cyclic possibility of the end groups will decrease with increase in TT content, which reveals that the oligomer content decreases in the copolyesters. With an increase in TT content, the cyclic possibility of the end groups will increase when TT is at a high composition, which indicates that the oligomer content increases in the copolyesters.

## Effects of composition on thermal behavior of the copolyesters

After their heat history is cleared up, the copolyesters are heated to melt at 10°C/min and cooled to room temperature, then the melt is cooled at 10°C/min. These DSC curves and their relative data for the copolyesters can be observed in Figures 6 and 7, and Table VI. Figure 6 shows that with an increase in TT content, $T_m$ of the copolyesters decreases first, then rises, while from Figure 7, it can be seen that with an increase in TT content the crystallization peak disappears first and then appears again, which reflects that the TT content obviously affects the melt and crystallization behavior of the copolyesters.

As mentioned earlier, the $T_g$ for PET is 78.5°C, and for PTT 43.5°C. The $T_g$ for the copolyesters is between that of the two homopolymers, and its value of $T_g$ decreases with the increase in TT content and basically fits in with the Gordon–Taylor equation[20]:

$$\frac{1}{T_g} = \frac{W_{PET}}{T_{gPET}} + \frac{W_{PTT}}{T_{gPTT}} \qquad (1)$$

where $W_{PET}$ and $W_{PTT}$ are weight fractions of PET and PTT, respectively.

Figure 8 shows that $T_g$ decreases with increase in TT content for the copolyesters owing to the different flexibility of the molecular chains. Usually, the alkyl units belong to flexible units and their flexibility corresponds to the number of methylenes. There are three and two methylenes in a chain segment unit of TT and ET, respectively, and therefore, the more the TT units, the more flexible the molecular chains are, and then the $T_g$ declines. In addition, only one value of $T_g$ is displayed for all the copolyesters instead of two points of $T_g$ for block copolymers of PET and PTT, which accounts for the fact that the copolyesters synthesized are all random copolymers whatever the TT content is.

In Figure 9, there exist $T_c$ and $T_m$ for some copolyesters and for others they do not, depending on their compositions. $T_m$ can be observed when monomer TT content in polyesters is less than 28.69% or more than 70.58%. When their TT content is between 41.45–65.04%, no melting peak can be detected. $T_m$ peak proves that copolyesters can crystallize under DSC measuring conditions; on the other hand, absence of $T_m$ peak means that the corresponding copolyesters
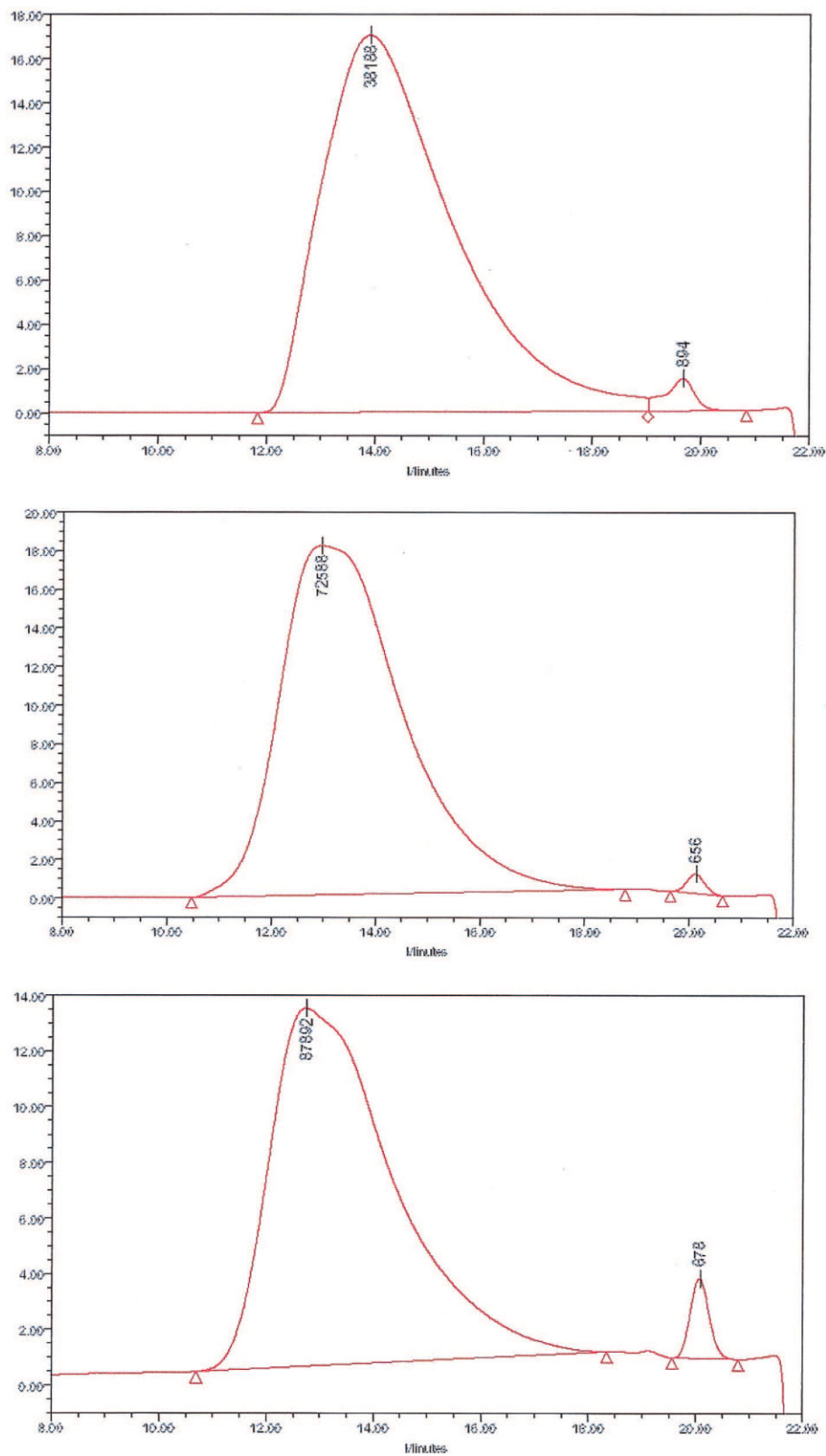
**Figure 4** MWD curves for PET (A), PETT50 (B), and PTT (C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

| PETT$n$ | IV (dL g$^{-1}$) | $M_n$ | $M_w$ | $M_p$ | $M_w/M_n$ | Oligomer $M_p$ | Oligomer Area (%) |
|---|---|---|---|---|---|---|---|
| PET | 0.637 | 19,030 | 35,154 | 38,188 | 1.85 | 894 | 1.93 |
| PETT10 | 0.655 | 29,080 | 60,654 | 57,600 | 2.09 | 914 | 1.50 |
| PETT20 | 0.662 | 29,210 | 64,353 | 67,690 | 2.20 | 715 | 1.10 |
| PETT30 | 0.687 | 29,483 | 68,445 | 71,871 | 2.32 | 676 | 0.95 |
| PETT40 | 0.701 | 36,978 | 69,752 | 64,076 | 1.89 | 659 | 0.45 |
| PETT50 | 0.719 | 38,089 | 73,444 | 72,588 | 1.93 | 656 | 0.79 |
| PETT60 | 0.741 | 38,444 | 75,757 | 74,208 | 1.97 | 641 | 1.11 |
| PETT70 | 0.765 | 30,301 | 78,171 | 77,166 | 2.58 | 645 | 1.67 |
| PETT80 | 0.744 | 26,639 | 64,144 | 50,932 | 2.41 | 655 | 1.95 |
| PETT90 | 0.766 | 28,631 | 73,093 | 57,885 | 2.55 | 650 | 2.21 |
| PTT | 0.771 | 38,848 | 76,190 | 87,892 | 1.96 | 678 | 3.28 |

cannot crystallize. $T_m$ decreases with the increase in TT content for the copolyesters with TT content less than 28.69%.

$$T_m = -2.030x + 255.3 \quad \gamma = -0.9948 \quad (2)$$

Similarly, $T_m$ decreases with the increase in ET content (i.e., $T_m$ increases with the increase in TT content) for the copolyesters when ET is at a low composition range (i.e., TT is at a high composition range).

$$T_m = 1.425x + 85.3 \quad \gamma = -0.9948 \quad (3)$$

Here, in the eqs. (2) and (3), $x$ is the TT content (mol %) of the copolyesters. These findings can be explained as follows. First, a little amount of comonomers in the polymers will destroy the regularity of the macromolecular chains, and hinder their sequential arrangement, playing a negative role in the process of crystal formation and reducing its crystallinity and crystal size. Next, a little amount of comonomers in the polymers will shorten the length of crystallizable homopolymer's segment in the macromolecular chains, and reduce their $T_m$ value. Finally, the chain segments with low composition can also be encapsulated in the crystal of block chains with high composition. These comonomers of low composition will weaken the crystallizable chain segment contents and lead to the crystallinity reduction of the copolyesters.

It is known that the crystalliable polymer has a melting endothermic peak in the DSC diagram. Figure 10 indicates a relation between heat absorption and the copolyester compositions. $\Delta H_m$ decreases with the increase in TT content for the copolyesters when TT content is low. That is

$$\Delta H_m = -1.2175x + 39.457 \quad \gamma = -0.9931 \quad (4)$$

Similarly, $\Delta H_m$ increases with the increase in TT content for the copolyesters when TT content is high. That is
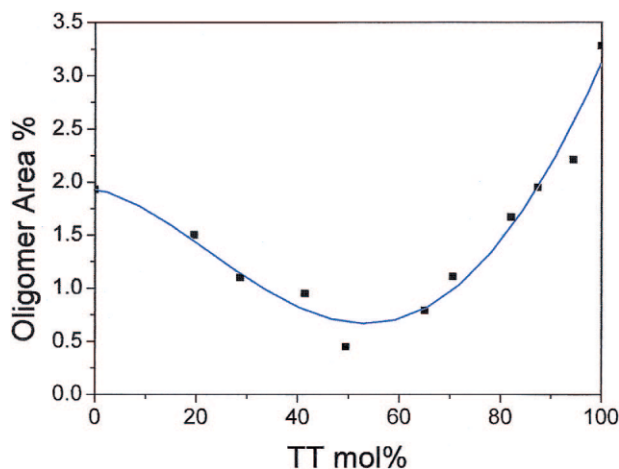


**Figure 5** Effect of the composition on the oligomer content of PETT copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
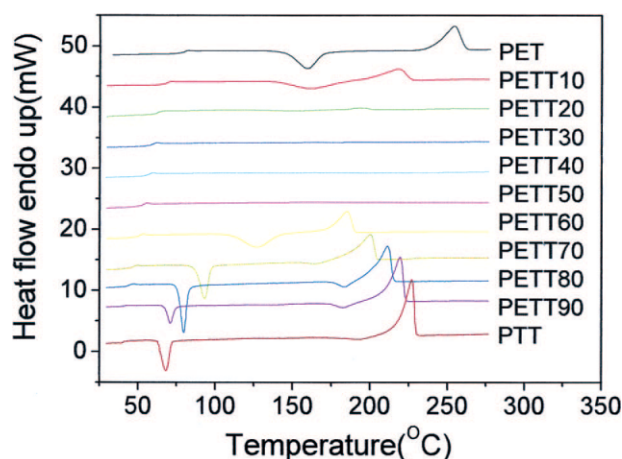


**Figure 6** DSC heating curves for PETT copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
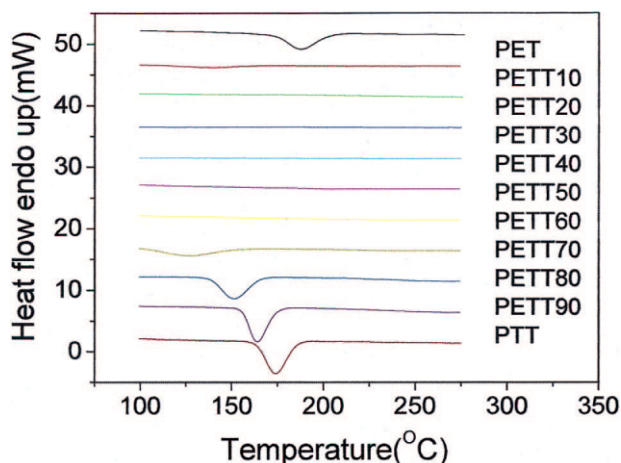
**Figure 7** DSC cooling curves for PETT copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
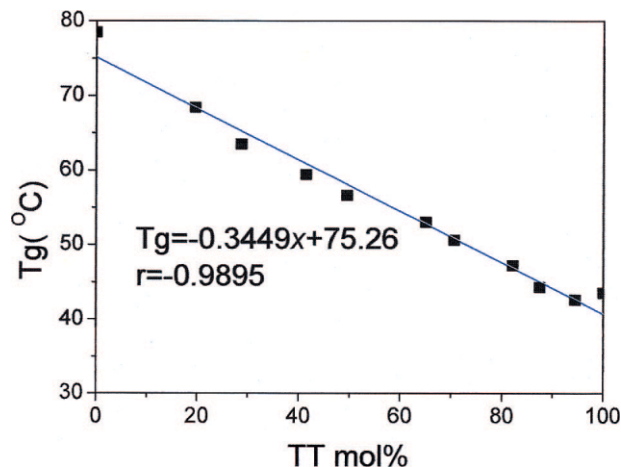


**Figure 8** $T_g$ of PETT copolyesters, as a function of TT %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\Delta H_m = 0.9708x - 39.576 \quad \gamma = 0.9957 \qquad (5)$$

Here, in eqs. (4) and (5), $x$ is the TT content (mol %) of the copolyesters.

The copolyester belongs to amorphous polymer if its $\Delta H_m$ is null, and $x = 32.4\%$ and $40.8\%$ can be deduced from eqs. (4) and (5), respectively. It can be inferred that copolyesters with TT contents of 32.4–40.8% must be amorphous, and the one with TT content more than 40.8% or less than 32.4% must be crystallizable polymer. Figure 10 shows that $\Delta H_m$ for PTT is higher than for PET, which means the crystallinity of PTT is greater than that of PET because of better flexibility of macromolecular chains for PTT.

In addition to the melting endothermic peak, an exothermic peak, generated by crystallization during DSC test, can still be exhibited between the glass transition and melting transition for some copolyesters.

From Figure 7, it is observed that the exothermic crystallization peak when cooling from melt is displayed for some copolyesters. Particularly, when the

copolyesters have a higher TT content, the crystallization temperature ($T_{mc}$) of cooling from melt increases with increase in TT content of the copolyesters, which manifests that TT chain segment unit develops to be a crystal nucleus easily (see Fig. 11).

## CONCLUSIONS

The copolyesters, poly(ethylene-co-trimethylene terephthalate)s, were synthesized by means of the PTA direct polycondensation technology and characterized by DSC, $^1$H NMR spectra and GPC. The electronegativity of oxygen atom in 1,3-PDO is stronger than that of oxygen atom in EG, and the rate of esterification reaction between 1,3-PDO and PTA is a little faster than that of esterification reaction between EG and PTA because the number of methylene in 1,3-PDO is one more than that in EG. The 1,3-PDO does not easily volatilize because the thermal stability of the chain segment unit of 1,3-PDO is poorer and the boiling point of 1,3-PDO is higher than that of EG. Therefore, the polymerization time of the

**TABLE VI**
**DSC Data for PETT Copolyesters**

| PETT$n$ | $x$ (%) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J g$^{-1}$) | $T_m$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $T_{mc}$ (°C) | $\Delta H_{mc}$ (J g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| PET | 0 | 78.5 | 159.2 | −34.9 | 254.2 | 38.7 | 187.7 | −41.0 |
| PETT10 | 19.58 | 68.4 | 162.5 | −16.9 | 219.0 | 18.0 | 140.0 | −8.5 |
| PETT20 | 28.69 | 63.5 | 153.7 | −2.6 | 194.7 | 2.9 | — | — |
| PETT30 | 41.45 | 59.4 | — | — | — | — | — | — |
| PETT40 | 49.52 | 56.6 | — | — | — | — | — | — |
| PETT50 | 65.04 | 53.0 | — | — | — | — | — | — |
| PETT60 | 70.58 | 50.6 | 127.7 | −28.3 | 185.7 | 29.5 | — | — |
| PETT70 | 82.09 | 47.2 | 93.9 | −27.9 | 200.7 | 40.1 | 126.1 | −33.2 |
| PETT80 | 87.37 | 44.3 | 80.3 | −30.1 | 212.2 | 44.5 | 152.0 | −41.6 |
| PETT90 | 94.42 | 42.6 | 72.7 | −11.1 | 220.2 | 50.9 | 164.7 | −46.1 |
| PTT | 100 | 43.5 | 69.0 | −15.3 | 226.7 | 58.9 | 174.5 | −48.3 |
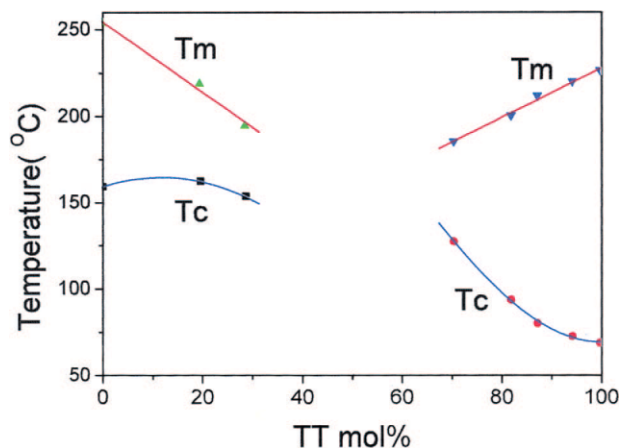
**Figure 9** $T_m$ and $T_c$ of PETT copolyesters, as a function of $x$%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



**Figure 11** $T_{mc}$ of PETT copolyester, as a function of $x$%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolyesters increases with the increase in the 1,3-PDO content. In all the copolyesters, the content of TT chain segment units is more than 1,3 PDO content in the feed ratio of diols, without exception. The minimum oligomercontent in the copolyesters can be obtained when the TT content is 49.52 mol %. The glass transition temperature for the copolyesters decrease monotonously from 78.5°C (for PET) to 43.5°C (for PTT) with increase of TT content. $T_m$ for the copolyesters varies with their composition. When TT is low, $T_m$ for the copolyesters decreases with the increase in TT content, namely, $T_m = -2.030x + 255.3$; When TT is high, $T_m$ for the copolyes-
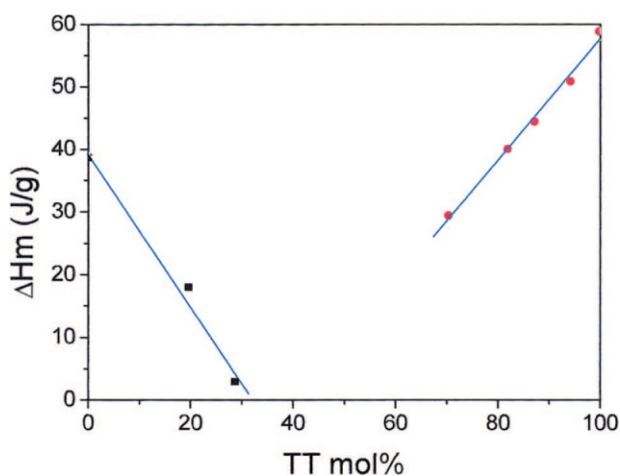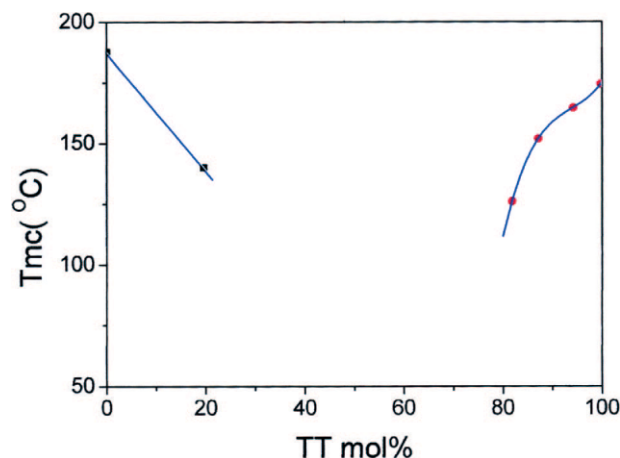
ters increases with the augment of TT content, namely, $T_m = 1.425x + 85.3$.

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**Figure 10** $\Delta H_m$ of PETT copolyesters, as a function of $x$%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]