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Synthesis and Thermal Behavior of Polyesters Derived from 1,3-Propanediol and Various Aromatic Dicarboxylic Acids

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Synthesis and Thermal Behavior of Polyesters Derived from 1,3-Propanediol and Various Aromatic Dicarboxylic Acids

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ABSTRACT

Seven aromatic dicarboxylic acids were esterified by melt polycondensation in two steps with 1,3-propanediol (1,3-PDO) in the presence of tetrabutoxytitanium as catalyst. The acids used were: terephthalic (TPA), isophthalic (IPA), naphthalene-2,6-dicarboxylic (2,6-NDA), naphthalene-1,4-dicarboxylic (1,4-NDA), biphenyl-4,4'-dicarboxylic (4,4'-BPDA), diphenylsulfone-4,4'-dicarboxylic (4,4'-DPSDA), and pyridine-2,6-dicarboxylic acid (2,6-PDA). In the first step, the esterification reaction was monitored, by measuring the distilled water. The prepared oligomers were polycondensated in a second step under high vacuum using the same catalyst as before. The received poly(propylene dicarboxylate)s were characterized by viscometry, carboxyl end-group content (CC), color measurement, and were studied by differential scanning calorimetry (DSC). From this study, the above polyesters could be classified to three classes: (a) easily crystallizing polyesters derived from TPA and 2,6-PDA, (b)

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slow crystallizing polyesters derived from IPA and 2,6-NDA, and (c) amorphous polyesters derived from 1,4-NDA, 4,4'-BPDA, and 4,4'-DPSDA.

Key Words: 1,3-Propanediol or 1,3-propyleneglycol or 1,3-trimethyleneglycol; Dicarboxylic acid; Poly(propylene dicarboxylate)s; Differential scanning calorimetry; PEN; Crystallization; Rigid amorphous phase.

INTRODUCTION

The synthesis of thermoplastic polyesters based on ethylene glycol (EG) or 1,4-butanediol (1,4-BDO) has been extensively investigated during the last decades. The most common polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and more recently, poly(ethylene naphthalate) (PEN) belong to this category of polymers. On the other hand, only a few papers dealing with polyesters of 1,3-propanediol (1,3-PDO), or 1,3-propyleneglycol, or 1,3-trimethylene glycol, have been published. This was a consequence of the fact that 1,3-PDO was not available in the market in sufficient quantity and purity in the past.^[1-3] However, in recent years more attractive processes have been developed for the production of 1,3-PDO, including selective hydration of acrolein followed by catalytic hydrogenation of the intermediate 3-hydroxypropionaldehyde,^[2,4] hydroformylation of ethylene-oxide^[4,5] and various other biotechnological methods. Currently, Du Pont's fiber-grade, or apparel-grade 1,3-PDO has successfully been prepared, by a fermentation process, based on corn sugar, a renewable resource.^[6] In addition, Shell announced the production of 1,3-PDO via an enzymic fermentation of glycerine.^[7]

The polyesters derived from 1,3-PDO and various dicarboxylic acids, called hereafter poly(propylene dicarboxylate)s, exhibit properties intermediate to those of the corresponding poly(ethylene dicarboxylate)s or poly(butylene dicarboxylate)s. Poly(propylene terephthalate) (PPT), is the most well known polyester of the series of 1,3-PDO based polyesters. Poly(propylene terephthalate) can be used in applications including mainly fibers, films and mechanical parts.^[5,8,9] Poly(propylene terephthalate) fibers comprise the advantages of polyesters and polyamides (high elasticity, excellent stretch recovery, dye and print capability, low electrostatic charging, and UV resistance).^[6,10] On the other hand, PPT films show good barrier properties in O₂ and H₂O.^[6]

Poly(propylene 2,6-naphthalate) (2,6-PPN) is also a new candidate for fiber production. These fibers exhibit good thermal properties, such as resistance in high temperature and UV radiation and good dyeability.^[11]

The synthesis of some copolymers based on EG and 1,3-PDO with naphthalene-2,6-dicarboxylic (2,6-NDA) and terephthalic acid (TPA) was reported.^[11-13]

Detailed thermal analysis was reported for PPT,^[14-16] while few data are available for 2,6-PPN.^[17] However, there is a lack of data for other poly(propylene dicarboxylate)s in the literature.

In this work, the synthesis and characterization of a series of polyesters of 1,3-PDO with seven aromatic dicarboxylic acids was tried by direct esterification of the corresponding acids in the presence of tetrabutoxytitanium. Moreover, the thermal analysis of these polyesters (some of them were prepared for the first time) was carried out by differential scanning calorimetry (DSC).





EXPERIMENTAL

Materials

1,3-Propanediol (CAS Number: 504-63-2, Purity: >99.7%), was kindly supplied by Du Pont de Nemours Co., Wilmington, DE. Terephthalic acid was purchased from Fluka (purum, 99%). Isophthalic (IPA) (99%) and pyridine-2,6-dicarboxylic (2,6-PDA) (99%) acids were purchased from Aldrich Chemical Co. Naphthalene-1,4-dicarboxylic (1,4-NDA), biphenyl-4,4'-dicarboxylic (4,4'-BPDA), and diphenylsulfone-4,4'-dicarboxylic (4,4'-DPSDA) acids were purchased from K&K and used without further purification. Dimethyl naphthalene-2,6-dicarboxylate (2,6-DMN) was a gift from Amoco Chemicals-Fine Acids (Chicago, IL). Tetrabutoxytitanium (99%) was purchased from Aldrich Chemical Co. and used as supplied.

Synthesis of Polymers

Poly(propylene dicarboxylate)s were synthesized by direct esterification of 1,3-PDO with the aromatic dicarboxylic acids mentioned below in two steps.

First Step (Esterification)

The polycondensation apparatus used in this work was similar to that used by Günther and Zachmann.^[18] A mol ratio of acid/diol = 1/1.2 was used and the amount of catalyst (5×10^{-4} mol of tetrabutoxytitanium per mol of acid) was added to the reactor. In this step the reactants were heated at 260°C, under a low vacuum (≈ 30 kPa) and with continuous stirring. Vacuum is applied to facilitate removal of the produced water as the reaction proceeds. This first step of esterification is considered to be complete after the collection of 8 mL of H₂O approximately, which was removed from the reaction mixture by distillation and collected in a graduated cylinder.

Second Step (Polycondensation)

In the following second step high vacuum (≈ 5 Pa) was applied. The temperature was maintained also at 260°C, while fresh catalyst of the same above quantity was added. This step seems to be completed in 90 min, in the case of PPT and maintained the same in all other polycondensations. Finally, all polyester samples were ground in a grind-mill, washed with methanol, and dried in vacuum at 50°C for 24 h.

Measurements

Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 25°C in a mixture of phenol/1,1,2,2-tetrachloroethane (60 : 40, w/w). The samples were maintained in the above mixture of solvents at 120°C for some time to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter (Teflon). Intrinsic viscosity was calculated after the Solomon-Ciuta equation.^[19]



Carboxyl end-group content (CC) of the resins was determined according to Pohl's method^[20] by titrating a solution of the resin in benzyl alcohol/chloroform with standard NaOH in benzyl alcohol in the presence of phenol red as indicator.

Color measurements were performed on homogeneous "spot" areas of 4 mm in diameter, under diffuse reflectance and $d/8^\circ$ geometry, using a MINOLTA CM-2022 portable spectrophotometer supplied with a memory card for data storage, a CM A32 zero calibration box and a CM-1 color data software. Color measurements representation was realized on a^* , b^* diagram, of the CIELAB (1976) uniform color system.

Differential scanning calorimetry study of the polyesters was performed on a Perkin-Elmer PYRIS 1 DSC (Perkin Elmer Cetus Instruments, Norwalk, CT), operating under nitrogen atmosphere. Several samples with various thermal histories were tested for all polyesters. Heating scans were performed at a rate $20^\circ\text{C}/\text{min}$, while cooling scans were performed at a rate $10^\circ\text{C}/\text{min}$. Samples of 10.00 ± 0.01 mg, were used in all tests. The calorimeter was calibrated using indium and zinc standards.

RESULTS AND DISCUSSION

Synthesis of Polyesters

In most of the papers published in the last years concerning poly(trimethylene terephthalate), this polymer is called briefly as 3GT or PTMT or mainly PTT, but this polyester should have a more suitable acronym harmonized with its homologues (PET and PBT) and which is **PPT**, as it is shown below:

Poly(ethylene terephthalate) PET
Poly(propylene terephthalate) PPT
Poly(butylene terephthalate) PBT

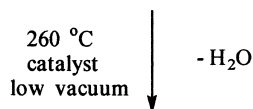
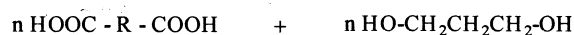
Furthermore, if someone wants to call PBT as poly(tetramethylene terephthalate), in this case its acronym will be also PTT.

The synthesis of poly(propylene dicarboxylate)s was performed with the direct esterification method of 1,3-PDO and the corresponding dicarboxylic acid in each case. This method involves melt polymerization in two steps. In the first step the reactants were heated at 260°C , under low vacuum and with continuous stirring. Vacuum is applied to facilitate removal of the produced water, as the reaction proceeds. After the removal and collection of the expected amount of water, this step is supposed to be completed. In the following second step high vacuum was applied. The temperature was also 260°C while fresh catalyst was added. This step was completed in 90 min (Sch. 1).

Table 1 contains the value of $[\eta]$ for polyesters prepared. These values ranged from 0.13 dL/g (2,6-PPP) to 0.74 dL/g (PPT). It is obvious that 2,6-PPP is a low molecular weight polymer, so it is an oligomer. For this reason, its preparation was carried out once again, but unfortunately with the same results. In this second preparation, a lower polycondensation temperature (170°C) was chosen, because of the low thermal stability of 2,6-PDA. Thermal decomposition of this acid was examined by determining the volume of CO_2 evolved.^[21] In the case of 4,4'-PPBP, it was impossible for intrinsic viscosity to be calculated, because this polyester was not soluble in polyester solvents.

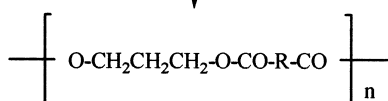
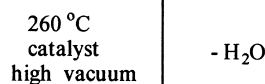


1st step: Esterification

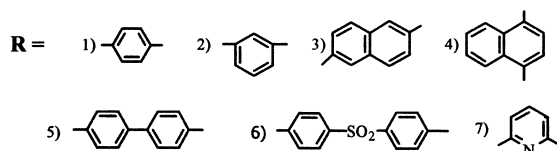


oligomers

2nd step: Polycondensation



where :



Scheme 1. Chemical reactions for the preparation of polyesters.

In Table 1, one can also see the CC for the polyesters. It is worthwhile noting that the CC value for 2,6-PPP is too high (241 $\mu\text{equiv/g}$) as a consequence of the low molecular weight.

Thermal Behavior

All of the polyesters of this series have the flexible trimethylene group in their repeating unit and they differ only in the aromatic moiety. Among these seven polyesters, one can recognize three classes of resins:

- Easily crystallizing polyesters, parted by PPT and 2,6-PPP.
- Slowly crystallizing polyesters, parted by 2,6-PPN and PPI.
- Amorphous polyesters, parted by 4,4'-PPDPS, 4,4'-PPBP, and 1,4-PPN.





Table 1. Intrinsic viscosity, carboxyl content, glass transition temperature, melting point, cold-crystallization temperature, and color of polyester samples.

Sample no.	Structure	Acronym	$[\eta]^a$ (dL/g)	CC (μequiv/g)	T_g^b (°C)	T_m^b (°C)	T_{cc}^b (°C)	L^*	a^*	b^*
1		PPT	0.74	17	44	230	75	78.15	-0.45	4.6
2		PPI	0.41	6	37	139	78.30	78.30	-0.45	8.9
3		2,6-PPN	0.61	12	82	201	80.55	80.55	-0.70	3.5
4		1,4-PPN	0.37	19	35					
5		4,4'-PPBP			88					
6		4,4'-PPDPS	0.58	25	58					
7		2,6-PPP	0.13	241	30	162				

^aIn phenol/tetrachloroethane 60/40, at 25°C.

^bAll DSC measurements conditions are mentioned in the experimental part.





Fast crystallization for the 2,6-PPP should be attributed to its low molecular weight, while the absence of crystallization of 1,4-PPN is connected with the bulky phenylene substituent.

Poly(Propylene Terephthalate)

Poly(propylene terephthalate) is a polymer that has been under research only for the last five years. Pyda and Wunderlich carried out some detailed thermal analysis of PPT.^[14,16] Our experimental data showed a T_g 44°C and a T_m 230°C, which are almost identical to these reported.^[14]

Poly(propylene terephthalate) is fast crystallizing. Our experience in this research field led us to the conclusion that PPT has slower crystallization rates than PBT and PBN, but faster than PET and PEN.^[22–25] The crystallization rates for these polyesters follow the order PBN > PBT > PPT > PET > PEN. Poly(propylene terephthalate) has a T_g (44°C), which is lower than that for PET (80°C) and PBN (48–82°C) and of course PEN (122°C), but it is in the range of the T_g values reported for PBT (22–48°C).^[22,25] It is important that PPT samples of quite low crystallinity can be obtained after quenching, in contrast to what is observed for PBN and PBT, for which no significant increment is observed in C_p at the glass transition region even for quenched samples due to high crystallinity.^[26]

Trace **a** in Fig. 1 corresponds to heating of an as-received PPT sample. It is obvious that high crystallinity was generated during slow cooling in the reactor. In addition, slow supplementary cold-crystallization probably occurs after the glass transition, but it is easily observable only above 200°C.

Trace **b** corresponds to a quenched PPT sample. In this case the glass transition (accompanied by a weak enthalpy relaxation), the cold crystallization and the final melting are observable. The main cold crystallization occurs at about 75°C. A slower process follows the original crystallization, up to about 150°C. Another exotherm is observed in the range 170–200°C, which is attributed to recrystallization, after partial melting of metastable crystals during the heating scan. The final melting for this initially quenched and cold crystallized sample is observed at about 226°C, that is a few degrees lower than for better-crystallised samples. In the same figure (trace **c**) a PPT sample of moderate crystallinity, obtained after fast cooling in the DSC, exhibits also a T_m of 226°C. Such low T_m is closely associated with pure metastable crystals formed during fast cooling or cold-crystallization. For this sample also, a cold-crystallization is observed at about 175–205°C, just before melting. Cold-crystallization (or recrystallization) exotherms in the melting temperature region are well known for PBT and PBN, since for these polymers recrystallization exotherms are observed in classical DSC traces.^[25] However, recrystallization also is very important for PET and PEN, as was proved by modulated-DSC traces.^[27,28]

Trace **d** in Fig. 1 shows the behavior of an as-received sample (which had significant initial crystallinity), after a two-step annealing procedure, involving a first step of annealing at 170°C for 3 h and a second step at 220°C for 15 min. In this case, the T_m was increased to 234°C due to crystal perfection, possibly through increase in lamellar thickness, or in general through reduction in surface energy. The narrower melting temperature region is indicative of a narrower crystal size/perfection distribution that resulted after the annealing steps.^[29]



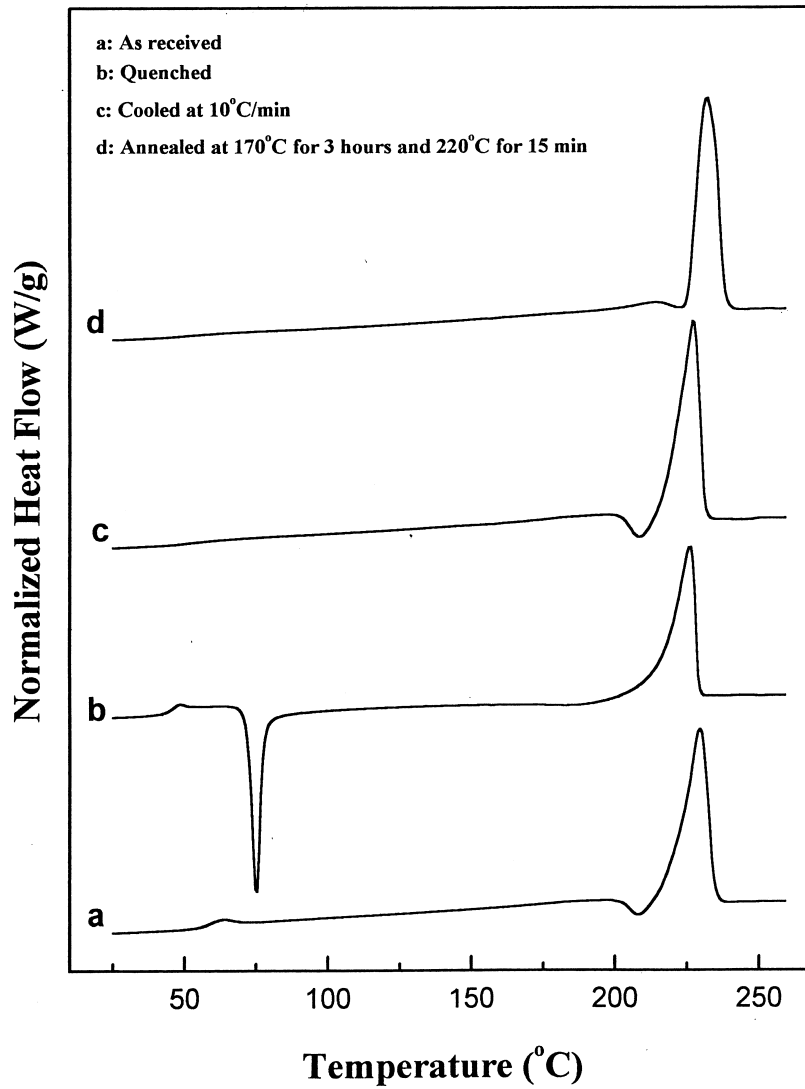


Figure 1. Differential scanning calorimetry traces for PPT samples with different histories.

Poly(Propylene Isophthalate)

For the study of the PPI behavior, two resins of different molecular masses were used. The one of lower molecular mass exhibited a $T_g = 27^\circ\text{C}$ (for quenched samples) and an ultimate melting point of 139°C . The as-received sample of higher molecular mass PPI exhibited very poor crystallinity, in contrast to the low-molecular mass as-received sample, due to reduced crystallization rates. Its' ultimate melting peak temperature was also 139°C



(Fig. 2, trace **a**). However, the T_g of the higher molecular mass PPI was increased to 37°C (Fig. 2, trace **b**). That is, the T_g is strongly dependent on the molecular mass, as was expected. However, no cold-crystallization was observed for both quenched PPI resins (high and low molecular mass), that is PPI exhibits slow crystallization rates.

After 5 h of annealing at 100°C of high molecular mass PPI, rather low crystallinity was formed, as was proved by the low melting enthalpy value and double melting peaks were recorded (Fig. 2, trace **c**). After a second step of annealing at 125°C the

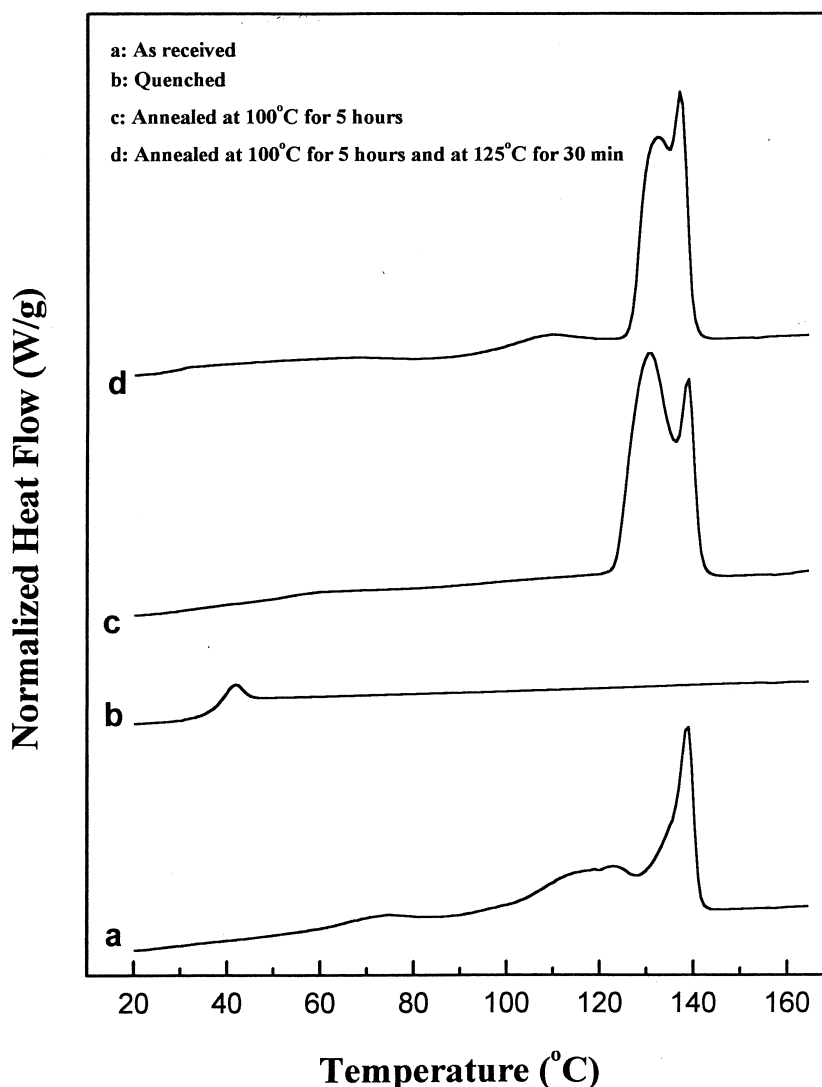


Figure 2. Differential scanning calorimetry traces for PPI samples with different histories.



crystallinity was reduced, but the crystal perfection was increased as is proved by the increase in the enthalpy of the ultimate peak.

Poly(Propylene-2,6-naphthalene Dicarboxylate)

In Fig. 3 four DSC traces for 2,6-PPN samples are shown. Trace **a** corresponds to a sample as-received from the reactor. A large enthalpy relaxation is indicative of the large amount of the amorphous phase. A cold-crystallization exothermic peak and a small melting peak are also recorded.

The behavior of a quenched 2,6-PPN sample is shown in trace **b**. A T_g of 82°C was found from this trace.

The next two traces are for annealed samples. Poly(propylene-2,6-naphthalate) after annealing at 150°C for 5 h exhibits a moderate crystallinity and a limited ΔC_p at glass transition as one can see in trace **c**. Two crystal distributions are associated with the corresponding melting peaks. The ultimate melting peak temperature slightly exceeds 200°C. After annealing at 170°C for 3 h, a lower crystallinity was generated as one can see

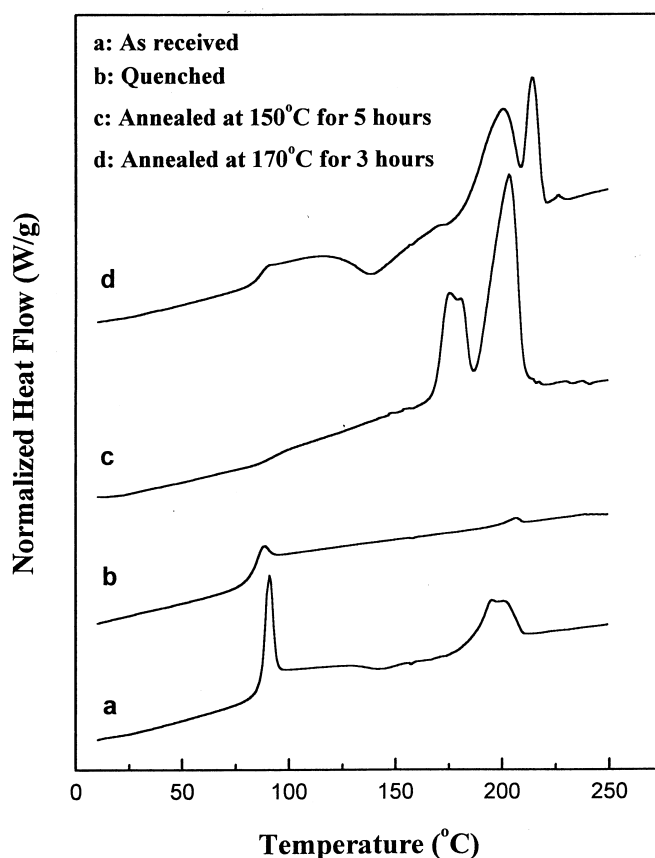


Figure 3. Differential scanning calorimetry traces for 2,6-PPN samples with different histories.

in trace **d**. A cold-crystallization at 140°C is most likely responsible for the dual melting, since it resulted in the formation of crystals melting at about 200°C. The peak at 208°C should be attributed to the melting of primary crystals formed during the isothermal stage.^[25]

Poly(Propylene-1,4-naphthalene Dicarboxylate) and Poly(Propylene-4,4'-diphenylsulfonyl Dicarboxylate)

For the 1,4-PPN and 4,4'-PPDPS, no significant information about melting was collected from the DSC traces. For 1,4-PPN, a $T_g = 35^\circ\text{C}$ was found (Fig. 4, trace **a**). The polyester did not crystallize even after 5 h of annealing at 110°C.

For 4,4'-PPDPS, the T_g was found to be 58°C (Fig. 4 trace **b**) and no evidence of crystallinity was observed after annealing at 170°C for 5 h. However, according to bibliographic data for 1,4-PPN a T_m 180°C and for 4,4'-PPDPS a T_m of about 320°C should be expected.^[30]

Poly(Propylene-4,4'-biphenyl Dicarboxylate)

4,4'-PPBP is a peculiarity of polyester. Its' behavior is a consequence of the presence of the rigid rod-like biphenylene moiety in the repeating unit. So, one should maybe expect this polyester not to crystallize, unless in the form of extended chain crystals. From the

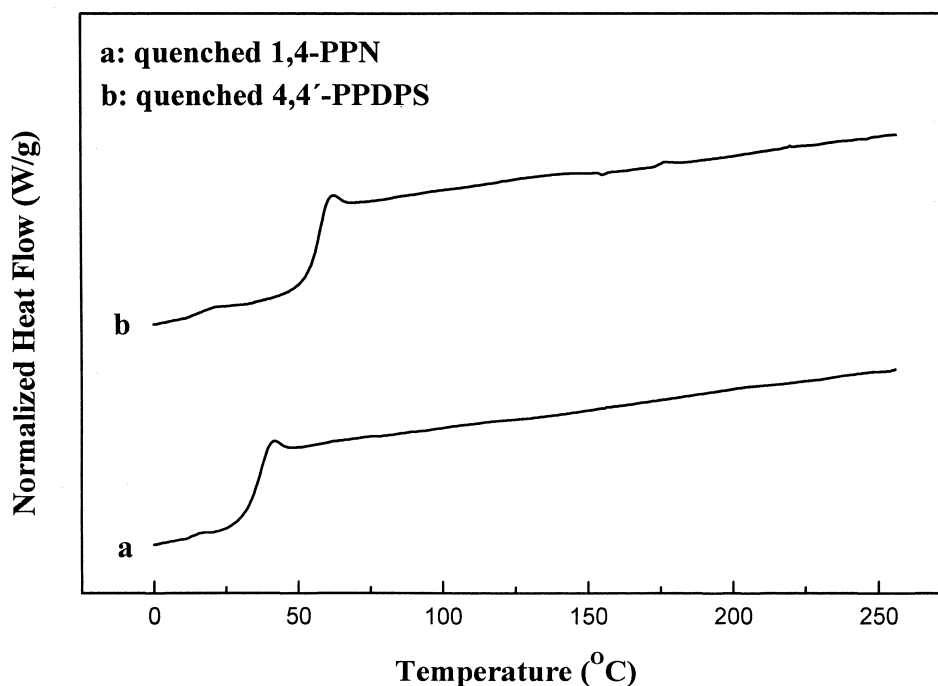


Figure 4. Differential scanning calorimetry traces for quenched 1,4-PPN and 4,4'-PPDPS samples.



DSC traces in Fig. 5 it is obvious that the T_g of 4,4'-PPBP is about 88°C. 4,4'-PPBP samples were annealed at 180°C for a period of 8 h. In the corresponding DSC heating scan (up to 360°C) only the so-called annealing peak was observed at 184°C, though a melting temperature of about 280°C was anticipated according to the literature.^[28] It is reasonable to suppose that folding for 4,4'-PPBP chains is impossible at low temperatures. It is also, obvious that extended chain crystals cannot form.

The observed endothermic peak should be discussed. An annealing peak is usually recorded for polymers 10–25°C above the annealing temperature, but it is very important that in principle it is the first and not the only one, since final melting is recorded at higher temperatures. The nature of the annealing peak is an open problem in polymer physics. It is usually associated with melting of fringed micelle type crystals.^[31] However, as it was revealed by modulated DSC, the annealing peak is probably the result of the overlap between melting of low stability crystals and recrystallization.^[32] The relation between the annealing peak and the relaxation of the rigid amorphous phase has also been discussed.^[33–35] The temperature of 180°C is rather low for polyester like 4,4'-PPBP, with such a rigid macromolecular chain, in order to crystallize. Maybe, one should not exclude formation of secondary fringed micelle type crystals which cannot recrystallize or suffer any perfection process during heating scan due to chain rigidity of 4,4'-PPBP. Moreover, relaxations of the rigid amorphous phase should also be taken into account in the case of 4,4'-PPBP.

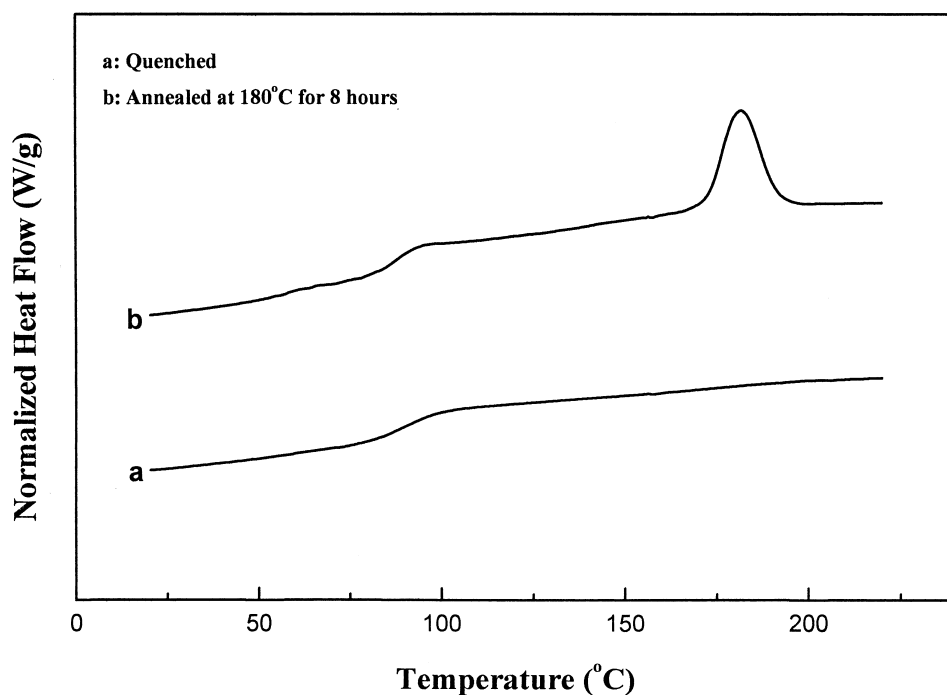


Figure 5. Differential scanning calorimetry traces for 4,4'-PPBP samples with different histories.

Poly(Propylene-2,6-pyridine Dicarboxylate)

Poly(propylene-2,6-pyridine dicarboxylate) has a behavior similar to that of PPT. However, it exhibits lower transition temperatures. It has a T_g equal to 30°C and melts at 162°C, as one can see (Fig. 6, trace **b**). A large cold-crystallization was observed between 80 and 125°C. From the heat of crystallization and heat of fusion, it is concluded that quenching results in almost purely amorphous 2,6-PPP.

CONCLUSION

A new series of polyesters based on 1,3-PDO were successfully synthesized by direct esterification of the respective dicarboxylic acids. The two-step polycondensation process was applied. The intrinsic viscosity values of the polyester samples were satisfactory for most of the polyesters despite the limitations in the synthesis conditions, which were introduced by the nature of the dicarboxylic acids in some cases.

The polyesters derived were studied by DSC to record their thermal behavior. Poly(propylene terephthalate) and 2,6-PPP exhibited fast crystallization kinetics, but they can also be obtained in the amorphous state after quenching. Poly(propylene 2,6-naphthalate) and PPI were found to be slowly crystallizing and thus they were always amorphous. Annealing, however, resulted in semicrystalline specimens. Among the

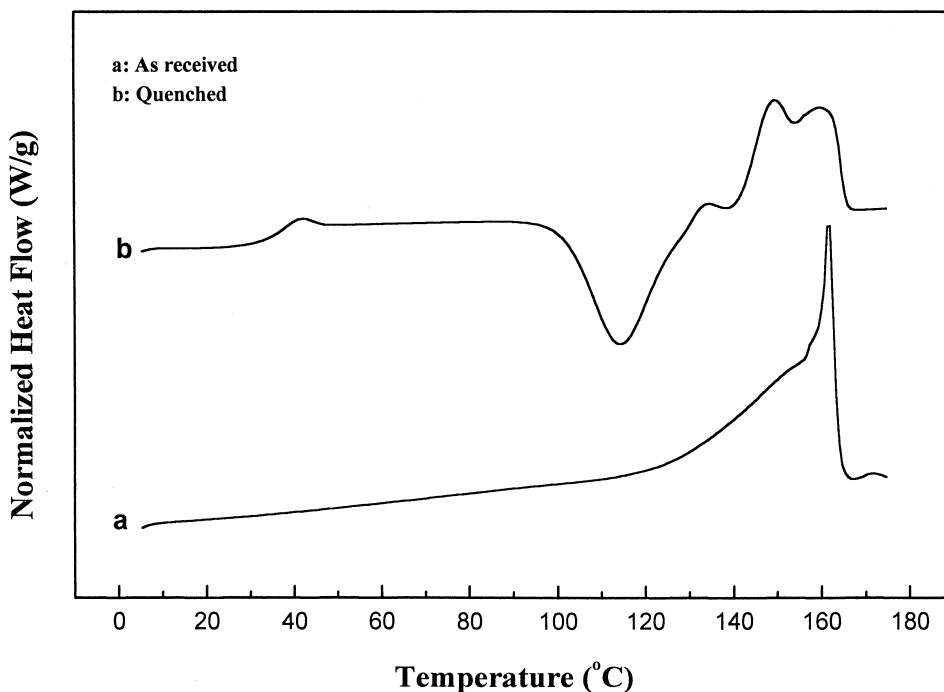


Figure 6. Differential scanning calorimetry traces for 2,6-PPP samples with different histories.





polyesters that were synthesized, those containing a large portion of aromatic moieties, namely 4,4'-PPDPS, 4,4'-PPBP, and 1,4-PPN, were amorphous. Especially 4,4'-PPBP after annealing only the annealing peak was observed.

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