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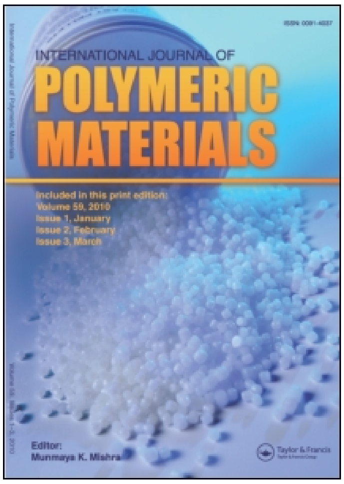

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
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To cite this Article Patel, Hemant S. and Patel, Keshav C.(2007) 'Synthesis and Characterization of Linear Homopolyesters Containing s-Triazine Rings', International Journal of Polymeric Materials, 56: 2, 93 — 105

To link to this Article: DOI: 10.1080/00914030600735130

URL: http://dx.doi.org/10.1080/00914030600735130

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International Journal of Polymeric Materials, 56:93–105, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600735130

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Synthesis and Characterization of Linear Homopolyesters Containing s-Triazine Rings

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Eight homopolyesters were synthesized by high temperature polycondensation of 2-(N-1-naphthylamine)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine [NANCCT] with each of the eight diols: Bisphenol-A(BPA), bisphenol-C(BPC), phenolphthalein(ph), resorcinol(R), hydroquinone(Hq), catechol(C), 1,5-dihydroxy naphthalene (1, 5-DHN), and ethylene glycol (EG). All the polyesters were characterized by solubility, density, viscosity measurements, IR spectra, NMR spectroscopy, and thermogravimetric analysis.

Keywords: characterization, polyesters, synthesis, triazine

INTRODUCTION

Great attention has recently been paid to synthesize high-performance polymers with increased thermal stability and heat resistance with good mechanical properties, as they are required in modern technological applications [1–2]. Extensive literature exists on thermally stable polymers in which aromatic and heteroaromatic rings are linked together in the main chain [3–4]. Due to increased demand of polymers with high performance characteristics in various fields including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers is growing steadily. However, these polymers are generally intractable and lack the properties essential

Received 27 March 2006; in final form 4 April 2006.

The authors express their sincere gratitude to the Head of the Department of Chemistry, Veer Narmad South Gujarat University, Surat for providing necessary research facilities.

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for successful fabrication into useful forms. These inherent problems have been tackled by many researchers over the last few decades by modifying the monomer structures [5–7]. As an approach to improve the processibility of heterocyclic polymers while maintaining the thermal stability, a number of published reports have described the synthesis and properties of s-triazine ring containing polymers, that is, polycyanurates, such as polyesters [8], polyamides [9], polyureas [10], polyimides [11], and so on. Polycyanurates are unique in the sense that they exhibit unusual combination of properties such as high softening temperature and thermal stability along with solubility, which are favorable properties to be considered as a useful high-performance engineering material [12–14]. In the class of polycyanurates, there are many reports describing the synthesis of polyesters and copolyesters by polycondensation of diacid chloride with diols [15–20]. The linear polyesters of high molecular weight afford synthetic fibres of excellent properties [21]. The presence of s-triazine ring in the main chain may alter the properties of polymers to great extent. Hence it was interesting to synthesize and characterize polyesters containing an s-triazine moiety.

The present paper describes the synthesis and characterization of linear homopolyesters froms 2-(N-l-naphthylamine)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine [NANCCT] and various diols such as bisphenol-A, bisphenol-C, catechol, ethylene glycol, and 1,5-DHN using high temperature polycondensation technique.

Materials

Cyanuric chloride (Fluka, m.p. l46°C) was purified by recrystallization from pure benzene. BPA (Resin grade, Cibatul, m.p.156°C) was repeatedly crystallized from 50% aqueous acetic acid and finally recrystallized from benzene. Phenolphthalein (BDH, m.p. 262°C) was purified by crystallization from ethanol. Resorcinol, catechol, and hydroquinone (Sisco lab) were purified by recrystallization from rectified spirit and 1,5-dihydroxy naphthalene (Sisco lab) was purified by recrystallization from aqueous alcohol. Ethylene glycol of better purity (Merck) was used as received.

EXPERIMENTAL

Material Synthesis

Bisphenol-C (BPC) was synthesized following a published procedure [22] and was crystallized from benzene (m.p. 187°C).

SYNTHESIS OF MONOMER [NANCCT]

The monomer 2-(N-1-naphthylamine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine (NANCCT) was synthesized as per the reaction scheme shown in Figure 1 by a method suggested by Dudely et al. [23].

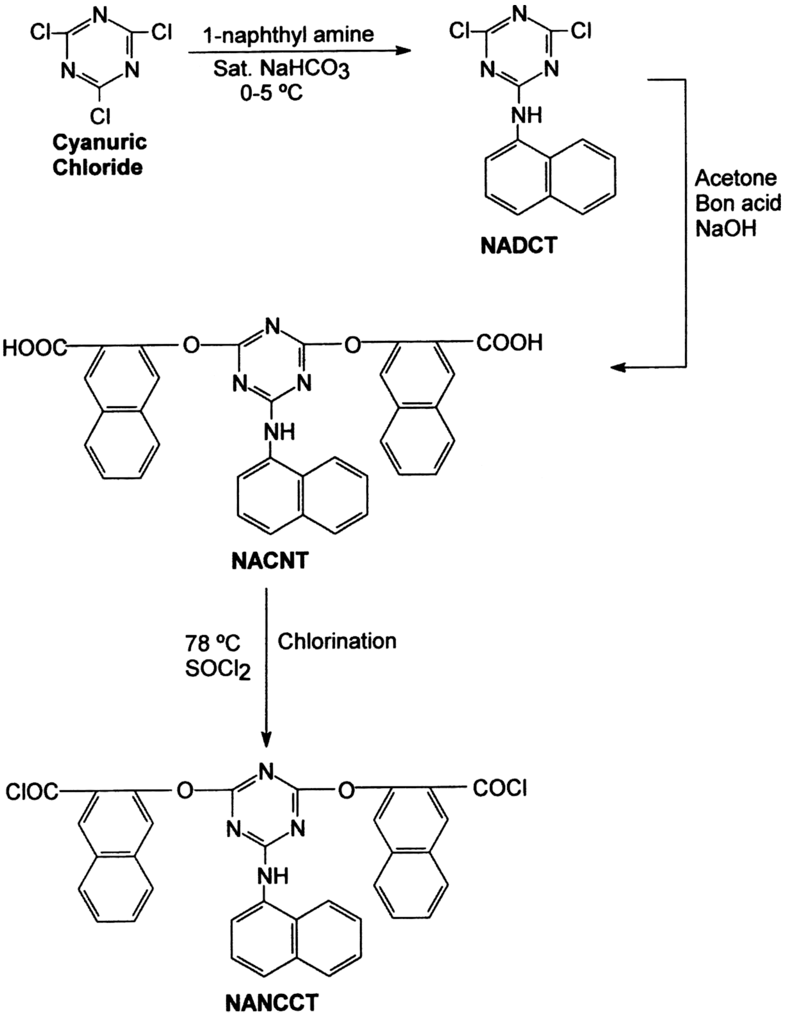

FIGURE 1 Reaction scheme for synthesis of monomer2-(N-α-naphthylamine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine [NANCCT].

[I] 2-(N-1-naphthylamine)-4, 6-dichloro-s-trazine [NADCT]

A solution of cyanuric chloride (18.44 g, 0.1 mol) in 60 ml acetone was added with stirring to a cold solution (0.5°C) of sodium bicarbonate (9.4 g, 0.1 mol) in 100 ml distilled water, in a three-necked flask (250 ml), equipped with a mechanical stirrer. This resulted in the formation of slurry of cyanuric chloride. A solution of 1-naphthylamine (14.3 ml, 0.1 mol) in 10 ml acetone was added to the cold slurry of cyanuric chloride. This reaction mixture was stirred for 2 h at 0–5°C. A light purple colored product was filtered and dried in a vacuum desiccator. The yield was 80% and m.p. 142°C.

[II] 2-(N-1-naphthylamine)-4,6-bis(2-carboxynaphthoxy)-s-triazine [NACNT]

A solution of 2-(N-1-naphthylamine)-4,6-bis dichloro-s-triazine (29.0 g, 0.1 mol) in 40 ml of acetone, a mixture of NaOH (16.0 g, 0.4 mol) and 3-hydroxy-2-naphtoic Acid (bon acid) (37.6 g, 0.2 mol) in 80 ml double distilled water, was added slowly at room temperature in a solution of NADCT with constant stirring. Reaction was continued for 4 h: First 2 h at room temperature and the rest at 80°C.

At the end of the reaction the green solid separated from the reaction mixture was filtered and suspended in acidified water. Finally it was filtered and washed several times with hot water and dried in vacuum at 100°C. The product was recrystallized from rectified spirit. The yield was about 80% and m.p. 210°C.

[III] 2-(N-1-naphthylamine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine [NANCCT]

2-(N-1-naphthyl amine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine (NACNT) (59.4 g 0.1 mol) and a molar excess of thionyl chloride were refluxed for 2 h at 78°C. At the end of the reaction the excess thionyl chloride was distilled off and the dry product was recovered. The residue obtained was taken up in hot benzene, heated with decolorizing carbon, filtered, and then cooled. The yield was about 80%, m.p. 178°C.

SYNTHESIS OF HOMOPOLYESTERS

The polymerization by high temperature polycondensation technique to synthesize polyesters, in Figure 2, is exemplified as follows:

A mixture of 2-(N-1-naphthyl amine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine (NANCCT) (6.62 g, 0.01 mol) in minimum quantity of DMF (~10 ml) was heated to about 150°C. Cetrimide (0.25 g) and

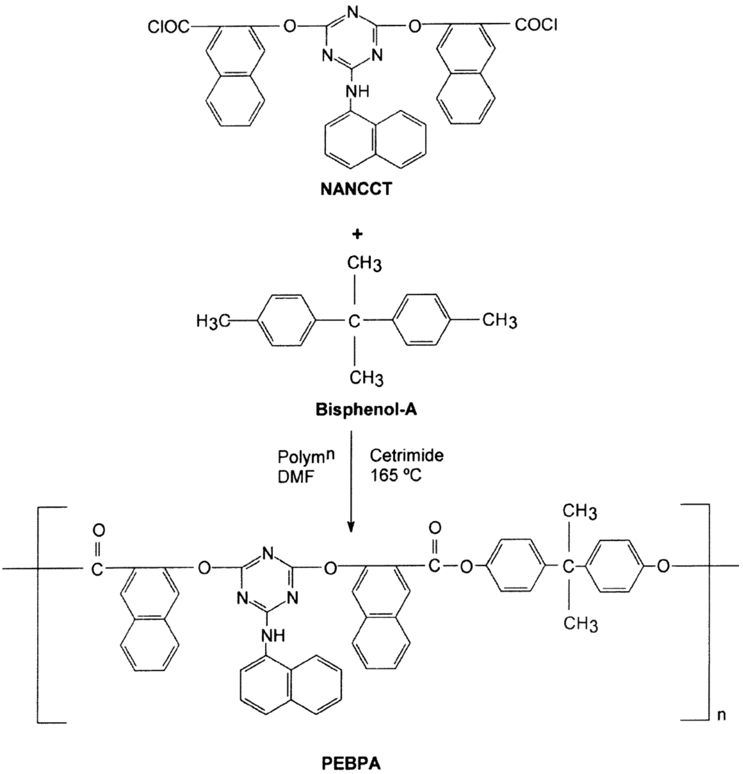

FIGURE 2 Reaction scheme for synthesis of polyester from NANCCT and Bisphenol-A.

then bisphenol-A (4.56 g, 0.02 mol) were added. The reaction temperature was raised to 165°C and kept there for 8 h. The reaction mixture was cooled and poured with constant stirring into 250 ml of ice cold water. The solid product was filtered, washed with hot water and finally with methanol to remove unreacted monomer, and dried; the yield was about 78%.

The other polyesters from NANCCT and various diols, such as bisphenol-C (BPC), phenolphthalein (Ph), Resorcinol (R), hydroquinone (Hq), Catechol (C), ethylene glycol (EG) and 1,5-DHN, were synthesized by the same method as shown earlier.

MEASUREMENTS

FTIR spectra of all the polyesters were recorded on Perkin Elmer FTIR Paragon 1000 SPIR S. No. 42825 using KBr pellet technique.

The thermograms were obtained on a thermobalance Metller TA-4000 system at a heating rate 10°C/min. The NMR spectra were recorded on a Perkin-Elmer Model-32 ^{1}H NMR spectrometer (300 MHz). Reduced viscosities of polyesters were determined for 1 gm/dl solution in DMF using an Ubbelohde suspended level viscometer.

RESULTS AND DISCUSSION

High temperature polycondensation of NANCCT with bisphenol-A has been investigated in detail to examine the effect of variables such as the nature of organic solvent, reaction time, and temperature. The remaining variables, such as concentration of reactants, their ratio, rate of stirring, and initiator used, were maintained nearly constant for all the experiments. The quantity and quality of the polyester of NANCCT and BPA obtained at various temperatures are presented in Table 1. Using these data, suitable reaction conditions have been selected for the synthesis of all polyesters of aromatic diols. The reduced viscosity of the polymer solution (1 gdl^{-1}) in dimethylformamide is used as a criterion of the quality of the polymer formed in a given set of reaction conditions. The polyesters obtained from different aromatic diols are highly soluble in polar aprotic solvents like N-methyl-2-pyrrolidinone (NMP), N,N′-dimethyl formamide (DMF), N,N′-dimethyl acetamide (DMA), and dimethylsulphoxide (DMSO). All polyesters are powdery substance. The trend in viscosity reflects relative reactivities of the diols used.

Viscosity Measurements

Typical Huggins and Krammers plots were used to obtain intrinsic viscosity and reduced viscosity for each of the polyesters. These data are presented in Table 2. The results reveal that among DMF soluble polyesters PEBPA has the highest whereas PEEG has the lowest

TABLE 1 Systematic Study of High Temperature Polycondensation for Optimization of Reaction Conditions

System	Reaction temperature (°C)	Yield (%)	Product appearance	η_{sp} (dl/g)
DMF	100	50	Powdery	0.615
DMF	125	58	Powdery	0.625
DMF	150	65	Powdery	0.703
DMF	165	82	Powdery	0.696
DMF	200	70	Powdery	0.635

TABLE 2 Physical Characteristics of Homopolyesters

Polymer code	Product appearance	Yield (%)	Density (g/ml)	$n_{sp/c}$ (dL/g)
PEBPA	Black	82	1.135	0.696
PEBPC	Dark brown	90	1.124	0.630
PEPh	Brown	85	1.192	0.675
PER	Brown	90	1.180	0.575
PEHq	Brown	90	1.182	0.585
PEC	Brown	85	1.184	0.592
PEDHN	Brown	85	1.187	0.620
PEEG	Brown	90	1.110	0.500

solution viscosity. The trend of these values reflects the order of relative reactivity of diols.

Density Mesurements

The density of all the polyesters was determined at 25 ± 1°C by suspension method in a pyknometer. The results are presented in Table 2. It varies from 1.110–1.192 gm/cm^3. The highest density among the synthesized polyesters is of PEPh, whereas the lowest is of PEEG.

The density of the polyesters obtained from NANCCT and various mixtures of diols decreases in the following order:

$$\text{PEPh} > \text{PEDHN} > \text{PEC} > \text{PEHq} > \text{PER} > \text{PEBPA} > \text{PEBPC} > \text{PEEG}.$$

FTIR Measurements

IR spectra of all the polyesters were scanned in KBr. The IR Spectra of the polyesters are shown in Figures 3 and 4, which exhibit several common characteristic absorption frequencies (cm^{-1}). The structural features of the monomer employed for polyester synthesis are such that all the polyesters formed will be linear.

A broad band, which is a characteristic of bonded −OH group, extends from 3020 to 3680 cm^{-1} with a maximum around 3420–3450 cm^{-1}, most probably due to −OH bond of end −COOH group of the polyesters. Certain inflections are observed in the above mentioned broad band. The inflection at 3010–3030 cm^{-1} is attributed to aromatic nucleus stretching [24–25]. The band in the region 2935–2980 cm^{-1}, is assigned to saturated C−H stretching vibration of aliphatic chain. The presence of carbonyl group is indicated by a strong band around 1720–1740 cm^{-1} in the spectra of all the

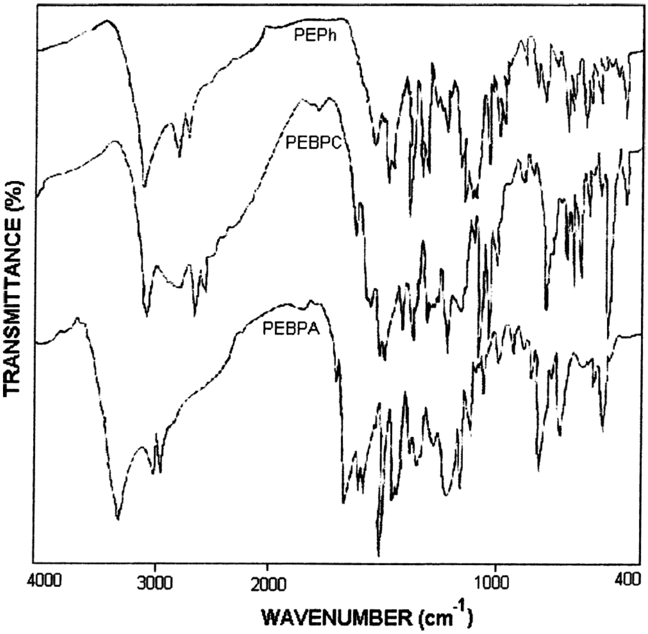

FIGURE 3 IR spectra of homopolyesters.

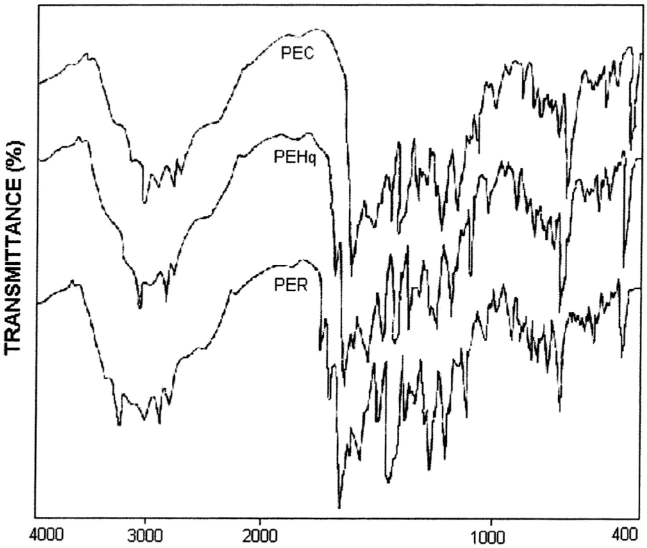

FIGURE 4 IR spectra of homopolyesters.

polyesters. The presence of s-triazine ring is supported by the appearance of a band at 1440–1510 cm^{-1}, which is due to in-plane bending vibration of s-triazine ring.

The bands observed around 1570–1600 cm^{-1} and 1630–1680 cm^{-1} are due to the presence of naphthalene ring. They were found to be difficult to distinguish because these regions are heavily crowded by stretching vibration of phenyl rings and bands at 1600 cm^{-1}, 1580 cm^{-1}, 1510 cm^{-1} and 1450 cm^{-1} attributed to the presence of a system of aromatic double bonds. The band in the region of 1590–1600 cm^{-1} is attributed to aromatic C−N stretching vibration. In spectra of all the polyesters two bands are observed, one at 1105–1200 cm^{-1}, (symmetric) and another at 1175–1240 cm^{-1} (asymmetric), which is attributed to C−O−C stretching [26]. In all the spectra, the bands in the region of 1170–1240 cm^{-1} and 970–1125 cm^{-1} may be attributed to aryl-ether linkage and in plane bending vibration of aromatic C−H bonds [27]. The homopolyesters involving the aromatic diols in their backbone exhibit bands in the region of 610–670 cm^{-1}, which may be due to out of plane bending vibrations of C−H bands of aromatic rings.

The band observed at 595 cm^{-1} in the spectrum of PEEG is attributed to the vibration of aliphatic chain. One band appearing at 560 cm^{-1} in the spectrum of PEBPA is attributed to the C−C deformation vibration of propyl link. In the spectrum of PEBPC, bands observed at 530 cm^{-1} and 900 cm^{-1} are attributed to C−C deformation vibration of cyclohexane ring.

NMr Spectral Characteristics

High resolution (300 MHz) spectra of solution of polyester samples were measured in deuterated (DMSO-d_6) using TMS as an internal reference. The NMR spectra of all the polyesters show a multiplet at around δ 6.42 to 7.90 ppm due to the presence of substituted aromatic phenyl ring systems. NMR spectrum of PEBPA is shown in Figure 5. The six protons of isopropyl group absorbed at δ 1.525 ppm. The three protons of $-CH_3$ group absorbed at δ 0.92 ppm and two protons of $-CH_2$ group absorbed at 4.1 ppm.

Thermal Analysis

All the thermograms of polyesters have been obtained at a heating rate of 10°C/min in the temperature range from ambient temperature to 800°C. Thermograms of some polyesters are shown in Figure 6.

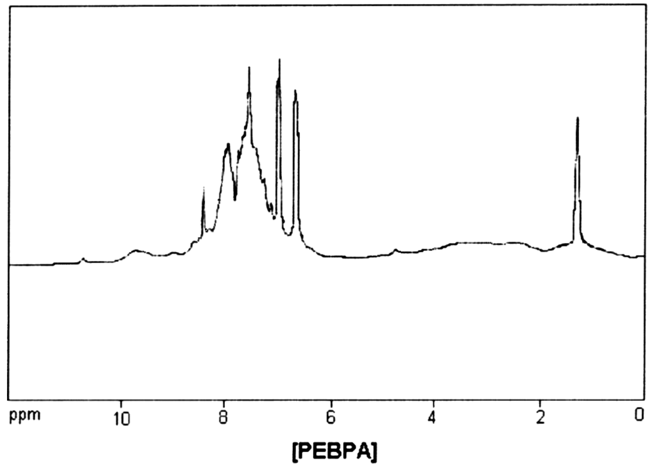

FIGURE 5 NMR spectrum of homopolyester PEBPA.

The characteristic temperatures for assessment of relative thermal stability of polymers such as initial decomposition temperature T_o, temperature T_{10} for 10% weight loss, temperature T_{max} for maximum rate of decomposition, temperature T_f for half volatilization, are

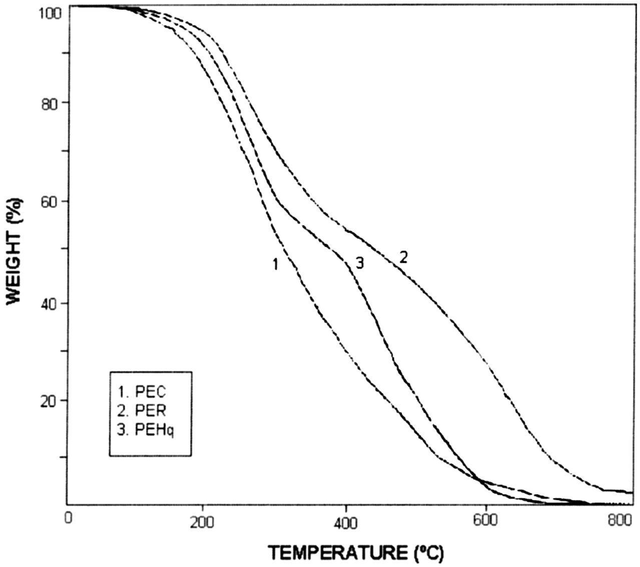

FIGURE 6 Thermograms of homopolyesters.

TABLE 3 Temperature Characteristics of Various Homopolyesters

Polymer	T_0 °C	T_{10} °C	T_{max} °C Step-I	T_{max} °C Step-II	T_s °C	Activation energy (kcal/mol) Step-I	Activation energy (kcal/mol) Step-II
PEBPA	140	265	300	600	475	9.9	14.52
PEBPC	175	275	365	660	540	11.08	19.36
PEPh	190	280	390	630	450	13.32	14.25
PER	130	250	300	575	425	11.74	10.80
PEHq	115	220	260	460	350	13.20	10.78
PEC	100	175	325	—	300	7.78	—
PEDHN	200	360	475	—	525	8.95	—
PEEG	165	275	450	—	440	8.49	—

presented in Table 3. The higher the value of T_{10} [28], the greater is the thermal stability of a polymer.

A comparison of T_s temperature of 50% weight loss for polyesters indicates the following decreasing order of stability:

$$\text{PEBPC} > \text{PEDHN} > \text{PEBPA} > \text{PEPh} > \text{PEEG} > \text{PER} > \text{PEHq} > \text{PEC}$$

A comparison based on T_{max} for copolyesters indicates the following order:

$$\text{PEDHN} > \text{PEEG} > \text{PEPh} > \text{PEBPC} > \text{PEC} > \text{PEBPA} = \text{PER} > \text{PEHq}$$

These trends show that the homopolyester of PEBPC has the higher thermal stability whereas the PEC has the lower thermal stability.

Values of activation energy [E_a] were calculated according to Broido's method [29], and range between 7.78 and 14.52 kcal/mol for the thermal decomposition of polyesters.

These studies reveal that the thermal stability of polyester is significantly related to the aromatic diol component in the molecular chain. They are directly proportional to the molecular size of the diol component.

CONCLUSION

A series of linear homopolyesters from 2-(N-1-naphthylamine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine [NANCCT] and various diols was synthesized successfully. In section of s-triazine rings and flexibilizing linkages in the backbone of aromatic homopolyesters afforded soluble polymers with high thermal stability. Thus, these polymers can be considered as promising, processable, high-temperature-resistant polymeric materials.

SYMBOLS AND ABBREVIATIONS

η_{sp}/c	Reduced viscosity
E_a	Activation energy
T_0	Initial decomposition temperature
T_{10}	Temperature for 10% weight loss
T_{max}	Maximum rate of decomposition temperature
T_S	Temperature for 50%weight loss
NADCT	2-(N-1-naphthylamine)-4,6-dichloro-s-triazine
NACNT	2-(N-1-naphthylamine)-4,6-bis(3-carboxynaphtoxy)dichloro-s-triazine
NANCCT	2-(N-1-naphthylamine)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine
PEBPA	Polyester of Bisphenol-A
PEBPC	Polyester of Bisphenol-C
PEPh	Polyester of phenolphthalein
PEDHN	Polyester of 1,5-dihydroxy naphthalene
PER	Polyester o resorcinol
PEHq	Polyester of hydroquinone
PEC	Polyester of catechol
PEEG	Polyester of ethylene glycol

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