

Synthesis and Characterization of Copolymers of Poly(ethylene terephthalate) and Cyclohexane Dimethanol in a Semibatch Reactor (Including the Process Model)

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ABSTRACT: Although poly(ethylene terephthalate) (PET) has excellent basic properties, this polymer tends to crystallize rapidly and has a rather high melting temperature, a low glass-transition temperature, and low impact on notched articles for some potential applications. Copolymerization is a reasonable method for improving the properties of PET. 1,4-cyclohexane dimethanol (CHDM) is one of the most important comonomers for PET. In this research, PET and PET copolymers containing 5–30% CHDM were prepared from comonomer mixtures by two-step melt polycondensation. The copolymers were synthesized in a home-made laboratory setup. The first synthesis step was conducted under pressure, and the second was performed *in vacuo* at a high temperature (230–290°C). The microstructure of the synthesized copolymers was studied with Fourier transform infrared and nuclear magnetic resonance. The comonomer content in the polymer chain was deter-

mined from the nuclear magnetic resonance spectrum. The presence of the comonomer in the copolymer chain was random. Differential scanning calorimetry was used to study the thermal properties of the copolymers to detect changes in the polymer properties. CHDM reduced the heat of fusion and melting and glass-transition temperatures of the PET copolymers. Process modeling was performed with mass balances of different functional groups and species. Equations of mass balances were integrated numerically. Numerical simulation and experimental results were in very good agreement. By modeling, the effects of the reaction temperature and feed molar ratio on the conversion and formation of diethylene glycol were studied. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3520–3532, 2009

Key words: computer modeling; modeling; polycondensation; polyesters; synthesis

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a linear polyester widely used as one of the important polymers for the synthesis of fibers, films, and food packaging materials. PET has excellent clarity, thermal and mechanical properties, colorability, and dimensional stability and good barrier properties with respect to oxygen and carbon dioxide; these qualities make PET a potential candidate in various industries and applications.¹ Moreover, this polymer is resistant to mineral oil, solvents, and acids.² PET is a tough polymer that does not break in unnotched impact strength tests at temperatures higher than -40°C ; however, one drawback is the brittleness of its final products.³ Moreover, its high melting temperature (T_m), low glass-transition temperature (T_g), and fast crystallization constitute other negative aspects of this polymer. Changes in the processing conditions

or molecular weights, the use of additives, alloying, blending, and copolymerization are various methods that confer desirable properties and make PET suitable for various applications.¹ Copolymerization has been investigated to modify properties such as the crystallizability and thermal properties.⁴ Copolymerization can be conducted with a diol or diacid. However, the content of the comonomer in the copolymer chains is an important parameter that plays a significant role in conferring suitable properties to PET. Amorphous copolyesters are applicable in articles without a crystalline structure that are produced by thermoforming and blow molding, and they are also applicable in nonoriented films, uniaxially oriented films, and biaxially oriented films.³ PET copolymers containing minor amounts of isophthalic acid as a secondary diacid have been extensively investigated because of their high importance to industry. The presence of isophthalic acid and any other comonomer reduces the crystallization of PET.⁵ However, isophthalic acid decreases the permeability of the copolyester to oxygen and carbon dioxide.^{6,7} 2,6-Naphthalene dicarboxylic acid (NDA) is another comonomer used in the copolymerization of PET. This comonomer improves the barrier

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property of the polymer with respect to oxygen and increases the heat and UV resistance of PET.^{7,8} 5-*tert*-Butyl isophthalic acid,^{4,9} 1,4-cyclohexane dicarboxylic acid,¹ and 6-hexane diol¹⁰ are the other comonomers most widely studied. Cyclohexane dimethanol (CHDM) is one of the most important diols used as a PET comonomer. CHDM has proven to be a valuable diol for commercial polyesters.¹¹ The presence of CHDM in the semiaromatic polyester structure produces a new group of polyesters with a wide crystallinity range (i.e., from amorphous structures to highly crystalline structures).³ The use of a small percentage of CHDM (<5%) improves the molding characteristic and assists in imparting enhanced clarity to stretch-blow-molded bottles for packing carbonated soft drinks. By modification of the crystallization characteristic of the PET backbone, the availability of CHDM spawned intense interest in CHDM-containing polyesters, especially at Eastman Co.¹¹ In 1980, Eastman performed studies on copolymers including cyclohexylene groups, and since then, they produced a group of PET copolyesters based on CHDM for food packaging, drugs, and molding parts for medical goods and electronics.³ Nevertheless, most studies on CHDM copolymer synthesis have been presented as patents,^{12–15} and very little information on CHDM copolymers has been published. Tsai et al.¹⁶ evaluated the effects of incorporating 5-*tert*-butylisophthalic acid and CHDM into the polymer chain of PET on the crystallization behavior and thermal, optical, and tensile properties of this polyester. Tsai et al.¹⁷ synthesized two series of amorphous copolyesters through the copolymerization of NDA, succinic acid (0–40%), CHDM, ethylene glycol (EG), and terephthalic acid (TPA). The compositions and molecular weights of the copolyesters were determined with ¹H-NMR spectroscopy and viscometry, respectively. The thermal and optical behavior was studied, too.

CHDM reduces the crystallinity and T_m and increases the toughness and T_g ; moreover, it improves the processability of PET. The geometrical configuration of the 1,4-cyclohexylene ring in the PET chain affects the structure and properties of PET. The chemical structure of CHDM is presented in Figure 1. Hence, the brittle behavior of PET changes to ductile behavior with an increase in the CHDM content. It is believed that the secondary relaxation is responsible for the aforementioned changes. A larger peak of the secondary stress relaxation is obtained with the increase in the CHDM content, without any change in its position.¹⁸ Secondary relaxation results from the conformational transition (chair–boat–chair) of the cyclohexylene ring.¹⁹ However, the rate at which CHDM increases toughness in copolyesters remains an active area of investigation.¹¹ With an increase in the CHDM con-

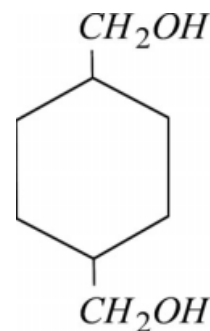


Figure 1 Chemical structure of CHDM.

tent up to 20–30 mol %, an amorphous polymer that shows no melting peak in differential scanning calorimetry (DSC) curves is produced. When the melting point is reduced, the processability of the copolyester is improved; therefore, less acetaldehyde (AA) will be produced in the molding cycle.³ Even though the presence of CHDM in PET chains has many benefits, it results in an increase in the gas permeability of the copolymer. An increase in chain mobility due to the presence of CHDM eases gas diffusion through the polymer chain.^{10,20}

PET can be produced by (1) the direct esterification of TPA and EG, (2) the alcoholysis of dimethyl terephthalate and EG, (3) the reaction between terephthaloyl chloride and EG, and (4) the reaction between TPA and ethylene oxide.² Until 1960, PET was mostly produced with the second method, and the first method was applied mainly because highly pure TPA was produced via recrystallization.³ The first method results in a higher reaction rate, less catalyst consumption, water as a byproduct, a higher molecular weight, and fewer products with COOH end groups. The first method also results in the production of high concentrations of diethylene glycol (DEG).² Today, 70% of PET in the world is produced by the direct esterification of TPA. The production of PET involves two steps. In the first step, which is called esterification, a reaction between carboxylic end groups and hydroxyl end groups occurs, and diol diesters are formed. In the second step, which is called polycondensation, transesterification between glycol esters and hydroxyl end groups occurs.³

In this article, the synthesis of PET copolymers with CHDM via the direct esterification of TPA and EG was studied to produce amorphous polymers. These copolyesters were abbreviated PETC_x (where x indicates the molar percentage of CHDM with respect to EG). The processing conditions for the production of PETC_x were determined. Synthesis was performed for various amounts of CHDM ranging from 5 to 30% in a laboratory-scale semibatch reactor. The water produced during the esterification

TABLE I
Some Properties of the Raw Materials

Property	Material			
	EG	TPA	CHDM	Antimony trioxide
IUPAC name	1,2-Ethanediol	Benzene-1,4-dicarboxylic acid	1,4-cyclohexane dimethanol	Antimony (III) oxide
Melting point (°C)	-12.9	402 (sublimation point)	41-61	656
Boiling point (°C)	197.3	—	284-288	—
Vapor pressure	0.06 mmHg at 20°C	1.19×10^{-5} mmHg at 25°C	1 mmHg at 96°C	1 mmHg at 574°C
Molecular weight (g/mol)	62.07	166.1	144.21	291.52

IUPAC = International Union of Pure and Applied Chemistry.

step, which indicated the extent of the reaction, was collected. Consequently, the microstructure of the copolyesters was studied with Fourier transform infrared (FTIR) and NMR spectra. The characterization of different groups and a comparative evaluation of some of their more relevant properties were performed.

EXPERIMENTAL

Materials and measurements

TPA and EG, used to produce the polymer, were supplied by Shahid Toundgoyan Petrochemical Complex (Mahshar, Iran). CHDM was purchased from Sigma-Aldrich Co. (London, England). Antimony oxide, a polycondensation catalyst, was bought from Merck Co. (Darmstadt, Germany). Some basic properties of these raw materials are summarized in Table I. The intrinsic viscosities of the polymers dissolved in highly pure dichloroacetic acid were measured with an Ubbelohde viscometer thermostated at $25 \pm 0.1^\circ\text{C}$. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker Avance (Switzerland) 400 spectrometer operated at 400 MHz and 25°C . Polyesters were dissolved in dichloroacetic acid, and a small amount of deuterated CHCl_3 was added to lock the spectrometer; the spectra were internally referenced to tetramethylsilane. Samples—20 or 60 mg—were dissolved in 0.8 mL of the aforementioned solvent and were used for ^1H - and ^{13}C -NMR spectroscopy, respectively. Infrared spectra were obtained at room temperature on a Nexus 670 spectrophotometer purchased from Nicolet Co. (Waltham, MA). A total of 1–2 mg of the polyesters was mixed with 100–200 mg of KBr to produce samples for FTIR. The thermal behavior of the polyesters was examined by DSC with a Mettler-Toledo (Columbus, OH) 822° calibrated with indium. DSC data were obtained from 4–6-mg samples at heating and cooling rates of 20 and 10 K/min, respectively, under

nitrogen circulation, with the heating and cooling carried out twice.

Setup

A laboratory-scale reactor was applied to produce PET and its copolymers. Figure 2 presents some different views of the setup. This was a home-made setup consisting of a stainless steel 1-L reactor, a condenser, and a vacuum pump. The reactor was heated with an electrical heater (1000 W), and ceramic-type insulation covered the reactor. The reactor could be heated up to 350°C . The reactor was cooled by air flow when needed. A nitrogen flow was used to maintain the required pressure. Moreover, nitrogen carried over the synthesized water during the esterification step. A stainless steel condenser, which was maintained at 160°C , returned EG into the reactor. Water vapor was cooled, gathered, and weighed on a regular basis (every 15 min) during the first step of the reaction as soon as the temperature reached 240°C . During the polycondensation step, a vacuum pump produced the required level of vacuum and extracted EG. Two chilled traps, in series, were used to prevent the entry of organic materials into the vacuum pump. Methanol at -30°C cooled the traps. All data acquisition and control tasks were performed with home-written Visual Basic code.

Synthesis of the copolyesters

EG, CHDM, and TPA with a hydroxyl group/acid group molar ratio of 1.3 were mixed before they were allowed to pass into the reactor so that the mixture would be homogeneous. The overall weight of the material was 650 g. A total of 245 ppm antimony trioxide was added to the mixture as a polycondensation catalyst. The paste was mixed for 30 min at 40 – 60°C under atmospheric pressure. The temperature and absolute pressure were then

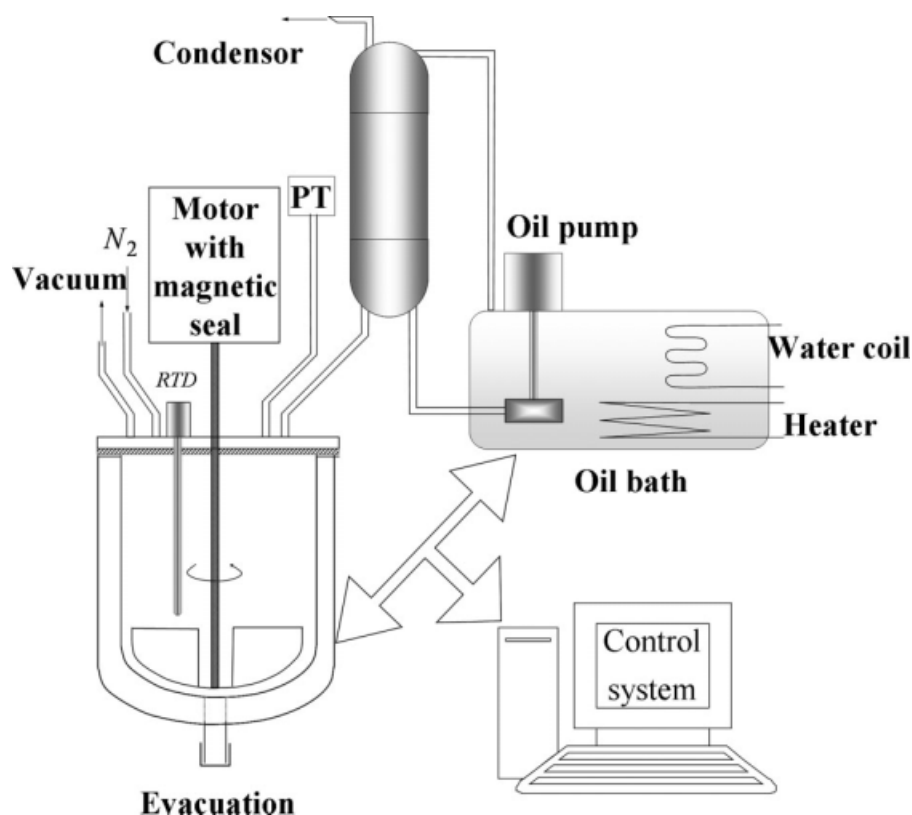


Figure 2 Schematic of the reactor. PT, pressure transducer; RTD, resistance temperature detector.

increased to 240°C and 4.5 atm, respectively, very rapidly. There was no nitrogen flow during the heating period. As soon as the temperature reached 240°C, nitrogen flow was initiated. The esterification step was performed until no more water was collected. The esterification step was continued for up to 3 h. The temperature was then raised to 280°C, and the pressure was reduced to 0.04 atm. Polycondensation was the predominant reaction in this step. EG, as a byproduct of the polycondensation reaction, was removed by a vacuum pump. This step was continued for 3–5 h. Finally, the pressure was adjusted to atmospheric pressure, and all the materials were evacuated by nitrogen pressure. This two-step melt polycondensation procedure is shown in Figure 3. The motivation for copolymerization was to produce an amorphous polyester. Hence, the

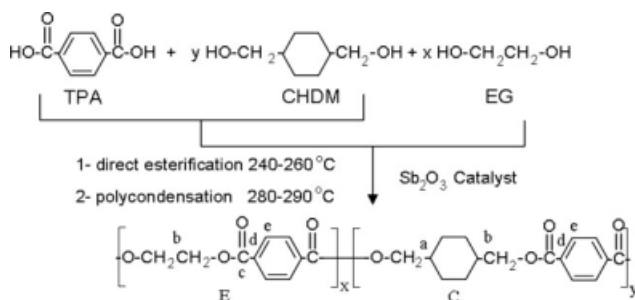


Figure 3 Different segments of the copolyester.

molar ratio of CHDM to EG was selected to be between 5 and 30%,^{16,17} and a higher ratio was beyond the scope of this research. A higher ratio could be an appropriate goal for further research. Figures 4 and 5 show typical temperature and pressure variations during the course of the reaction, respectively.

RESULTS AND DISCUSSION

The compositions of differently synthesized copolyesters, reaction times, and randomness degrees

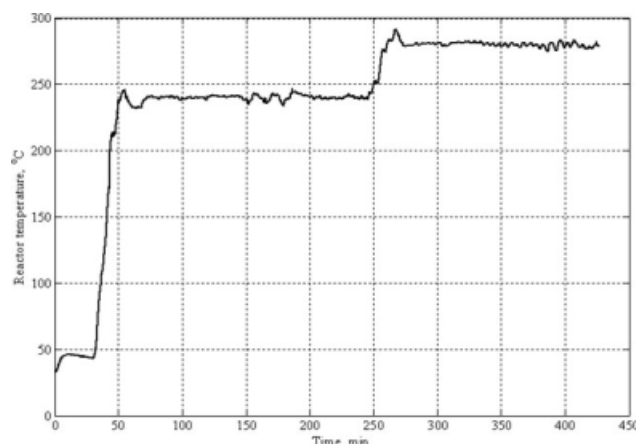


Figure 4 Reactor temperature during the copolymerization of PETC₅.

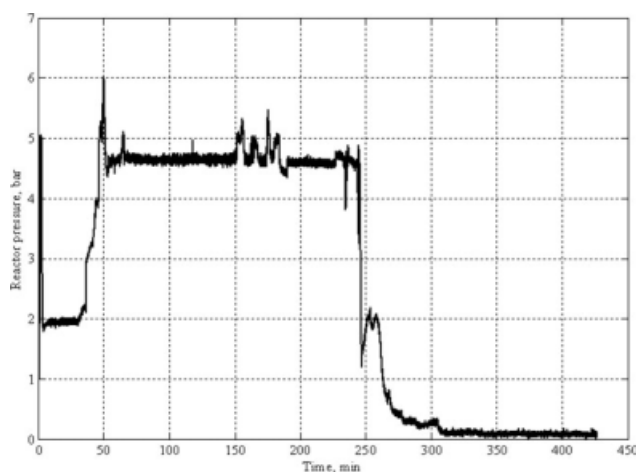


Figure 5 Pressure during the copolymerization of PETC₅.

based on NMR spectra and the intrinsic viscosities of the produced copolyesters are listed in Table II. Figure 6 shows the FTIR spectra of PET and PETC₅. There is good agreement between the spectra for all the copolyesters. The wide peak around 1100–1200 cm⁻¹ corresponds to the C–O bond in the ester group. The peak at 1715 cm⁻¹ corresponds to the C=O carbonyl group. The O–H bond of carboxylic acids shows a wide peak around 2400–3400 cm⁻¹. The O–H bond of alcoholic groups shows a wide peak around 3300–3400 cm⁻¹. These peaks overlap with the peak corresponding to the C–H bond: 2968 cm⁻¹ for aromatic C–H and 2907 cm⁻¹ for aliphatic C–H. The =CH bond shows a sharp peak at 725 cm⁻¹. Although the spectra of the copolyesters show some differences, it is not easy to draw any quantitative conclusions based on FTIR. Figures 7 and 8 show ¹H- and ¹³C-NMR spectra of the copolyesters, respectively. The percentage of the comonomer in the polymer chains was estimated, and it is given in Table II. As shown in Figure 7, the protons of the CH₂ group connected to cyclohexylene have two peaks: one at 4.17, which is related to the cis isomer, and one at 4.2, which is related to the trans isomer. Hence, the ratio of the cis isomer to the trans isomer for the CHDM comonomer in the polyester

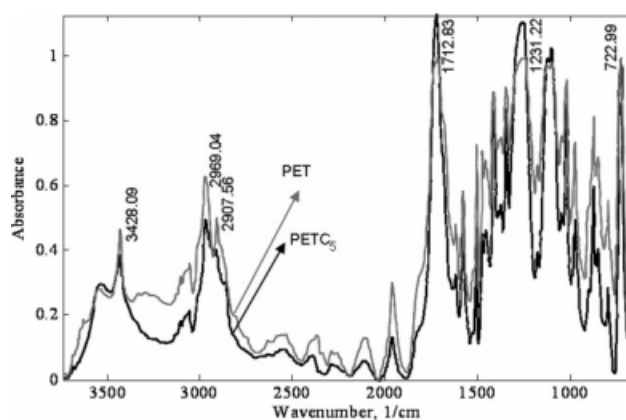


Figure 6 FTIR spectra of PET and PETC₅.

chain is given in Table II. The molar ratio of CHDM to EG in the polymer chains is higher than the ratio in the initial feed. Figure 9 shows the molar ratio of CHDM to EG in the copolymer chains and also in the initial feed. This event may be explained by the low vapor pressure of CHDM, which results in less evaporation of CHDM in comparison with EG at the reaction temperature; therefore, CHDM shows more reactivity. Figure 10 shows the ¹³C-NMR spectrum of PETC₃₀. From the ¹³C-NMR spectra of the copolyesters, the degree of randomness and mean length of the sequences could be estimated with the dyad sequence distribution. The carbon of the terephthalate group, which is labeled “d” in Figure 3, produces four signals related to ethylene terephthalate cyclohexylene dimethylene (ETC) at 133.987 ppm, cyclohexylene dimethylene terephthalate cyclohexylene dimethylene (CTC) at 133.776 ppm, ethylene terephthalate ethylene (ETE) at 133.384 ppm, and cyclohexylene dimethylene terephthalate ethylene (CTE) at 133.171 ppm (see Fig. 10). The areas under these four peaks, defined as f_{ETC} , f_{CTC} , f_{ETE} , and f_{CTE} , respectively, give the degree of randomness. To calculate the degree of randomness, the molar ratios of the ethylene terephthalate groups (P_E) and cyclohexylene dimethylene terephthalate groups (P_C) can be calculated with the following equations:

TABLE II
Compositions, Reaction Times, Randomness Degrees (Based on NMR), and Viscosities of the Copolyesters

Polyester	Feed composition ([CHDM]/[EG]) ^a	Copolymer composition ([CHDM]/[EG]) ^b	Total time (h)	Polycondensation time (h)	Intrinsic viscosity (dL/g) ^c	Randomness degree	Trans/cis
PET	0	0.0	6	2.42	0.279	0	—
PETC ₅	0.05	0.075	7.18	3	0.244	0.755	26.84/73.15
PETC ₁₅	0.15	0.25	8.55	4.33	0.336	0.983	28.57/71.43
PETC ₃₀	0.30	0.45	8.45	4.00	0.409	0.9963	29.01/70.99

^a Initial molar ratio.

^b Molar ratio in the copolyester determined by ¹H-NMR.

^c Measured in dichloroacetic acid.

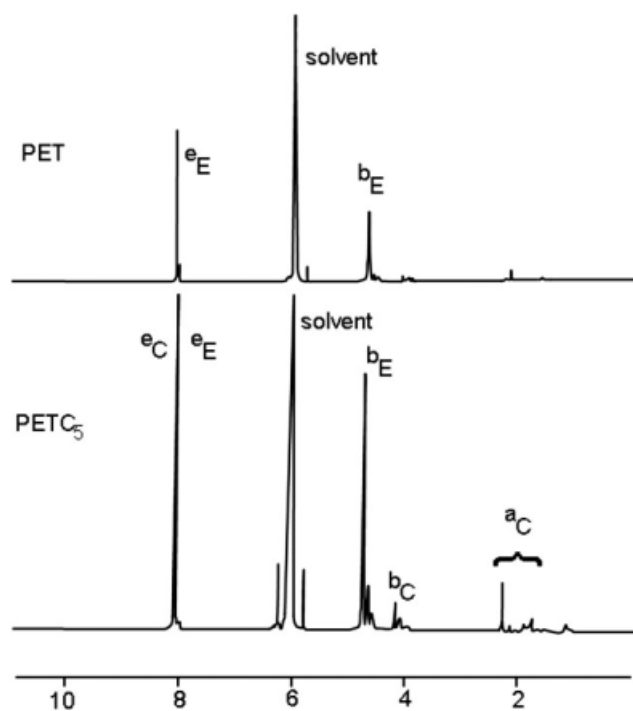


Figure 7 $^1\text{H-NMR}$ spectra of PET and PETC_5 .

$$P_E = \frac{f_{\text{ETC}} + f_{\text{CTE}}}{2} + f_{\text{ETE}}$$

$$P_C = \frac{f_{\text{ETC}} + f_{\text{CTE}}}{2} + f_{\text{CTC}}$$

If we could analyze one copolymer chain, the probability of finding one ethylene group next to one cyclohexylene group and the probability of finding one cyclohexylene group next to one ethylene group could be defined as P_{EC} and P_{CE} , respectively:

$$P_{\text{EC}} = \frac{f_{\text{ETC}} + f_{\text{CTE}}}{2P_E}$$

$$P_{\text{CE}} = \frac{f_{\text{ETC}} + f_{\text{CTE}}}{2P_C}$$

In the end, the degree of randomness is calculated as follows:

$$\text{Degree of randomness} = P_{\text{CE}} = P_{\text{EC}}$$

Whenever the value is close to 1.0, more random copolyester is obtained. The curve of the dyad sequence versus the moles of 1,4-cyclohexane dimethylene terephthalate (CT) is presented in Figure 11.

The thermal behavior of the copolyesters was studied with DSC. Figure 12 shows the heating and cooling curves for the determination of the crystallization temperature (T_c), T_g , T_m , and heat of fusion. Table III shows the results obtained from the DSC

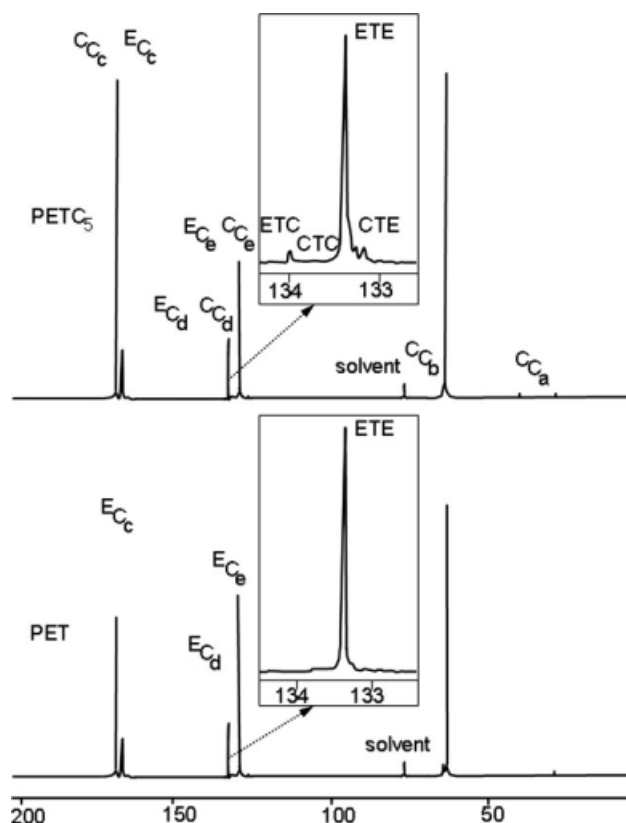


Figure 8 $^{13}\text{C-NMR}$ spectra of PET and PETC_5 .

traces. T_g increases with an increase in the amount of the comonomer. The rigidity of the cyclohexane unit (compared with EG) in the polymer chain could explain the increase in T_g . The increase in T_g is one of the desirable effects of a comonomer on the properties of PET. T_m , T_c , and the heat of fusion decrease with an increase in the amount of the comonomer.

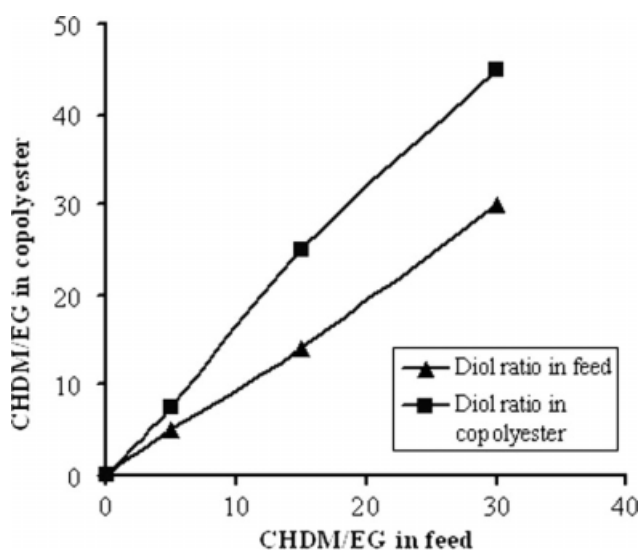


Figure 9 CHDM/EG percentage in the copolyester chain versus the CHDM/EG percentage in the feed: (■) diol ratio in the copolyester chain and (▲) diol ratio in the feed.

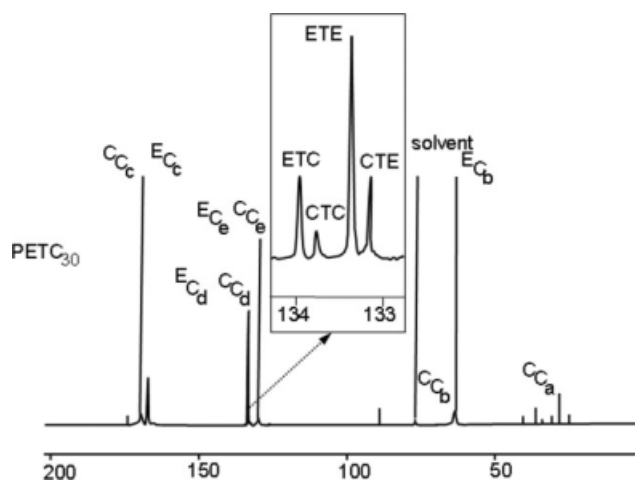


Figure 10 ^{13}C -NMR spectrum of PETC_{30} .

Accordingly, PETC_{30} is completely amorphous. This may be explained by the increase in the randomness of the polymer chains, so the comonomer units prevent the formation of crystals of isomorphous PET units. Moreover, the polymer chain will be less flexible because of the presence of rigid cyclohexane units in the chain.

PROCESS MODELING

Modeling the process gives us a better understanding of its features. The modeling of PET synthesis in continuous and semicontinuous reactors has been studied by various researchers. Ravindranath and Mashelkar²¹⁻²⁴ reviewed different aspects of the

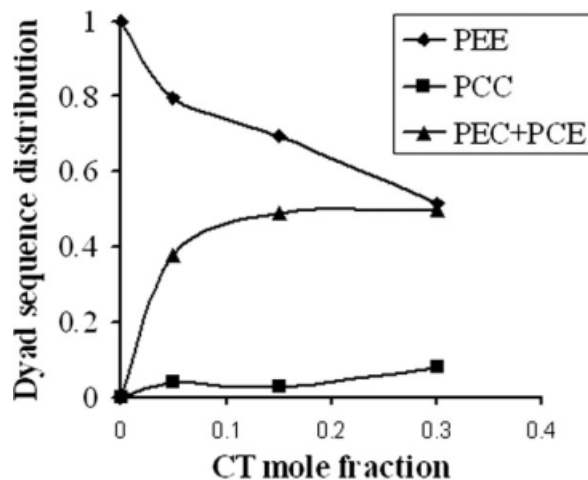


Figure 11 Experimental dyad sequence distribution.

mechanism and kinetics of PET synthesis, and they have published some research articles. They modeled a semicontinuous ester exchange reactor for PET via dimethylene terephthalate. Zinc acetate was used as the catalyst in their research. Their results were qualitatively acceptable.²¹ Then, they presented a mathematical model for a continuous transesterification reactor.²² They used models for investigating the effects of process and plant parameters on the byproducts. These parameters were the temperature and its profile, the residence time, and the number of reactors. Ravindranath and Mashelkar also presented a mathematical model for a continuous direct esterification process.²³ They studied the effects of the temperature distribution, residence

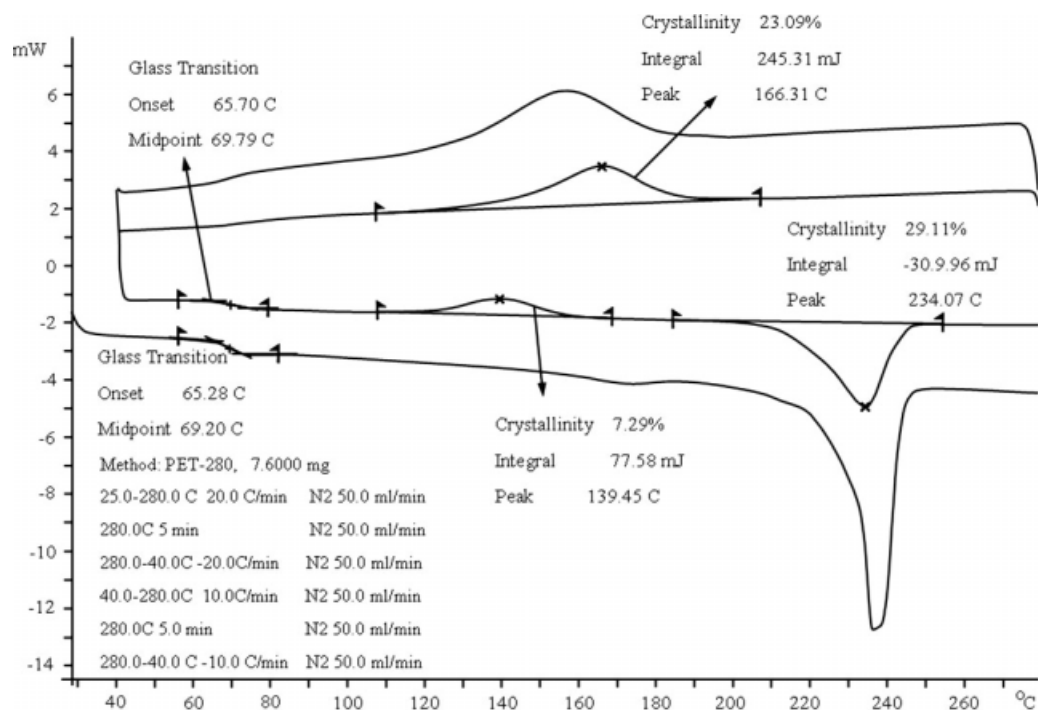


Figure 12 DSC trace of PETC_5 .

TABLE III
Thermal Behavior of the Copolyesters Based on DSC

Copolyester	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PET	74.24	247.29	48.187	187.42	-53.1
PETC ₅	69.79	234.07	40.78	139.45	-10.21
PETC ₁₅	72.97	212.36	9.187	164.93	-6.92
PETC ₃₀	75.24	— ^a	— ^a	— ^a	— ^a

^a Not observed. ΔH_m and ΔH_c are heat of fusion and crystallization, respectively.

time distribution, recycling of bishydroxyl ethyl terephthalate, pressure, and EG/TPA ratio on the reactor performance. They did not compare simulation results with any experimental data. However, their results were qualitatively acceptable. Then, they modeled the final stage of a continuous polycondensation reactor.²⁴ In their final article, they presented a model for the molecular weight distribution of PET products. They introduced all possible reactions in this model. By using the moment concept, they gave the theoretical result for the molecular weight distribution. Reimschuessel et al.²⁵ presented kinetic parameters for the reaction of hydroxyl groups and carboxylic acid groups by studying the equilibrium reaction between benzoic acid and EG, ethane diol monobenzoate, and water in the presence of anti-

mony as the catalyst. Then, Reimschuessel²⁶ studied whether data from the previous article were valid for PET. His results showed that the functional groups are important in condensation reactions. Kang et al.²⁷ modeled a direct esterification reaction for PET synthesis in a semibatch reactor; Rafizadeh et al.²⁸ presented a model for esterification and polycondensation steps. In this research, reactions among functional groups were studied for modeling PET synthesis. Different segments present in the reaction media are listed in Table IV. Table V lists the reactions considered for the presented model. In this table, k_i ($i = 1-13$) denotes the effective reaction rate constant, and K_i ($i = 1-10$) is the equilibrium constant. Reactions (1)–(8) are esterification reactions, and reactions (9) and (10) are polycondensation

TABLE IV
Molecular Structures of Different Segments

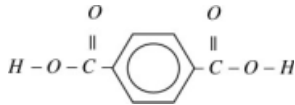
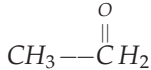
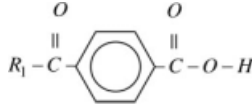
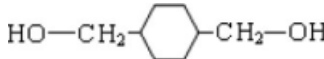


Molecule/functional group	Symbol	Molecular structure
Ethylene glycol	EG	HO—CH ₂ —CH ₂ —OH
Terephthalic acid	TPA	
Acetaldehyde	AA	
Water	W	H ₂ O
EG end group	tEG	R ₁ —O—CH ₂ —CH ₂ —OH
EG repeat unit	bEG	R ₁ —O—CH ₂ —CH ₂ —O—R ₂
TPA end group	tTPA	
DEG repeat unit	bDEG	R ₁ —O—CH ₂ —CH ₂ —O—CH ₂ —CH ₂ —O—R ₂
Cyclohexane dimethanol	CHDM	
Cyclohexylene dimethylene end group	tCHDM	R ₁ —O—CH ₂ —  —CH ₂ —OH
Cyclohexylene dimethylene repeat unit	bCHDM	R ₁ —O—CH ₂ —  —CH ₂ —O—R ₂

TABLE V
Reactions Included in the Model

Number	Reaction	k_i^r, k_i
1	EG + tTPA \rightleftharpoons tEG + W	$k_1/K_1, k_1$
2	CHDM + tTPA \rightleftharpoons tCHDM + W	$k_2/K_2, k_2$
3	EG + TPA \rightleftharpoons tEG + W	$k_3/K_3, k_3$
4	CHDM + TPA \rightleftharpoons tCHDM + W	$k_4/K_4, k_4$
5	tEG + tTPA \rightleftharpoons bEG + W	$k_5/K_5, k_5$
6	tCHDM + tTPA \rightleftharpoons bCHDM + W	$k_6/K_6, k_6$
7	tEG + TPA \rightleftharpoons bEG + W	$k_7/K_7, k_7$
8	tCHDM + TPA \rightleftharpoons bCHDM + W	$k_8/K_8, k_8$
9	2tEG \rightleftharpoons bEG + EG	$k_9/K_9, k_9$
10	2tCHDM \rightleftharpoons bCHDM + CHDM	$k_{10}/K_{10}, k_{10}$
11	tEG \rightarrow tTPA + AA	k_{11}
12	tEG + EG \rightarrow tTPA + DEG	k_{12}
13	2tEG \rightarrow tTPA + tDEG	k_{13}

reactions. Side reactions are shown in reactions (11)–(13), which produce AA and DEG. AA and DEG have more effects on polymer properties than other byproducts. Some researchers^{3,26} believe that DEG is produced in esterification and in the beginning stage of the polycondensation step and that AA, acid end groups, and vinyl end groups are produced at the end of polycondensation. Water and EG are removed in the esterification and polycondensation steps, respectively. It has been assumed that the mechanism of transfer function is film diffusion:

$$\text{Water flow rate} = AK_G[W] \quad (1)$$

$$\text{Ethylene glycol flow rate} = AK_G[EG] \quad (2)$$

where A is the effective mass transfer area, K_G is the overall mass transfer coefficient, and $[W]$ is the concentration of water. EG is returned to the reactor during the esterification step by means of the condenser.

Mass balances of various species were written for the semicontinuous reactor:

$$\frac{1}{m} \cdot \frac{d(m.[\text{tTPA}])}{dt} = -R_1 - R_2 - R_5 - R_6 + R_{11} + R_{12} + R_{13} \quad (3)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{tEG}])}{dt} = R_1 + R_3 - R_5 - R_7 - 2R_9 - R_{11} - R_{12} - 2R_{13} \quad (4)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{bEG}])}{dt} = R_5 + R_7 + R_9 \quad (5)$$

$$\frac{1}{m} \cdot \frac{d(m.[W])}{dt} = R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7 + R_8 - \dot{m}_W(t) \quad (6)$$

$$\frac{1}{m} \cdot \frac{d(m.[EG])}{dt} = -R_1 - R_3 + R_9 - R_{12} - \dot{m}_{EG}(t) \quad (7)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{tDEG}])}{dt} = R_{12} + R_{13} \quad (8)$$

$$\frac{1}{m} \cdot \frac{d(m.[AA])}{dt} = R_{11} - \dot{m}_{AA}(t) \quad (9)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{TPA}])}{dt} = -R_3 - R_4 - R_7 - R_8 \quad (10)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{tCHDM}])}{dt} = R_2 + R_4 - R_6 - R_8 - 2R_{10} \quad (11)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{bCHDM}])}{dt} = R_6 + R_8 + R_{10} \quad (12)$$

$$\frac{1}{m} \cdot \frac{d(m.[\text{CHDM}])}{dt} = -R_2 - R_4 + R_{10} \quad (13)$$

where tTPA is the TPA end group, tEG is the EG end group, bEG is the EG repeat unit, tDEG is the DEG end group, tCHDM is the cyclohexylene dimethylene end group, and bCHDM is the cyclohexylene dimethylene repeat unit. m is the mass of the reactive mixture, m_{AA} is the mass of AA, m_W is the mass of water, and m_{EG} is the mass of EG. R_i ($i = 1$ –13) is the reaction rate:

$$R_1 = r_1 - r_1^r = 2k_1[\text{tTPA}][\text{EG}] - k_1^r[\text{tEG}][W] \quad (14)$$

$$R_2 = r_2 - r_2^r = 2k_2[\text{tTPA}][\text{CHDM}] - k_2^r[\text{tCHDM}][W] \quad (15)$$

$$R_3 = r_3 - r_3^r = 4k_3[\text{TPA}][\text{EG}] - k_3^r[\text{tEG}][W] \quad (16)$$

$$R_4 = r_4 - r_4^r = 4k_4[\text{TPA}][\text{CHDM}] - k_4^r[\text{tCHDM}][W] \quad (17)$$

$$R_5 = r_5 - r_5^r = k_5[\text{tTPA}][\text{tEG}] - 2k_5^r[\text{bEG}][W] \quad (18)$$

$$R_6 = r_6 - r_6^r = k_6[\text{tTPA}][\text{tCHDM}] - 2k_6^r[\text{bCHDM}][W] \quad (19)$$

$$R_7 = r_7 - r_7^r = 2k_7[\text{TPA}][\text{tEG}] - 2k_7^r[\text{bEG}][W] \quad (20)$$

$$R_8 = r_8 - r_8^r = 2k_8[\text{TPA}][\text{tCHDM}] - 2k_8^r[\text{bCHDM}][W] \quad (21)$$

$$R_9 = r_9 - r_9^r = k_9[\text{tEG}]^2 - 4k_9^r[\text{bEG}][\text{EG}] \quad (22)$$

$$R_{10} = r_{10} - r_{10}^r = k_{10}[\text{tCHDM}]^2 - 4k_{10}^r[\text{bCHDM}][\text{CHDM}] \quad (23)$$

where r_i and r_i^r are forward and backward rate of i^{th} reaction in Table V with regarding k_i and k_i^r as rate constants, respectively.

TABLE VI
Molecular Weights of the Species

	Component					
	tTPA	tEG	bEG	W	EG	tDEG
Molecular weight	209	209	356	18	62	106
	Component					
	AA	TPA	tCHDM	bCHDM	CHDM	
Molecular weight	45	166.1	291	418	144.2	

$$R_{11} = r_{11} = k_{11}[\text{tEG}] \quad (24)$$

$$R_{12} = r_{12} = 2k_{12}[\text{tEG}][\text{EG}] \quad (25)$$

$$R_{13} = r_{13} = k_{13}[\text{tEG}]^2 \quad (26)$$

where [TPA] is the concentration of dissolved TPA in the reactive mixture. It should be mentioned that

TPA is partially soluble in EG and in PET oligomers. It is assumed that EG is saturated with TPA during the paste mixing step; therefore, the terephthalic concentration remains constant as long as there is enough TPA to saturate the reactive mixture ($[\text{TPA}]_{\text{sat}}$). The following solubility formula is applied:²²

$$\log[\text{TPA}]_{\text{sat}} (\text{mol/kg of EG}) = 4.6503 - (2475/T) \quad (27)$$

where T is the temperature. As the reaction progresses, m increases because of the increases in the amounts of bis(2-hydroxyethyl terephthalate) (BHET) and PET oligomers and the increases in the solubility of EG, TPA, BHET, and PET oligomers in one another. The solubility of TPA in BHET is defined as follows:

$$[\text{TPA}]_{\text{sat}} (\text{mol/kg of EG}) = \exp(1.9 - (1420/T)) \quad (28)$$

Mass changes (m_i) during a reaction are computed as follows:

$$\frac{dm}{dt} = \frac{dm_{\text{TPA}_{\text{sat}}} + dm_{\text{w}} + dm_{\text{EG}} + dm_{\text{CHDM}} + dm_{\text{tEG}} + dm_{\text{AA}} + dm_{\text{bEG}} + dm_{\text{tDEG}} + dm_{\text{tCHDM}} + dm_{\text{bCHDM}}}{dt} \quad (29)$$

The molecular weights of species are reported in Table VI. Table VII presents the kinetic parameters that are used in this model.²⁵ All rates and rate constants are per kilogram; details of the kinetic parameter calculations via nonlinear regression have been reported elsewhere.²⁵ Table VIII gives the values of A and K_G . The reactor is a cylinder tank type, so mass transfer occurs via the upper interface, which can be assumed to be constant. Reaction rates are the Arrhenius type:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (30)$$

where A_i is constant, E_i is activation energy, and R

is global gas constant. Furthermore, the rate constants are functions of acid end groups, antimony, and their interactions:

$$k_i = k_i^0 + k_i^c[\text{tTPA}] \quad (31)$$

$$k_9 = k_9^0 + k_9^c[\text{tTPA}] + k_9^m[\text{Sb}] + k_9^{cm}[\text{tTPA}][\text{Sb}] \quad (32)$$

In these equations, the superscripts 0, c , m , and cm denote constants for the uncatalyzed reaction (0), reactions catalyzed by carboxyl groups (c), reaction catalyzed by the metal catalyst (m), and reactions entailing interactions between the carboxyl groups and the antimony catalyst (cm).

TABLE VII
Kinetic Parameters

k_i	A_i	E_i (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)
k_1^0 (kg mol ⁻¹ min ⁻¹)	2.55×10^{-5}	0		
k_1^c (kg mol ⁻¹ min ⁻¹)	8.672×10^5	86.647		
k_5^0 (kg mol ⁻¹ min ⁻¹)	8.426×10^8	124.782		
k_5^c (kg mol ⁻¹ min ⁻¹)	7.564×10^1	43.302		
k_9^0 (kg mol ⁻¹ min ⁻¹)	5.038×10^{17}	206.472		
k_9^c (kg mol ⁻¹ min ⁻¹)	3.325×10^6	91.812		
k_9^m (kg mol ⁻¹ min ⁻¹)	4.071×10^{14}	115.92		
k_9^{cm} (kg mol ⁻² min ⁻²)	3.6×10^2	0		
k_{11} (min ⁻¹)	1.04×10^8	125		
k_{12} (kg mol ⁻¹ min ⁻¹)	1.04×10^5	125		
k_{13} (kg mol ⁻¹ min ⁻¹)	1.04×10^5	125		
K_5			-45.1	-23.7
K_9			-80.3	-38.1

ΔH and ΔS are enthalpy and entropy of reaction.

TABLE VIII
A and K_G

A	$7.85 \times 10^{-3} \text{ m}^2$
K_G for water transfer	$3.185 \times 1/\text{min m}^2$
K_G for EG transfer	$127.388 \times 1/\text{min m}^2$

Polymer chains consist of bEG, bCHDM, and their end groups; therefore, the degree of polymerization could be estimated:

$$\text{Number of chains} = \frac{[t\text{TPA}] + [t\text{EG}] + [t\text{CHDM}]}{2}$$

$$\bar{P}_n = \frac{[b\text{EG}] + [b\text{CHDM}]}{\text{Number of chains}} \quad (33)$$

Finally, a set of initial nonlinear ordinary equations was obtained. This set could be integrated by different approaches; the Runge–Kutta fourth-order method was applied to obtain a solution for these equations. Figure 13 shows the flow chart of the solution.

Modeling results and discussion

The modeling results are shown in Figures 14–18. These results correspond to esterification at 240°C, polycondensation at 280°C, a hydroxyl group/acid

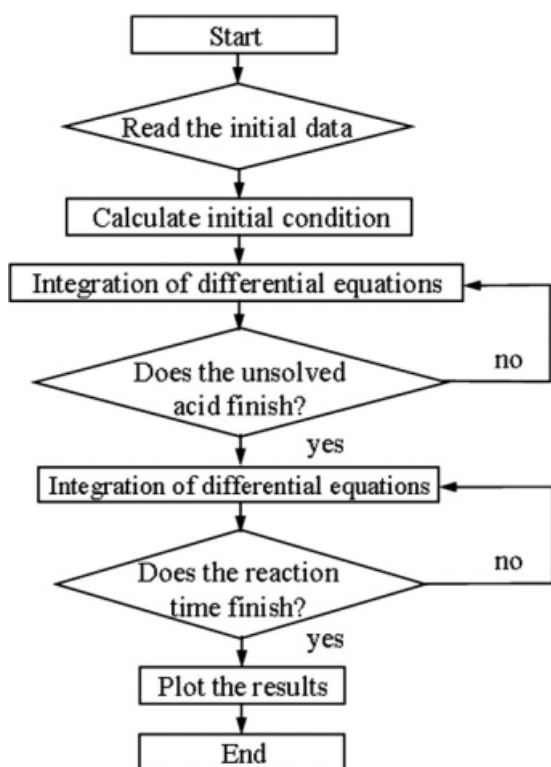


Figure 13 Flow chart of the solution to the model.

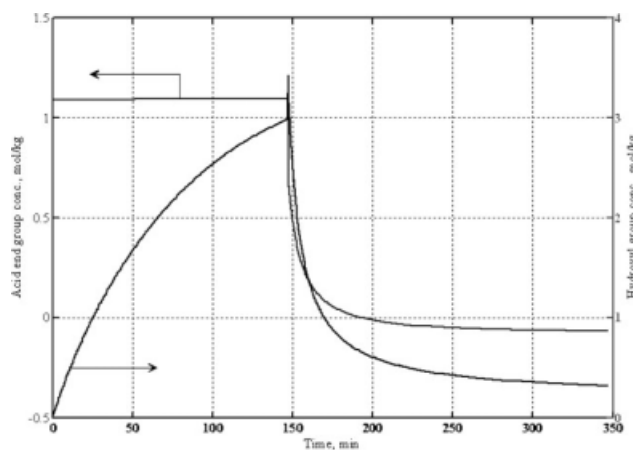


Figure 14 Concentration of carboxyl and hydroxyl end groups (feed ratio = 1.3, temperature = 240°C).

group ratio of 1.3, and a 5% concentration of the comonomer. Figure 18 presents a comparison of the experimental and simulation results for the amount of collected water. In the simulation, reactions among functional groups were considered. This figure shows that there is no important difference between the measured data. There is good agreement between the simulation and experimental data.

The model could be used to study the effects of the temperature and diol molar ratio in the feed on DEG and the conversion of acid end groups. Figure 19 shows the effect of temperature on the formation of DEG. There is a decrease in the amount of DEG with an increase in the temperature; however, the rate of DEG production is increased with an increase in temperature. Figure 20 shows the conversion of acid end groups during the reaction. With an increase in temperature, the conversion rate increases. Nevertheless, it does not reach 1 because

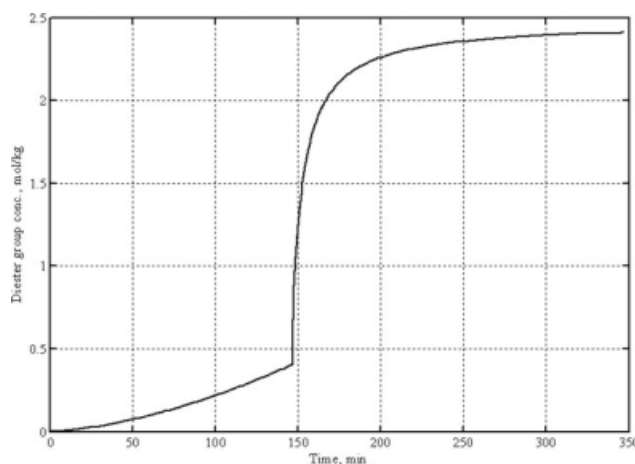


Figure 15 Concentration of ester groups (feed ratio = 1.3, temperature = 240°C).

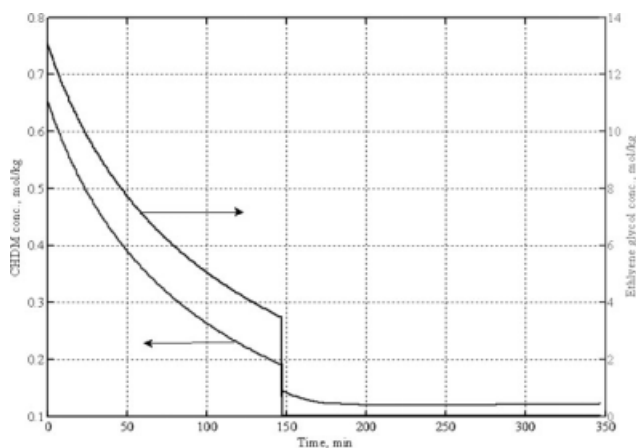


Figure 16 Concentration of CHDM and EG (feed ratio = 1.3, temperature = 240°C).

of the equilibrium nature of the reaction. Figures 21 and 22 show the effect of the diol group/acid group ratio on DEG formation and conversion. On the basis of Figure 21, the rate and amount of DEG formation increase with the diol group/acid group ratio because the probability of etherification increases. Figure 22 shows that the conversion of acid groups increases with the diol group/acid group ratio because of an increase in the solubility of TPA in EG.

CONCLUSIONS

The synthesis of PET copolymers with CHDM via two-step melt polycondensation was studied. Copolymers were produced in a house-made, laboratory-scale research reactor. The intrinsic viscosity of the copolymers was around 0.24 and increased with the

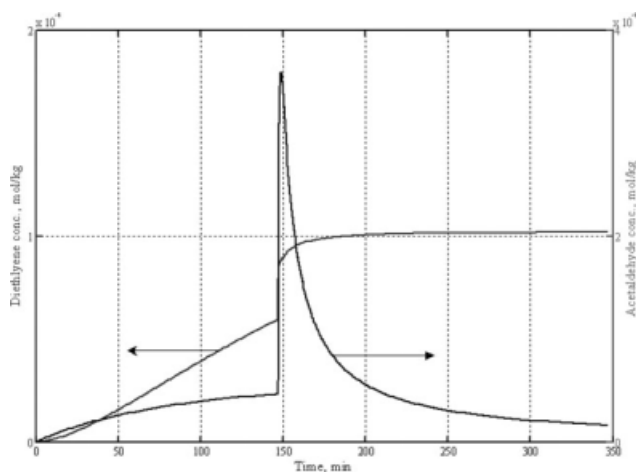


Figure 17 Concentration of the byproducts (DEG and AA) of the reaction (feed ratio = 1.3, temperature = 240°C).

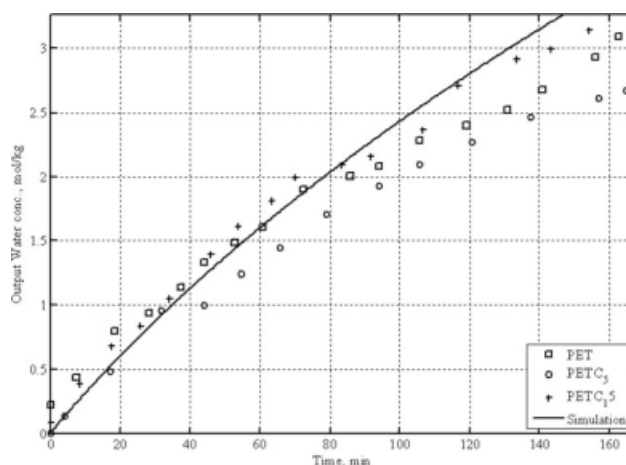


Figure 18 Experimental and modeling results for the produced water (feed ratio = 1.3, temperature = 240°C).

polycondensation time. The FTIR spectra of the products showed peaks for carbonyl and carboxyl bonds, as expected. The amount of cyclohexylene in the polymer chain was determined from $^1\text{H-NMR}$ spectra. It was determined that the amount of CHDM in the polymer chain was greater than the amount of CHDM in the feed. Hence, CHDM has a greater tendency to participate in the reaction in comparison with EG. $^{13}\text{C-NMR}$ spectra, based on the dyad sequence distribution, showed that the copolymers were randomly distributed. The DSC curves of the products showed that the heat of fusion decreased with an increase in CHDM; hence, the melting point of the products decreased. A copolymer with more than 15% CHDM was basically amorphous. T_g of the copolymers increased with an increase in CHDM because of a decrease in the chain mobility. Moreover, modeling of the process was studied by the derivation of mass balances of

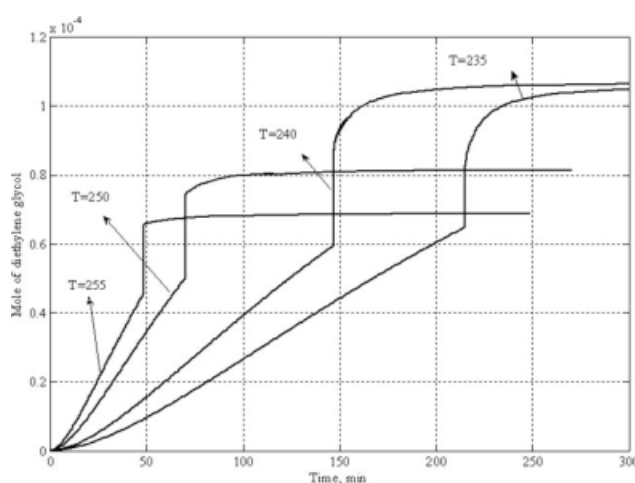


Figure 19 Effect of the reaction temperature on the formation of DEG (feed ratio = 1.3).

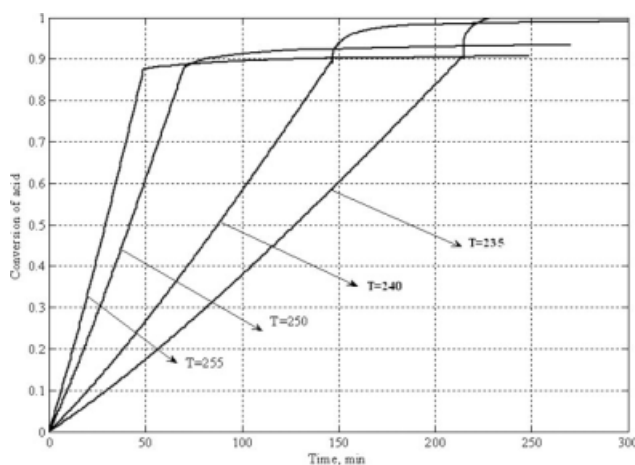


Figure 20 Effect of the reaction temperature on the conversion of the acid end groups (feed ratio = 1.3).

different species in a semibatch reactor. In the modeling, the reactions between functional groups were considered. The water produced was used to validate the model. The experimental and simulation results for the amounts of water produced showed very good agreement. With the process model, the effects of important parameters such as the ratio of EG to TPA and temperature were studied. With an increase in the EG-to-TPA ratio, the acid conversion and DEG production increased, and this could be due to the presence of more EG in the reaction mixture; therefore, more etherification occurred, and more TPA dissolved in the reaction mixture. With an increase in the temperature of the reaction, the reaction rate increased; nevertheless, this temperature increase reduced the conversion rate, and this could be explained by the increase in the number of reverse reactions.

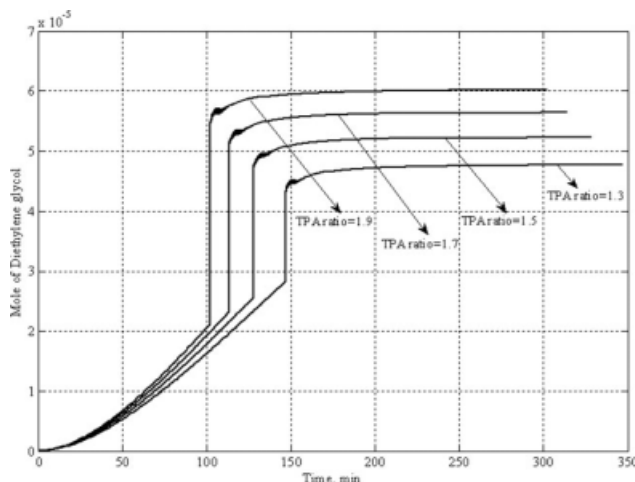


Figure 21 Effect of the monomer feed ratio on the formation of DEG (temperature = 240°C).

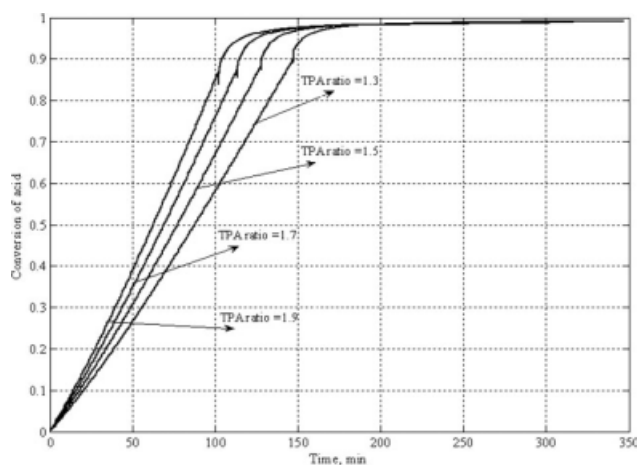


Figure 22 Effect of the monomer feed ratio on the conversion of the acid end groups (temperature = 240°C).

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