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Optimization of poly(1,4-cyclohexylidene cyclohexane-1,4-dicarboxylate) (PCCD) preparation for increased crystallinity

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Abstract

A key factor, which affects the crystallization temperature on cooling (T_c) of PCCD is the cis/trans isomer ratio of the cyclohexyl diester in the polymer. Isomerization of pure dimethyl-*trans*-1,4-cyclohexanedicarboxylate can occur during the polymerization, and the T_c on cooling decreases along with the trans content. The isomerization reaction is enhanced with temperature, time and catalyst amount, and these variables should be minimized to prepare PCCD polymers with high T_c. However, these same variables also control the molecular weight growth of the polymer, and so a compromise between the best conditions for high T_c and those for high M_w must be made. A set of optimized conditions were obtained leading to PCCD polymers with M_w of 75,000–80,000 and T_c on cooling of 164–167 °C. Solid state polymerization was used to prepare high molecular weight PCCD with a high level of crystallinity (T_c on cooling ~193 °C). It was also shown that adding small amounts of supplementary diols facilitates PCCD preparation by ensuring that high molecular weight PCCD polymers will be obtained even when the stoichiometry of monomer feed is off by >3%, i.e. conditions which would otherwise lead to low M_w. Finally, less crystalline PCCD's have been prepared via either incorporation of diethylene glycol or increasing the cis-diester amount in the polymer.

Keywords: PCCD; Polyester; Crystalline polymer

1. Introduction

Poly(1,4-cyclohexylidene cyclohexane-1,4-dicarboxylate) (PCCD) polymers are of current interest as weatherable materials. PCCD does not absorb UV due to the fact that it is completely aliphatic, therefore photo-induced degradation is less important than with other polyesters such as PBT. Although photo-oxidation can occur, stabilizers to prevent such processes are available. PCCD's are partially crystalline, provide some enhancement in ductility, and have good flow and solvent-resistant properties. PCCD polymers are prepared by melt polymerization of 1,4-cyclohexanedimethanol (CHDM) and dimethyl *trans*-1,4-cyclohexanedicarboxylate (DMCD) in the presence of a catalyst such as titanium (IV) isopropoxide (TPT) (Fig. 1).

PCCD polymers have been known since 1950s [1], but were not sold commercially until recently, probably due to the difficult process conditions required for their preparation. Unlike poly-(butylene terephthalate) [PBT] and poly(ethylene terephthalate) [PET] which can be prepared starting with a large molar excess of diol, CHDM has low volatility, and cannot be used in large excess over the diester component; careful stoichiometry control is necessary to achieve high molecular weight. Furthermore, acid end groups can be continually generated in PBT and PET preparation, whereas acid (or ester) functionality can be depleted during PCCD preparation via distillation or sublimation of DMCD. Copolymers having high levels of relatively volatile comonomers such as ethylene glycol or 1,4-butanediol, are easily prepared and are sold commercially. However, The copolymers are amorphous materials, do not crystallize from the melt, and have poor solvent resistance.

For use as a weatherable blend-stock material, it is desirable to have a polymer that crystallizes rapidly from the melt, in order to achieve solvent-resistance properties. The PCCD polymer prepared by conventional polymerization has a melting temperature (T_m) of 225 °C and a crystallization temperature on cooling (T_c) of 130–152 °C, with a crystallization exotherm of about 10 J/g (standard conditions for differential scanning calorimetry [DSC] are heating to 250 °C at 20 °C/min, hold for 5 min, then cool at 20 °C/min to 50 °C). Often the polymer does not crystallize from the melt during isolation, although a crystallization event can be seen during heating in the DSC. In contrast, PBT has a T_m of 226 °C and a T_c on cooling of 182 °C.

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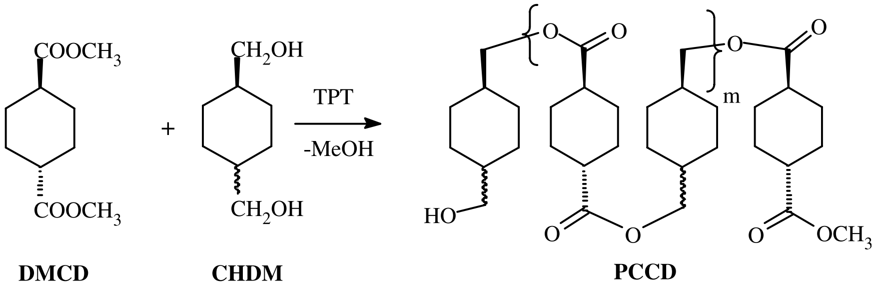

Fig. 1. PCCD polymerization from CHDM and DMCD.

The crystallization of PCCD was not studied at all in early PCCD work [1]. Recent work by Patel [2] described the optimization of conditions for obtaining high molecular weight while maintaining a high melting point. The effect of process variables on T_c was not studied at that time. There have been attempts to use low levels of amide functionality to increase crystallization temperature and rates in polyesters such as PET and PBT [3]. Brunelle reported that PCCD crystallization temperatures were increased by 15–40 °C when bisesteramides made from DMCD and hexamethylenediamine (HMDA) were incorporated into the PCCD polymers at levels of 0.5–2.5% [4].

In this report, we describe methods to increase both crystallization temperature and molecular weight by controlling the reaction conditions. Optimum conditions were obtained by controlling variables such as maximum reaction temperature (T_{max}), reaction time at T_{max}, and catalyst amount and addition mode. The key variable for obtaining high molecular weight polymer with high T_c on cooling was minimization of the maximum temperature and time at that temperature. Solid state polymerization was used to prepare high molecular weight PCCD with a high level of crystallinity ($T_c \sim 193$ °C). Conversely, we have also shown that high molecular weight but very amorphous PCCD polymers can easily be obtained by incorporating volatile diols such as butanediol, ethylene glycol, and diethylene glycol. We have also shown that the preparation of PCCD can be simplified by use of small amounts of accessory diol. The diol becomes incorporated into polymer, minimizing stoichiometry imbalance effects, but can be largely removed in the later stages of polymerization. Finally, we compare our optimized PCCD's to those obtained using the bisamide additives.

2. Experimental

2.1. Materials

CHDM (99%, mixture of 69% *cis* and 31% *trans* isomers) and titanium (IV) isopropoxide (97%) were received from Aldrich, and t-DMCD (98% trans isomer) from Eastman Chemical Co. The monomers and the catalyst were used as received without further purification. Reagent grade 1,4-butanediol (BD), ethylene glycol (EG) and diethylene glycol (DEG) were obtained from Aldrich.

2.1.1. 1,6-Bis-(4-carbomethoxycyclohexanecarboxamide) [Cy-6-Cy]

A mixture of 4.0 g (20 mmol) of DMCD and 1.0 mL of a 4.0 M solution of 1,6-hexamethylenediamine in toluene (4 mmol) was heated at 160 °C in a nitrogen atmosphere, with stirring. After 1.5 h, the entire reaction mixture was solid, and no amine was detected by vapor phase chromatographic analysis. The solid was triturated with ethylacetate to remove excess DMCD, separated by filtration and dried in vacuum, yielding 1.28 g (71%) of the desired 1,6-bis-(4-carbomethoxycyclohexane carboxamide), having a melting point of 240 °C. Analysis by GPC showed the presence of about 75% (by weight) of the monomeric bisamide, and 25% of the triamide from 2 equiv. of amine and 3 equiv. of DMCD.

2.2. Instrumentation

GPC analysis was performed on a Perkin–Elmer instrument using 3% isopropanol/chloroform eluent using a 300 mm PLgel 5 μm mixed-C column (Polymer Labs) at 0.85 mL/min flow rate. A Hewlett Packard model HP1047A RI detector was used for polymer detection. Molecular weights by GPC were based on calibration with polystyrene standards, with the calculation carried out by Turbogel® Software.

The melt temperatures and crystallization temperatures were measured on a Perkin–Elmer DSC-7 with Pyris® software. The typical DSC sample size was 5–10 mg and the DSC heating and cooling rates were 20 °C/min. The melting temperatures given in this report were taken from the endothermic peak of the second heating cycle. When double melting peaks were seen, the peak from the higher temperature was reported as T_m. The crystallization temperatures were taken from the exothermic peak of the second cooling cycle.

^{1}H NMR spectra were run at 300 MHz on a GE NMR Instrument QE-300 NMR spectrometer. Samples were prepared in deuterochloroform with TMS as an internal standard.

2.3. Melt polymerization of PCCD polymers

2.3.1. Polymerization at low temperature (PCCD 14)

A tubular glass reactor (23 cm long and 4 cm wide in diameter) was charged with 20.20 g of t-DMCD (98% trans) (100.9 mmol), 14.45 g of CHDM (69% trans) (100.2 mmol) and 30 μL of titanium(IV) isopropoxide (TPT). The reactor was fitted to a melt polymerizer (Fig. 2) equipped with a stirrer,

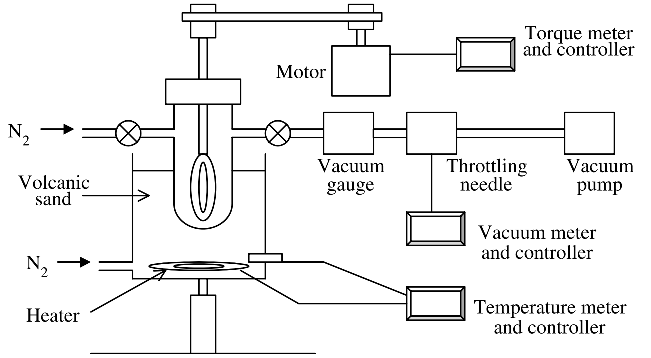

Fig. 2. Melt polymerizer equipped with a stirrer, a temperature programmer, a vacuum controller and torque meter. Volcanic sand in the heating bath is fluidized with a nitrogen stream for even heating.

a temperature programmer, a vacuum controller and a torque meter. Low vacuum was applied to seal the reactor, and held at 500 Torr. The reaction mixture was heated with stirring (150 rpm) from 160 to 230 °C over 30 min, and then the pressure was gradually reduced to 1 Torr over 20 min, while methanol distilled. The temperature was again raised to 245° over 10 min and held there for 60 min. The reactor was detached from the melt polymerizer and the polymer was collected by scooping it out quickly with spatulas and cooling in cold water. Molecular weight of the polymer was 54,500 by GPC, and DSC analysis showed a T_c on cooling of 172 °C ($\Delta H_c = 27$ J/g) and a T_m of 234 °C ($\Delta H_m = 28$ J/g).

2.3.2. Polymerization at optimum temperature (PCCD 24)

20.22 g of DMCD (101.0 mmol) and 14.41 g of CHDM (99.9 mmol) were weighed into a tubular glass reactor. The reactor was set into a melt polymerizer (Fig. 2). When the reaction mixture was melted in a thermostated sand bath at 160 °C, 0.10 mL of 0.1 N TPT solution in toluene was added to the mixture. The reaction was heated from 160 to 180 °C over 60 min with stirring (150 rpm) and then from 180 to 230 °C over 20 min, allowing methanol to distill. Vacuum was applied and the pressure was gradually reduced to 1.0 Torr over 20 min, while the temperature was raised from 230 to 253 °C. The reaction was continued at 253 °C for 100 min, during which torque increased sharply in the first 10 to 20 min and then kept increasing gradually, indicating that the molecular weight was building up continuously. The reactor was disassembled from the melt polymerizer and the polymer was scooped out quickly and cooled in cold water. Molecular weight of the polymer was 79,700, and DSC analysis showed a T_c on cooling of 183 °C ($\Delta H_c = 29$ J/g) and a T_m of 234 °C ($\Delta H_m = 25$ J/g).

2.3.3. Polymerization with 1,6-bis-(4-carbomethoxycyclo hexanecarboxamide) [Cy-6-Cy] (PCCD 16)

19.84 g of DMCD (99.1 mmol), 14.44 g of CHDM (100.1 mmol) and 1.030 g of Cy-6-Cy (2.00 mmol) were charged into a tubular glass reactor [4]. The reactor was fitted in a melt polymerizer (Fig. 2). The mixture was warmed in a sand bath at 160 °C, when 0.3 mL of 0.1 N TPT solution in toluene was added to the mixture using a syringe and needle. The mixture was stirred at 150 rpm and the temperature was gradually raised to 180 °C over 1 h, while methanol distilled at atmosphere pressure. Then the temperature was raised to 230 °C over 20 min. Vacuum was applied and the pressure was gradually reduced to 1.0 Torr over the next 20 min, and at the same time the bath temperature was raised to 253 °C. The reaction was continued at 253 °C for the next 100 min. The reactor was detached from the melt polymerizer and the polymer was quickly collected and cooled in cold water. GPC analysis indicated $M_w = 74{,}900$ and the polymer had T_c of 179 °C ($\Delta H_c = 28$ J/g) and a T_m of 224 °C ($\Delta H_m = 26$ J/g).

2.3.4. Polymerization with 1,4-butanediol (BD) (PCCD 50)

20.22 g of DMCD (98% trans) (101.0 mmol), 14.13 g of CHDM (69% trans) (98.0 mmol) and 0.45 g of BD (5.0 mmol) were charged in a glass tube reactor (23 cm long and 4 cm wide in diameter). The reactor was set into a melt polymerizer equipped with a stirrer, a temperature programmer, a vacuum controller and a torque meter. The reaction mixture was heated in a thermostated sand bath at 160 °C. When the mixture was melted, 0.15 mL of 0.1 N solution of titanium (IV) isopropoxide (TPT) in toluene was added to the mixture. The reactor was heated at 160–180 °C over 60 min with stirring of 150 rpm, allowing methanol to distill. 0.15 mL of the catalyst solution was added again to the mixture, and then the reactor was heated from 180 to 230 °C over 20 min. Vacuum was applied and gradually reduced to 1.0 Torr, while the temperature was raised from 230 to 253 °C over 20 min. The stirring was continued at 253 °C for 100 min, during which the torque increased sharply in the first 10–20 min and then kept increasing gradually, indicating that the molecular weight was building up continuously. The reactor was disassembled from the melt polymerizer and the polymer was collected by scooping it out quickly with spatulas while it was hot. Then, the polymer was cooled in cold water. The amount of BD incorporated in the polymer was 4.9 mol% by NMR study. Molecular weight of the polymer was 81,800, and DSC analysis showed a T_c on cooling of 157 °C ($\Delta H_c = 25$ J/g) and a T_m of 222 °C ($\Delta H_m = 24$ J/g).

2.3.5. Polymerization with ethylene glycol (EG) (PCCD 51)

Similar polymerization was carried out under the same conditions described above with a change of using 0.33 g of EG (5.0 mmol) instead of BD. NMR analysis indicated that 1.5 mol% of EG was incorporated in the polymer. Molecular weight of the polymer was 92,900, and DSC showed T_c on cooling of 150 °C ($\Delta H_c = 24$ J/g) and $T_m = 223$ °C ($\Delta H_m = 24$ J/g).

2.3.6. Polymerization with diethylene glycol (DEG) (PCCD 52)

Similar polymerization was carried out under the same conditions described above with a change of using 0.53 g of DEG (5.0 mmol) instead of BD. NMR analysis indicated that 2.0 mol% of DEG was incorporated in the polymer. Molecular

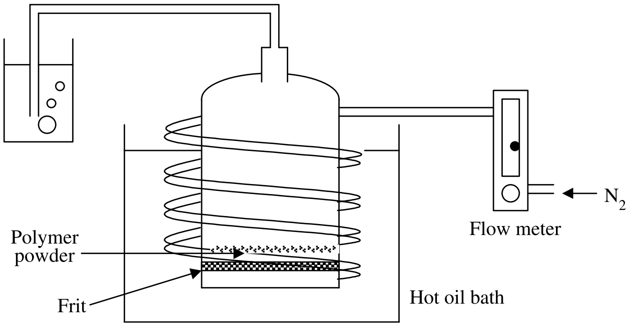

Fig. 3. Solid state polymerization apparatus. Powdered polymer sample is charged in a glass chamber bottomed with a glass frit. Hot nitrogen gas flows through the frit and warms the powder, removing volatiles.

weight of the polymer was 76,600, and DSC showed T_c on cooling of 161 °C ($\Delta H_c = 21$ J/g) and $T_m = 225$ °C ($\Delta H_m = 25$ J/g).

2.4. Solid state polymerization

PCCD polymer chunks were chilled in liquid nitrogen for at least 3 min and then immediately ground mechanicaly to fine powder. About 5 g of powdered polymer was charged into a solid state polymerization vessel shown in Fig. 3. The vessel had a glass frit on the bottom and a glass coil was wrapping around the vessel, such that nitrogen flowing through the coil would be heated when the vessel and coil was immersed in hot oil. Effluent was taken overhead through a glass joint to a receiver. The vessel was immersed in hot oil bath at 205–210 °C while a gentle flow of nitrogen (about 100 mL/min) was passed through the coil, then through the polymer and finally out the receiver. Samples were taken periodically to determine molecular weight.

2.5. Isomerizations

2.5.1. DMCD

50 g of DMCD (29% trans/71% cis, TCI America) and 0.1 g of TPT (0.2 wt%) were refluxed at 270 °C for 2 h under nitrogen. The mixture was sampled periodically and the samples were subjected to ^{1}H NMR measurement in $CDCl_3$ to determine their *trans*/*cis* ratios.

2.5.2. CHDM

According to a European patent [5], isomerization to prepare *trans*-1,4-cyclohexane-dimethanol was attempted. Fifty grams of CHDM (69% trans) and 5.0 g of 50% NaOH solution (5 wt%) were placed in a 250 mL round bottomed flask and were heated at 200 °C for 5 h. The mixture was cooled down to room temperature, and then neutralized with conc. HCl. The neutralized CHDM was distilled under vacuum using 12 in. long Vigirous column. The first 10 g of CHDM was collected (bp 100–110 °C at 0.5 Torr) and subjected to ^{1}H NMR spectroscopy.

3. Results and discussion

3.1. Melt polymerization studies

Typically, polyesters are produced by condensing a diol with a diester or diacid in two stages. The first stage is called ester interchange (EI), in which a diester or diacid reacts with excess diol resulting in low molecular weight hydroxyalkyl-terminated oligomers along with evolution of a byproduct such as methanol (when dimethyl esters are used) or water (from diacids). When most of the byproduct is removed, the Transesterification (TE) stage follows. The TE stage is normally run under vacuum and at high temperature to remove excess diol and drive the polymerization to high molecular weight (Fig. 4).

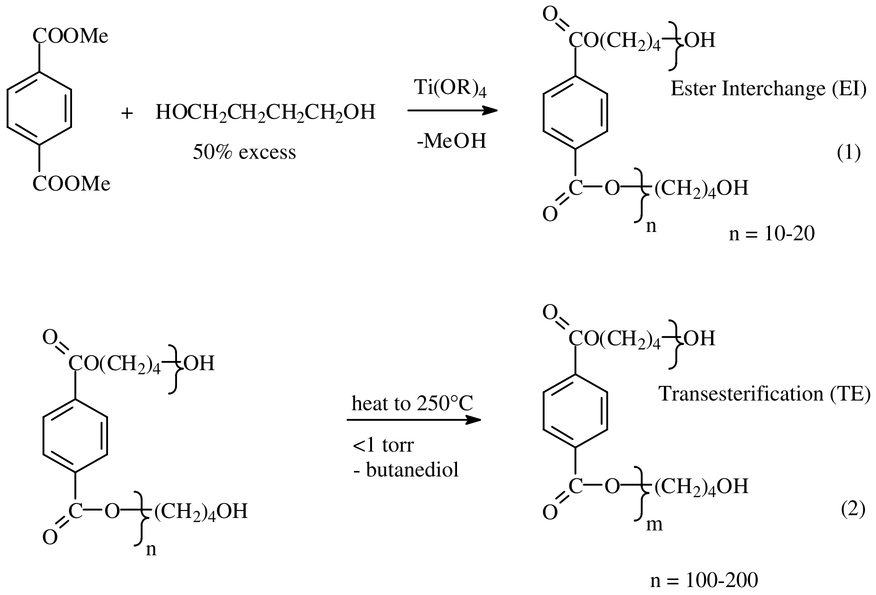

Fig. 4. Ester interchange and transesterification steps in preparation of a polyester.

In the case of PET and PBT, 30–100% molar excess of diol (ethylene glycol for PET or butanediol for PBT) is used in EI stage and the excess portion is removed in TE stage. During TE, many possiblities for reaction exist: (1) attack of an ω-hydroxyalkyl end group on a carbonyl can either be unimolecular (backbiting), leading to a shortened chain and a cyclic, (2) degenerate attack internally on another chain, providing two molecules with the same average DP as the starting molecules, or (3) productive attack at the ester of an end group with cleavage and removal of diol monomer, statistically doubling the molecular weight. Furthermore, at elevated temperatures, chain scission reactions can occur via β-hydrogen elimination, reforming carboxylic acid. In the particular case of PBT, back-biting of a hydroxybutyl group can form THF and a carboxylic acid. As long as sufficient hydroxyalkyl end groups remain, direct esterification of acid and alcohol can also occur, building molecular weight.

PCCD polymerization is significantly different. CHDM cannot be used in large excess in PCCD preparation because (1) CHDM has low volatility (bp 283 °C) and is hard to remove even under high vacuum, and (2) The PCCD polymer is significantly more sterically hindered than PET or PBT, slowing the productive transesterification reactions mentioned above [1,2]. Furthermore, neither scission via β-hydrogen abstraction nor acid generation via ether formation have been observed, and so it is easily possible to deplete carboxylic acid functionality. Because of these facts, careful stoichiometric control of the monomers in the EI stage becomes critical in order to get high molecular weight PCCD polymers [1,2]. While running experiments, we also observed that DMCD was quite sublimable and condensed around the top portion of the glass reactors and even in vacuum hoses. To compensate this loss of DMCD, we used a slight excess DMCD (about 0.5–1 mol%) in all polymerizations. However, we recommend that the amount of excess DMCD used for PCCD preparation should be determined experimentally for each system because the loss from sublimation would be different depending on the shape and size of the reactor, heating method, vacuum degree, etc.

A typical temperature profile for PCCD melt polymerization is shown in Fig. 5. The EI reaction was carried out at 160–253 °C for about 100 min. It was started with very slight vacuum to hold the reactor in a steady position and the vacuum increased gradually along with the temperature. It should be noted that gradual increase of vacuum and temperature was very important for gentle removal of methanol. If methanol boils out abruptly, the monomers, especially CHDM, could be carried over along with methanol, resulting in an imbalance of stoichiometry.

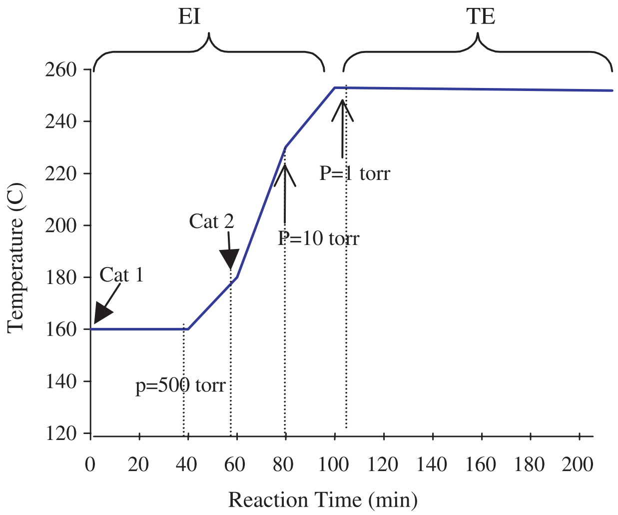

Fig. 5. Temperature and pressure profile during melt polymerization. Most of methanol is removed during ester interchange (EI) period and the molecular weight builds up quickly during transesterification (TE) period.

When the temperature reached 253 °C and the pressure 1 Torr, most of the methanol was removed. The TE stage could be monitored by the increasing torque on the stirrer as shown in Fig. 6. The torque increased sharply initially and then slowly approached a maximum as the reaction reached its completion. This indicates that the molecular weight builds up quickly as the hydroxy and ester endgroups of the PCCD oligomers undergo ester interchange reaction, but then that transesterification takes place more slowly (if at all), while the number of end groups are depleted. The fact that methyl ester end groups are detected even in high molecular weight polymers suggests that true TE (i.e. loss of CHDM monomer) may not occur.

3.2. Solid state polymerization

PCCD polymers prepared under certain conditions such as low T_{max} or/and short reaction time had low molecular weights. The molecular weight could be increased by solid state polymerization (SSP). SSP of PCCD has previously been studied by Patel and Smith, but effects on T_c were not mentioned [6]. Ground polymer powders were heat-treated at 210 °C in a solid state polymerization apparatus by passing hot nitrogen gas through the sample. Samples were taken periodically, and the molecular weights and crystallization temperatures of each sample were measured and depicted in

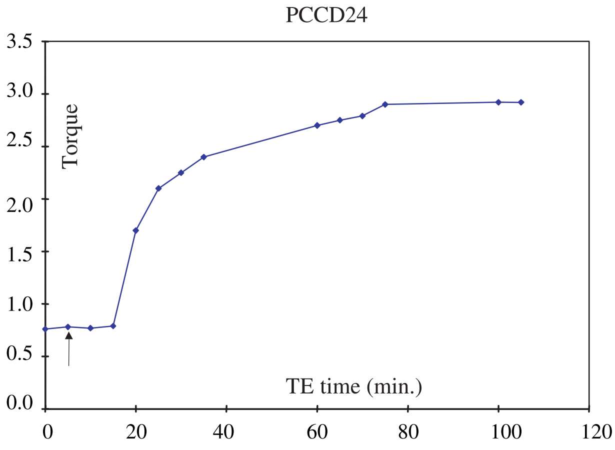

Fig. 6. Torque changes during TE period of PCCD melt polymerization. The torque (representing molecular weight) increased sharply initially and then approached a maximum slowly as the reaction approached completion.

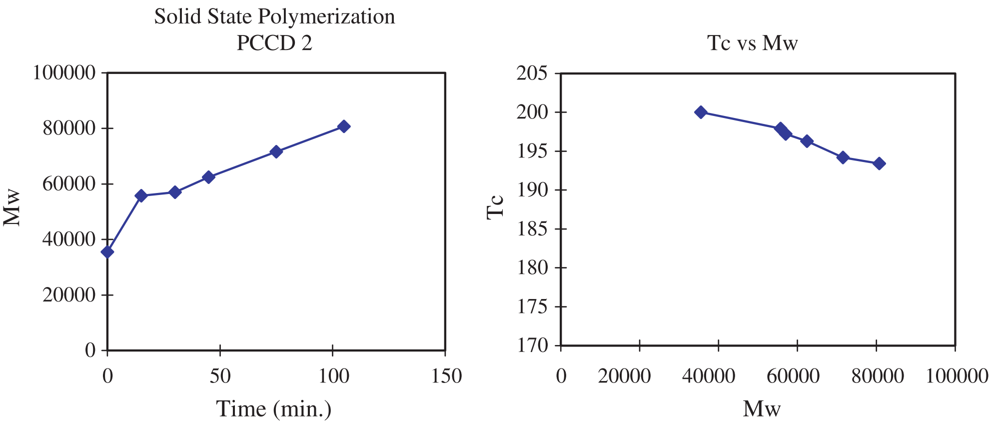

Fig. 7. Solid state polymerization of PCCD2 at 210 °C; the molecular weight changes over heat treatment time and the correlation between crystallization temperature (T_c) and molecular weight.

Fig. 7. The molecular weight increased rapidly in the early stage of heat treatment and then slowed down. While the molecular weights increased with heat treatment, the crystallization temperatures decreased. It is anticipated that higher molecular weight polymers will crystallize more slowly, due to less chain mobility. The results of solid state polymerizations of low M_w PCCD's are summarized in Table 1. They all showed a similar trend.

It should be noted that solid-state polymerization is a vehicle to attain highly crystalline PCCD's, since less cis/trans isomerization occurs at the lower SSP temperatures. Polymerization to moderate molecular weight polymer at a low temperature (∼240 °C), followed by SSP at 205–210 °C affords polymers with M_w of ∼80,000 and T_c on cooling ∼180–90 °C. As will be seen in the next section, conventional melt polymerization, even under optimized conditions provides similar molecular weights, but with T_c of only 166 °C.

3.3. PCCd polymerization optimization

Patel, in his previous work on PCCD synthesis [2] identified several key variables as significant in making PCCD polymers with high molecular weight and high melting points (T_m). Among the list of variables, three machine variables for a DOE were chosen: stirring rate, reaction temperature ramp, and batch size. He showed that polymerization at 265 °C was optimum for maintenance of T_m while obtaining high polymer melt viscosity, but did not use the crystallization rate or T_c as a measurable.

Table 1
Solid state polymerization of PCCD polymers

Samples	Temp (°C)	Time (min)	Init. M_w	Final M_w	Init. T_c	Final T_c
PCCD2	205	105	35,527	80,740	200	193
PCCD3	210	90	50,410	65,550	190	185
PCCD4	210	60	63,231	78,250	177	185
PCCD7	210	90	58,872	79,825	185	180
PCCD9	210	60	64,210	79,674	191	188
PCCD14	210	150	54,491	75,615	172	182

In investigation of the use of amide-containing components to enhance crystallization of PCCD [4], an optimization was carried out by Brunelle to determine the key variables controlling the T_c on cooling of PCCD. It was known that the difference between T_m and T_c should be minimized in order to obtain a fast crystallizing material [3]. While T_m of the PCCD polymers did not vary significantly using various preparation conditions, the T_c varied considerably. When the amide level was zero, certain conditions played a dramatic role in changing T_c: the maximum temperature of the polymerization and the time held at that temperature. A maximum polymerization temperature of 253 °C gave high M_w as well as high T_c on cooling, leading to polymers which crystallized quickly from the melt.

Based on this information, an optimization DOE was carried out to obtain optimum conditions for high T_c and high molecular weight of PCCD polymers without incorporating any amide segments. The key variables were (1) the time at the maximum temperature of 253 °C (80 and 120 min), (2) catalyst amount (15 and 30 μL or 86 and 172 ppm) and (3) catalyst addition mode (catalyst was added either all at once at the beginning or in two equal portions at the start and 1 h later). For measureables, the molecular weight of the polymer was checked by GPC with detection by refractive index, T_m and T_c were measured by DSC, and the cis/trans ratio was determined by ^{1}H NMR. The ratio of monomers (1.0% excess DMCD) and the EI step (60 min at 160 °C) were held constant. The detailed reaction conditions for the DOE and all measurable results are summarized in Table 2.

Analysis showed that there was no interaction between the variables for M_w and only one interaction between catalyst amount and catalyst mode for T_c. The 3D surface plot shown in Fig. 5 summarizes the result that high catalyst amount and long reaction time will yield high molecular weight. On the contrary, the high crystallization temperature is achieved with low catalyst amount and short reaction time. Therefore, one cannot obtain maximum M_w and T_c at the same time, and a compromise between the two requirements must be made (Figs. 8 and 9).

The optimum conditions found above were validated with five scale-up reactions (PCCD 61–65). The monomers were

Table 2
DOE conditions and results for PCCD polymers with high M_w and high T_c

	Conditions					DSC				GPC	NMR	
	DMCD (mmol)	CHDM (mmol)	TPT (μL)	Temp (°C min)	Pres (Torr)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	M_w	DMCD	
										RI-GPC	cis	trans
PCCD35	101	100	15	160(60)-253-(120)	1.0	165	28	228	26	84,802	3.2	96.8
PCCD37	101	100	15+15	160(60)-253-(120)	1.0	172	30	227	27	89,924	4.9	95.1
PCCD39	101	100	15	160(60)-253-(80)	1.0	169	28	230	27	75,886	2.7	97.3
PCCD40	101	100	30	160(60)-253-(120)	1.0	151	22	224	24	100,588	4.6	95.4
PCCD41	101	100	15+15	160(60)-253-(80)	1.0	165	27	229	27	75,701	1.5	98.5
PCCD42	101	100	7.5+7.5	160(60)-253-(80)	1.0	168	27	230	28	68,203	1.4	98.6
PCCD43	101	100	30	160(60)-253-(80)	1.0	163	26	229	27	74,202	3.8	96.2
PCCD44	101	100	7.5+7.5	160(60)-253-(120)	1.0	158	28	230	28	72,699	2.2	97.8

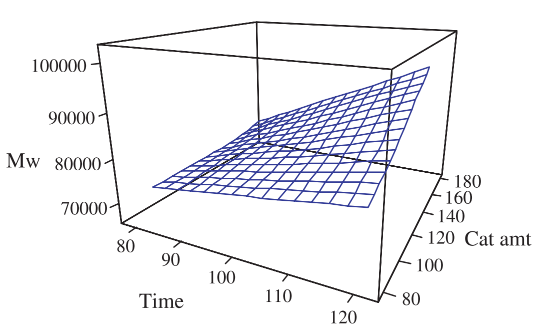

Fig. 8. 3D surface plots for effects of time and catalyst amount on molecular weight (left) and crystallization temperature (right).

scaled up 10 times to 1 mol. These reactions were carried out using specially designed glass reactors with a nipple tip on the bottom so that when the tip was knocked off at the completion of polymerization the polymer resin could be stranded out through the hole with nitrogen pressure. The reaction conditions and characterization results are summarized in Table 3.

3.4. Isomerization of DMCD

DMCD is technically accessible from dimethyl terephthalate via hydrogenation. Catalytic hydrogenation provides DMCD with only about 26% trans content, but isomerization with a variety of catalysts can lead to the thermodynamic mixture of about 70% trans content. Kricheldorf [7] has reproduced work reported in patents [8], and reports that some salts (LiCl) and strong proton acids are good isomerization catalysts. The 70% trans-content is the thermodynamic level, with the same mixture being obtained by isomerization of 100% trans starting material. Recrystallization from methanol can then lead to DMCD with >99% trans content, recycling the cis isomer back to isomerization. The properties of PCCD polyesters depend on the trans/cis ratio; only the polymers rich in trans isomer afford high melting points or fast crystallization.

Running the polymerization at high temperature for long times decreased the T_c on cooling of PCCD polymers. It was believed that the drop in T_c was directly related to the drop in trans content of the cyclohexyl diesters driven by isomerization reaction under polymerization conditions. In contrast to Kricheldorf's report [7], titanate was shown to be a catalyst for isomerization. Heating a 26% *trans*-DMCD in the presence of titanate led to a higher trans content (Table 4). Although titanate was not as effective as LiCl or *p*-toluenesulfonic acid, isomerization nonetheless occurred.

Measurement of the isomerization rate of the diester segments in the polymer chain was also studied. PCCD polymer was heated above its melting temperature for several hours, pulling samples and analyzing by ^{1}H NMR spectroscopy

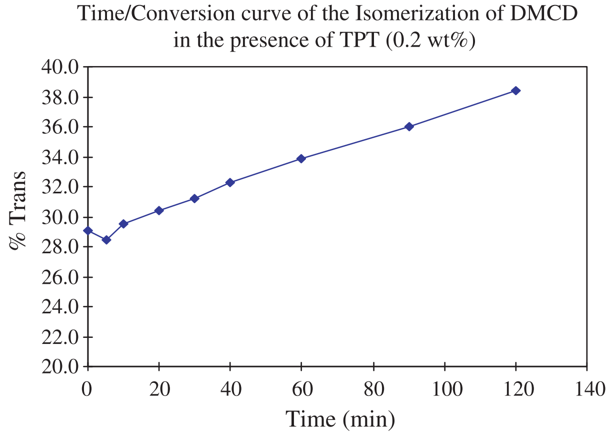

Fig. 9. Isomerization of 29% *trans*-DMCD at 270 °C in the presence of TPT catalyst.

Table 3
Scale-up reactions for validation of the optimized conditions

	DMCD (mmol)	CHDM (mmol)	TPT (μL)	Temp (°C min)	Pres (Torr)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	M_w	DMCD	
										RI-GPC	cis	trans
PCCD61	1010	1000	100+100	160(60)-253-(80)	1.1	167	26	228	26	76,443	3.1	96.9
PCCD62	1010	1000	100+100	160(60)-253-(80)	1.5	165	24	228	26	75,249	2.7	97.3
PCCD63	1010	1000	100+100	160(60)-253-(80)	1.2	164	29	228	27	76,561	2.1	97.9
PCCD64	1010	1000	100+100	160(60)-253-(80)	1.3	167	28	228	28	74,263	2.0	98.0
PCCD65	1010	1000	100+100	160(60)-253-(80)	1.1	167	27	227	27	79,839	2.7	97.3

for trans/cis ratio and carrying out DSC analysis for T_c changes. The results are summarized in Table 5 and depicted in Fig. 10. As anticipated, a significant amount of isomerization occurred during the heat treatment at a temperature of 270 °C. Furthermore the reduction in the T_c on cooling was proportional to the decrease in the trans content. At 250 °C, both the isomerization and the reduction of T_c were slower. Curiously, these conditions are more severe than those used in the polymerizations carried out in Mt Vernon by Patel, yet the T_c did not degrade as much as in his work. Whereas the T_c declined from 180–190 to ~170 °C in our study, PCCD from the Patel work has T_c of 130–150 °C. Exposure to metals or higher catalyst levels may be the reasons for this behavior.

Isomerization of CHDM with base has also been patented. Since this result seemed surprising, and had not been observed during polymerization, we attempted to reproduce the literature method. Heating 69% *trans*-CHDM with 50% NaOH at 200 °C for 6 h gave no change in the cis/trans ratio. Distillation through a 12-in. vigreaux column, as in the patent, did enhance the trans content, but the pot-residue was similarly enhanced in cis isomer. It seems that the patent technique is simply trans-enhancement via fractional distillation, rather than isomerization.

3.5. Copolymerization with bisesteramide

Incorporation of amide functionality into polyesters has been found to enhance the crystallization of the polymers [4]. Brunelle reported that a bisesteramide (Cy-6-Cy; Fig. 11) prepared from hexamethylenediamine (HMDA) and DMCD increased the crystallization temperature of PCCD polymers by 15–40 °C. The copolymers were prepared by melt-polymerization at 230 °C and either subsequent solid state polymerization at 205–215 °C, or by standard melt polymerization at 265 °C; they had T_c on cooling of 173–187 °C. A large-scale reaction produced a 2% Cy-6-Cy PCCD copolymer by melt-polymerization at 265° and it had T_c of 168 °C. For comparison, PCCD homopolymers prepared under similar conditions had T_c of 130–150 °C.

Table 4
Isomerization of DMCD with various catalysts (2%) at 280 °C

Catalyst	Time (h)	% trans
None	2	26
$Ti(OBu)_4$	1	34
$Ti(OBu)_4$	2	38
LiCl	1	35
LiCl	2	50
LiBr	2	40
p-TsOH	4	49
$ZnCl_2$	4	41

We needed to determine whether the bisesteramide (Cy-6-Cy) would help to increase T_c of the PCCD polymers prepared under optimized temperature 253 °C. As shown in Table 6, a series of copolymers were prepared with 0–5 mol% of Cy-6-Cy. In Fig. 12, the crystallization temperatures (179–181 °C) and the trans content ratio (97.0–98.2%) of DMCD segments in the polymer chains did not change much with the level of amide content. Surprisingly, the control sample (PCCD homopolymer) had a higher T_c on cooling than the amide-containing copolymers.

With these observation, we conclude that the presence of low levels of amide functionalities enhance T_c of PCCD polymers prepared under somewhat abusive polymerization temperatures (i.e. temperature above 255 °C), but that their presence does not enhance crystallization temperatures if the polymers are prepared under optimized conditions. The high T_c of PCCD 18 (Table 6) may be partly due to the fact that the polymer has a lower M_w than the other PCCD's, or it may reflect the fact that a pure PCCD crystallizes more readily than an ester-amide copolymer when the trans content is very high. A second observation is that the amount of amide functionality within the range of 0.5–5.0 mol% did not seem to make any difference. Finally, the presence of amide functionality had no effect on cis–trans isomerization of the PCCD, as seen in Fig. 12.

Table 5
cis/trans Isomerization of the ester functionality in a PCCD polymer

Sample	Temp (°C)	Time (h)	% trans (NMR)	T_c (°C)	ΔH (J/g)
PCCD18	270	0	96.8	178	30
	270	1	96.2	178	30
	270	2	95.3	177	29
	270	3	95	175	28
	270	4	94	173	27
	270	5	93.7	171	26
PCCD2	250	0	98.9	190	30
	250	1	97.6	185.7	25.9
	250	2	96.8	180.6	26
	250	3	96.7	178.3	27
	250	5	96.2	172	26

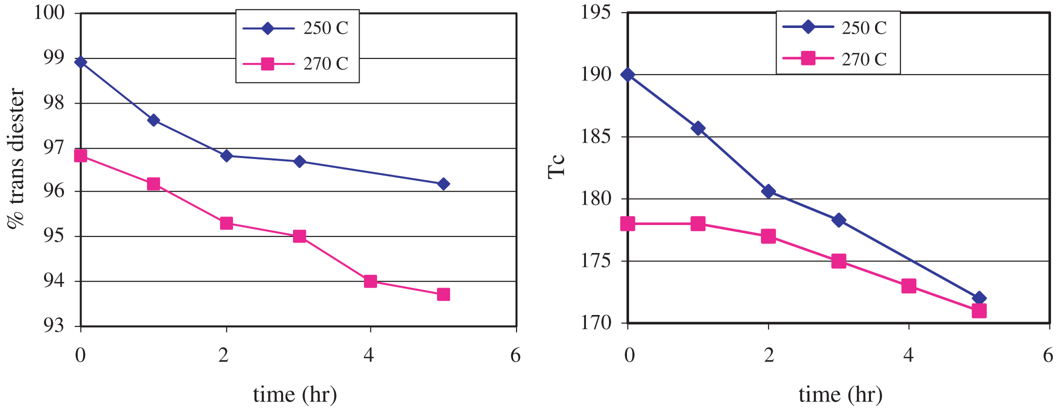

Fig. 10. Changes of trans-ester content and T_c of PCCD by heating.

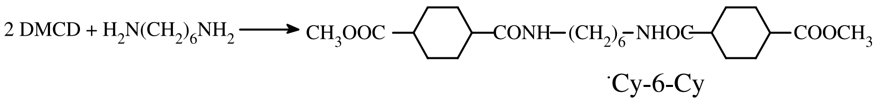

Fig. 11. Esteramide monomer from DMCD and hexamethylenediamine.

Table 6
Preparation and characterization of PCCD copolymers with Cy-6-Cy at 253 °C

Sample	DMCD (mmol)	CHDM (mmol)	Cy-6-Cy (mmol)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	M_w	DMCD	
								RI-GPC	cis	trans
PCCD18	101.1	99.9	0.0	189	31	232	27	50,340	3.2	96.8
PCCD15	100.8	100.8	0.5	180	28	231	25	67,100	2.8	97.2
PCCD13	100.5	100.1	1.0	181	28	223	26	70,040	2.8	97.2
PCCD16	99.1	100.1	2.0	179	28	224	26	74,940	2.7	97.3
PCCD17	98.1	100.1	3.0	179	30	226	27	42,340	1.8	98.2
PCCD19	97.3	100.1	4.0	179	26	224	24	100,760	3.0	97.0
PCCD20	96.3	100.1	5.0	180	27	224	24	82,670	2.3	97.7

3.6. Copolymerization with volatile diols: simplification of stoichiometry control

It has been pointed out that one of the major operational issues with the preparation of PCCD polymers is control of the reaction stoichiometry [2]. Most polyester syntheses use a large excess of diol (50–100%) which is subsequently removed by distillation during the TE stage. However, the most efficient polymerizations of DMCD with CHDM use only 0.5–1.0% of the diester component, since it is difficult to remove CHDM by distillation. Because of this fact, slight imbalances in stoichiometry can easily lead to loss of control during polymerization, leading to lower molecular weights than expected, due to depletion of one of the monomers. Unlike PET and PBT, which are predominantly capped with hydroxyethyl or hydroxybutyl groups which can be cleaved as diols and removed, PCCD polymers have approximately equal amounts of alcohol and methyl ester end groups.

We have identified a very simple process change, which can facilitate stoichiometry control during PCCD polymerization: adding a small amount of a supplemental, more volatile diol to the reaction mixture. The second diol will esterify along with the CHDM, forming alcohol-terminated oligomers or build into the polymer. Excess diol (equal to the amount of supplement added) will then be present throughout most of the polymerization. Near the end of the polymerization, transesterification will free the second diol, which is removed by distillation, as in PBT or PET synthesis, resulting in polymer which has only a small amount of the supplemental

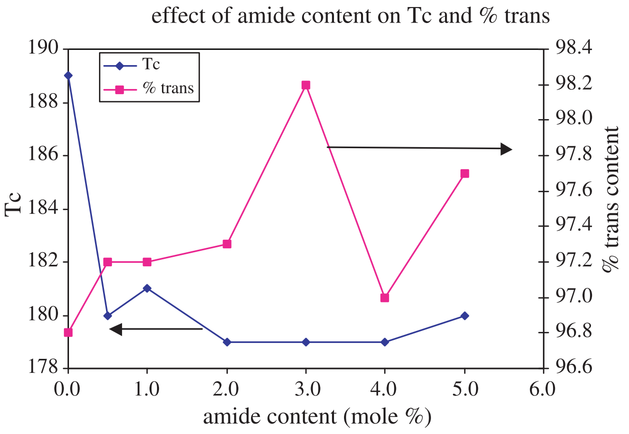

Fig. 12. The effect of amide content in PCCD copolymers on their glass transition temperatures, T_c and trans content of the diester in the polymer.

Table 7
Incorporation of volatile diols (and a bisamide Cy-6-Cy) into PCCD polymers

	DMCD (mmol)	CHDM (mmol)	Diol (mmol)	Cy-6-Cy (mmol)	T_c (°C)	ΔHc (J/g)	T_m (°C)	ΔH_m (J/g)	M_w
									RI-GPC
Example 1	101	98	BD 5.0		157	25	222	24	81,774
Example 2	101	98	EG 5.0		150	24	223	24	92,885
Example 3	101	98	DEG 5.0		161	21	225	25	76,564
Example 4	101	95	DEG 9.7		149	23	222	25	76,359
Example 5	101	90	DEG 19.5		141	22	212	23	91,631
Example 6	100	98	BD 5.1	1.0	166	25	220	24	76,575
Example 7	100	98	EG 5.0	1.0	163	21	222	23	85,871
Example 7	100	98	DEG 5.0	1.0	165	23	222	23	78,463

Polymerizations were carried out at 253 °C for 100 min in the presence of 114–172 ppm of TPT catalyst added in two portions.

Table 8
Less crystalline PCD's via increased cis content or incorporation of diethylene glycol

DEG (mol%)	cis-Diester (mol%)	Polymer M_w ($\times 10^{-3}$)	T_m (°C)	ΔH (J/g)	T_c (°C)	ΔH (J/g)
5	0	63.9	223	25	169	29
10	0	76.4	222	25	149	23
20	0	91.6	212	23	141	22
0	12	86.4	214	24	137	11
0	26	82.7	198	30	128	2
20	12	98.5	198	22	124	4

diol incorporated. Using this technique, high polymer molecular weights can be achieved, even when the stoichiometry of DMCD/CHDM is mismatched by >3%. Importantly, the melting point and the crystallization temperature of the polymer can be maintained, even though a copolymer is being formed, as long as the amount of copolymer at the end of reaction is small. Examples of the incorporation of several diols into PCCD polymers are shown in Table 7.

The data in Table 7 shows that high M_w PCCD could be obtained even when the CHDM/DMCD stoichiometry was 3–6% off. Also note that the molecular weights achieved are typically higher than those obtained under the same optimized conditions in the absence of supplemental diol (Table 4, M_w's 74–79,000). NMR analysis showed that when 5% butanediol (example 1), ethylene glycol (example 2), or diethylene glycol (example 3) were added, 4.9, 1.5, and 2.0% became incorporated into the polymers, respectively. Finally, even though 5% of the diol was added, the melting points were undepressed, and the crystallization temperatures remained high. Ideally, this procedure should prove most effective if one attempts to balance the DMCD/CHDM ratio, adding only 2–5% supplemental diol, to make sure that ester functionality does not deplete.

3.7. Less crystalline PCCD's

Reducing the crystallization temperature of PCCD proved very easy. Either incorporation of a second diol (diethylene glycol) or a large increase in cis-diester led to PCCD's with significantly reduced T_c on cooling and sometimes barely discernable crystallization exotherms. cis-Diester was prepared by using a mixture of 99%-*trans*-DMCD and commercially available 26%-*trans*-DMCD. Results are shown in Table 8.

4. Conclusion

A key factor, which affects the crystallization temperature of PCCD is the cis/trans isomer ratio of the cyclohexyl diester in the polymer. Isomerization of the 99% trans diester starting material occurs during the polymerization, and the T_c on cooling decreases along with the trans content. The isomerization reaction is enhanced with temperature, time and catalyst amount, and these variables should be minimized to prepare PCCD polymers with high T_c. However, these same variables also control the molecular weight growth of the polymer, and so a compromise between the best conditions for high T_c and those for high M_w needs to be made. A set of optimized conditions derived from transfer functions that were obtained from a DOE were established. Using these optimized conditions, PCCD polymers that had M_w of 75,000–80,000 and T_c of 164–167 °C could be prepared. Solid state polymerization of PCCD prepared under controlled conditions at 210 °C led to high molecular weight PCCD's with T_c as high as 193 °C. The presence of amide functionality at low levels helps to keep the T_c high in cases where the polymerization conditions were not optimal. We have also shown that adding small amounts of supplementary diols facilitates PCCD preparation by ensuring that high molecular weight PCCD polymers will be obtained even when the stoichiometry of monomer feed is off by >3%, conditions which would otherwise lead to low M_w. Finally, we have prepared less crystalline PCCD's via either incorporation of diethylene glycol or increasing the cis-diester amount in the polymer.

References

[1] (a) J.R. Caldwell, R. Gilkey, US Patent 2,891,930 (1959)(b) C.J. Kibler, A. Bell, J.G. Smith, US Patent 2,901,466 (1959); both to Eastman Kodak;(c) Kibler CJ, Bell A, Smith JG. J Polym Sci, Part A 1964;2:2115.

[2] B.R. Patel, G.F. Smith, T.E. Banach, US Patent 5,986,040 (1999, to GE).

[3] Gaymans RJ, de Haan JL. Polymer 1993;34:4360.

[4] Brunelle DJ, US Patent 5,939,519 (1999, to GE).

[5] European Patent 0 353 990 B1 (1994).

[6] Patel B, Smith G, US Patent 6,455,664 (2002, to GE).

[7] Kricheldorf HR, Schwarz G. Makromol Chem 1987;188:1281–94.

[8] (a) Levin SZ, Diner IS, Gurevich GS, CAN 61:61413; (b) Thweatt JG, McConnell WV, Def Publ US Pat Off, US 892024, CAN 76:33861; (c) Sumner Jr CE, Choate WE, US Patent 5,231,218 (1993, to Eastman Kodak).