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Copolyesters based on *s*-triazine moiety: Synthesis and characterization

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Ten copolyesters have been synthesized by high temperature polycondensation of 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] with each of the mixture of diols:[Bisphenol-A(BPA)+ Bisphenol-C(BPC)], [BPA+Hydroquinone(Hq)], [BPA+1,5-Dihydroy naphthalene(1,5-DHN)], [BPA+1,4–Dihydroy anthraquinone(1,4-DHA)], [BPA+Catechol(C)], [BPA+Resorcinol(R)], [BPA+Ph], [Ph+1,4-DHA], [Ph+C] and [Ph+R]. All the copolyesters have been characterized by solubility, density, viscosity measurements, IR and NMR spectra, and thermogravimetric analysis. All the copolyesters are soluble at high temperature in acetone, dimethylformamide (DMF), dimethylsulphoxide (DMSO), dimethylacetamide (DMA), *etc.* and have reduced viscosity in the range 0.400-0.641 dL/g in DMF at 30°C. Copolyester derived from diol mixture[BPA+1,4-DHA] show greater thermal stability than the other copolyesters.

Keywords: Copolyesters, *s*-triazine, IR, NMR, thermogravimetric analysis

Extensive literature exists on thermally stable polymers in which aromatic and heteroaromatic rings are linked together in the main chain[1,2]. Aromatic polymers are well known as high performance materials with useful properties such as outstanding thermal stability, good chemical resistance and excellent mechanical properties[3-5]. Due to increased demand of polymers with high performance characteristics in various fields including the aerospace, automobiles and microelectronic industries, the use of these aromatic polymers is growing steadily. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful form. Many researchers have tackled these inherent problems over the last few decades by modifying the monomer's structures[6,7]. The promising approach for modifying the properties of aromatic polymers is the introduction of aromatic pendent groups[8] or heterocyclic rings[9] into the polymer backbone, which imparts good solubility and thermal stability. As an approach to improve the stability and processibility of heterocyclic polymers while maintaining thermal stability, a number of published reports have described the synthesis and properties of *s*-triazine ring containing polymers, *i.e.* polycyanurates such as polyesters[10], polyamides[11], polyimides[12], *etc.* 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 favourable properties to be considered as a useful high performance engineering material[13,14]. In the class of polycyanurates, there are many reports about synthesis leading to synthesis of polyesters and copolyesters from polycondesation of diacid chloride with diols[15-22].

Many of the problems arising while processing and fabrication , for example, decomposition at processing temperature, melt stiffness, *etc.* with homopolymers can be reduced or almost solved by using copolymers. Furthermore, copolymerization is a method for improving the polymer properties to meet specific requirements[23]. Since the linear polyesters and co-polyesters of high molecular weight afford synthetic fibres of excellent properties and have a wide range of

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Symbols and abbreviations

NADCT	2-(β-naphthylamino)-4,6-dichloro-*s*-triazine
NACNT	2-(β-naphthylamino)-4,6-bis(3-carbonyl naphthoxy)-*s*-triazine
NANCCT	2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine
PE(BPA+BPC)	Copolyester of (bisphenol-A+bisphenol-C)
η_{sp}/c	Reduced viscosity
E_A	Activation energy

application[24], the present investigation focuses on synthesis and characterization of copolyesters derived from 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] and various mixtures of diols.

Materials and Methods

DMF, methanol, acetone and other common chemicals used were laboratory grade reagents. Cyanuric chloride (Fluka) was purified by recrystallization from pure benzene (m.p. 146°C). BPA (Resin grade, Cibatul, m.p. 156°C) was repeatedly recrystallized from 50% aqueous acetic acid and finally recrystallized from benzene. Commercially available phenolphthalein (BDH, m.p. 262°C), resorcinol, catechol and hydroquinone (Sisco Lab) were purified by recrystallization from rectified spirit. 1,5-DHN and 1,4-DHA (Merck) were used as received. BPC was synthesized by the published procedure[25] and was recrystallized from benzene (m.p. 187°C).

Reduced viscosities of copolyesters were determined with 1 g/dL solutions in DMF at 30°C using Ubbelohde suspended level viscometer. The densities of polyesters were determined at 30°C using the suspension method[26]. IR spectra of all the copolyesters were scanned using KBr pellets on a Perkin-Elmer FT-IR Paragon 1000 SPIR 43825 instrument. The NMR spectra were recorded on a Perkin-Elmer Model-32 ^{1}H NMR spectrometer (200 MHz) using DMSO-d_6 as solvent and TMS as an internal standard. TGA of the copolyesters were performed using thermobalance Universal VI-12E TA instrument at a heating rate 10°C/min in an inert atmosphere. The samples were kept in a vacuum desiccator for 24 hr before analysis.

Results and Discussion

High temperature polycondensation of NANCCT (6.62 g, 0.01 mol) with equimolar (0.01 mol) mixture of diols [BPA+BPC] 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 molar ratio, rate of stirring and initiator used, were maintained nearly constant for all the experiments. The quantity and quality of the copolyester of [BPA+BPC] obtained at various temperature are presented in **Table I**. Based on these data, suitable reaction conditions have been selected for the synthesis of all the copolyesters of various mixtures of aromatic diols. The reduced viscosity of the polymer solution (1 g/dL) in DMF is used as a criterion of the quality of the polymer formed under a given set of reaction conditions.

Solubility

Solubilities of the copolyesters was determined for powdery samples in excess solvents. All the copolyesters are partly soluble at RT in DMA, DMSO, dioxane, acetone and *n*-butanol with complete dissolution at higher temperature. DMF and ethyl acetate are good solvents for all the copolyesters. Aliphatic hydrocarbon and chlorinated solvents are non-solvents for the copolyesters. The solubility of the copolyesters markedly decreases with decrease in the content of the phenyl moiety in the polymer.

Density measurements

Density of the copolyesters was determined at 25 ± 3°C by a pyknometer and results are presented in **Table II**. The density of the copolyesters synthesized was found to be in the range 1.180-1.258 g/cm^3. The density of the copolyesters decreases in the following order: PE(BPA+1,5-DHN) > PE(BPA+Ph) > PE(Ph+C) > PE(BPA+BPC) > PE(BPA+1,4-DHA) > PE(Ph+R) > PE(BPA+R) > PE(Ph+1,4-DHA) > PE(BPA+C) > PE(BPA+Hq).

Viscosity measurements

Examination of reduced viscosity of the copolyesters given in **Table II** reveals that the copolyester of (BPA+Ph) has the highest whereas the copolyester of (Ph+R) has the lowest solution viscosity. The trends of these values reflects the order of relative reactivity of diols. BPA is the least acidic and hence most reactive towards nucleophilic displacement reaction, which leads to the formation of high molecular weight polymers. The reduced viscosity of the copolyesters decreases in the following order:

PE(BPA+Ph) > PE(BPA + BPC) > PE(BPA + 1,5-DHN) > PE(BPA + 1,4-DHA) > PE(Ph + 1,4-DHA) > PE(BPA + C) > PE (BPA + R) > PE (Ph + C) > PE (BPA + Hq) > PE (Ph + R).

IR spectral characteristics

IR spectra of some copolyesters are shown in **Figure 1**. They exhibit several common characteristic absorption frequencies (cm^{-1}). The bands at 800-810 cm^{-1} and 1410-1450 cm^{-1}, respectively, are attributed

Table I — Systematic study of high temperature polycondesation of NANCCT and mixture of diols (BPA+BPC) for optimization of reaction conditions

System	Reaction Temperature (°C)	Yield (%)	Product appearance	η_{sp} (dL/g)
DMF	100	53	Powdery	0.515
DMF	125	60	Powdery	0.535
DMF	150	62	Powdery	0.605
DMF	165	75	Powdery	0.584
DMF	200	70	Powdery	0.538

to out of plane vibrations of the *s*-triazine ring, and the band at 1170-1280 cm^{-1} is attributed to vibration involving the aryl ether linkage[27,28]. In the IR spectra of all the copolyesters, two bands are observed, one at 1140-1160 cm^{-1} and another at 1260-1300 cm^{-1} which are attributed to the symmetric and asymmetric stretching vibrations of C-O-C (ester) group. In the IR spectra of all the copolyesters, a band around 1720-1740 cm^{-1} is observed which confirms the presence of –C=O group[29]. The band at 1665-1670 cm^{-1} may be due to β-substituted naphthalene ring vibration.

The IR spectra of copolyesters of [BPA+BPC], [BPA+Ph], [BPA+1,4-DHA], [BPA+1,5-DHN], [BPA+C] and [BPA+R] exhibit distinct bands around 550-560 cm^{-1} confirming the presence of C-C deformation vibration of propyl link due to BPA. The spectra of copolyesters of [BPA+BPC] show absorption bands around 530 cm^{-1} and 1180 cm^{-1} due to deformation vibration of cyclohexane ring of BPC. The spectra of PE(BPA+Ph), PE(Ph+1,4-DHA), PE(Ph+C) and PE(Ph+R) exhibit strong bands around 1750-1760 cm^{-1} due to C-O stretching vibration of lactone ring of phenolphthalein.

NMR analysis

The ^{1}H NMR spectra of PE(BPA+BPC) (not shown) exhibit signals in the range δ 6.60-7.93 due to the presence of aromatic protons. The signal due to –NH appears around δ 8.19. The six protons of the isopropyl group produce a singlet at δ 1.39, while the ten protons of the cyclohexyl ring appear as singlets at δ 2.70 and 2.86.

Thermal decomposition characteristics

Thermograms of some copolyesters are shown in **Figure 2**. The characteristic temperatures for assessment of relative thermal stability of polymers such as initial decomposition temperature T_0, temperature for 10% weight loss T_{10}, temperature for maximum rate of decomposition T_{max}, temperature for half volatilization T_f and activation energy E_A are presented in **Table III**. The thermal stability of copolyesters on the basis of initial decomposition temperature T_0 is as follows:

PE(Ph + C) > PE (BPA + Ph) > PE (Ph + R) > PE (BPA + Hq) > PE(Ph + 1,4-DHA) > PE (BPA + 1,4-DHA) > PE (BPA + 1,5-DHN) > PE (BPA + BPC).

The higher the value of T_{10}, the greater is the thermal stability of a polymer[30]. A composition of T_{10} for copolyesters indicates the following decreasing order of stability:

PE (BPA+Ph) > PE (BPA+Hq) > PE (Ph+R) > PE (Ph+1,4-DHA) > PE (Ph+C) > PE (BPA+1,4-DHA) > PE (BPA+1,5-DHN) > PE (BPA+BPC).

The observations of the above thermal stability trends show that the copolyesters involving resorcinol, catechol and 1,4-DHA have higher stability as compared to the copolyesters involving phenolphthalein.

Values of activation energy [E_A] given in **Table III** were calculated according to the Broido's[31] method, which range between 5.05 and 16.00 KCal/mol for the thermal decomposition of copolyesters.

These studies reveal that the thermal stability of copolyesters is significantly related to the aromatic diol component in the molecular chain. It is directly proportional to the molecular size of the diol component in the main chain of polymer.

Experimental Section

Synthesis of monomer NANCCT

The monomer 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine was synthesized by the reported method[32] as shown in **Scheme I**.

Synthesis of copolyesters

A high temperature polycondensation is exemplified for the synthesis of copolyesters from 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] with a mixture of diols [BPA+BPC] which is given in **Scheme II**.

NANCCT (6.62 g, 0.01 mol) in a minimum quantity of DMF was heated to about 150°C. Cetrimide (0.25 g) and then the mixture of [BPA (2.28 g, 0.01 mol) + BPC (2.68 g, 0.01 mol)] were added. The reaction temperature was raised to 165°C and heated for 8 hr. The reaction mixture was cooled and poured with constant stirring into 250 mL of ice cold water. The solid was filtered and washed with hot water and finally with methanol to remove unreacted monomer and dried. The yield was about 75%.

Table II — Physical characteristics of copolyesters

Polymer code	Product appearance	Yield (%)	Density (g/mL)	$\eta_{sp/C}$ (dL/g)
PE(BPA+1,4 - DHA)	Grey powder	70	1.215	0.488
PE(BPA+1,5 - DHN)	Reddish brown	80	1.258	0.536
PE(BPA+BPC)	Red	75	1.218	0.584
PE(BPA+C)	Green	85	1.189	0.456
PE(BPA+R)	Black	85	1.211	0.432
PE(BPA+Hq)	Black	80	1.180	0.408
PE(BPA+Ph)	Black	80	1.239	0.641
PE(Ph+1,4 - DHA)	Grey	90	1.208	0.472
PE(Ph+C)	Black	80	1.222	0.432
PE(Ph+R)	Reddish brown	85	1.212	0.400

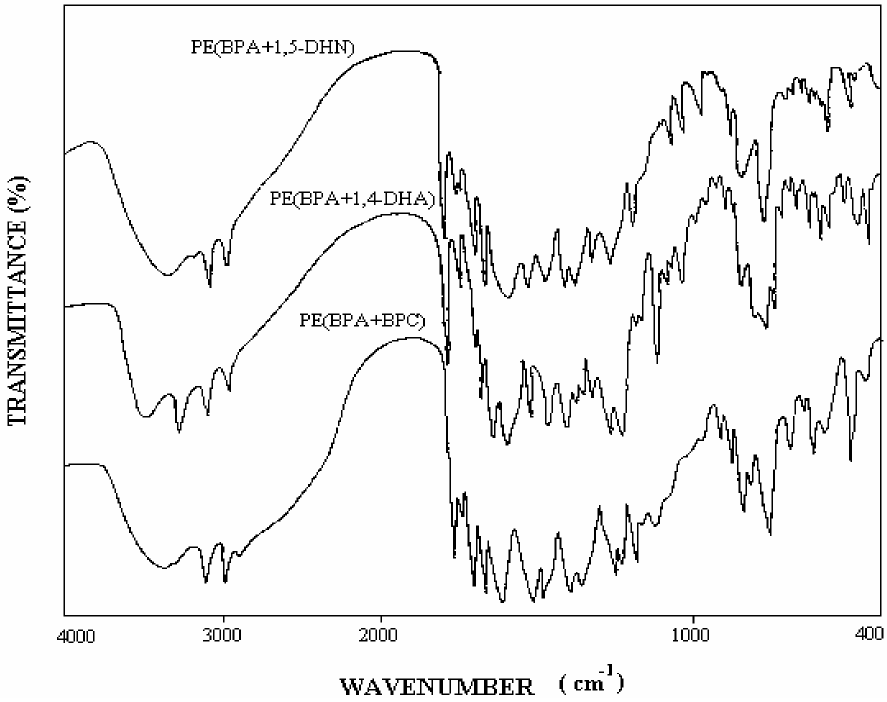
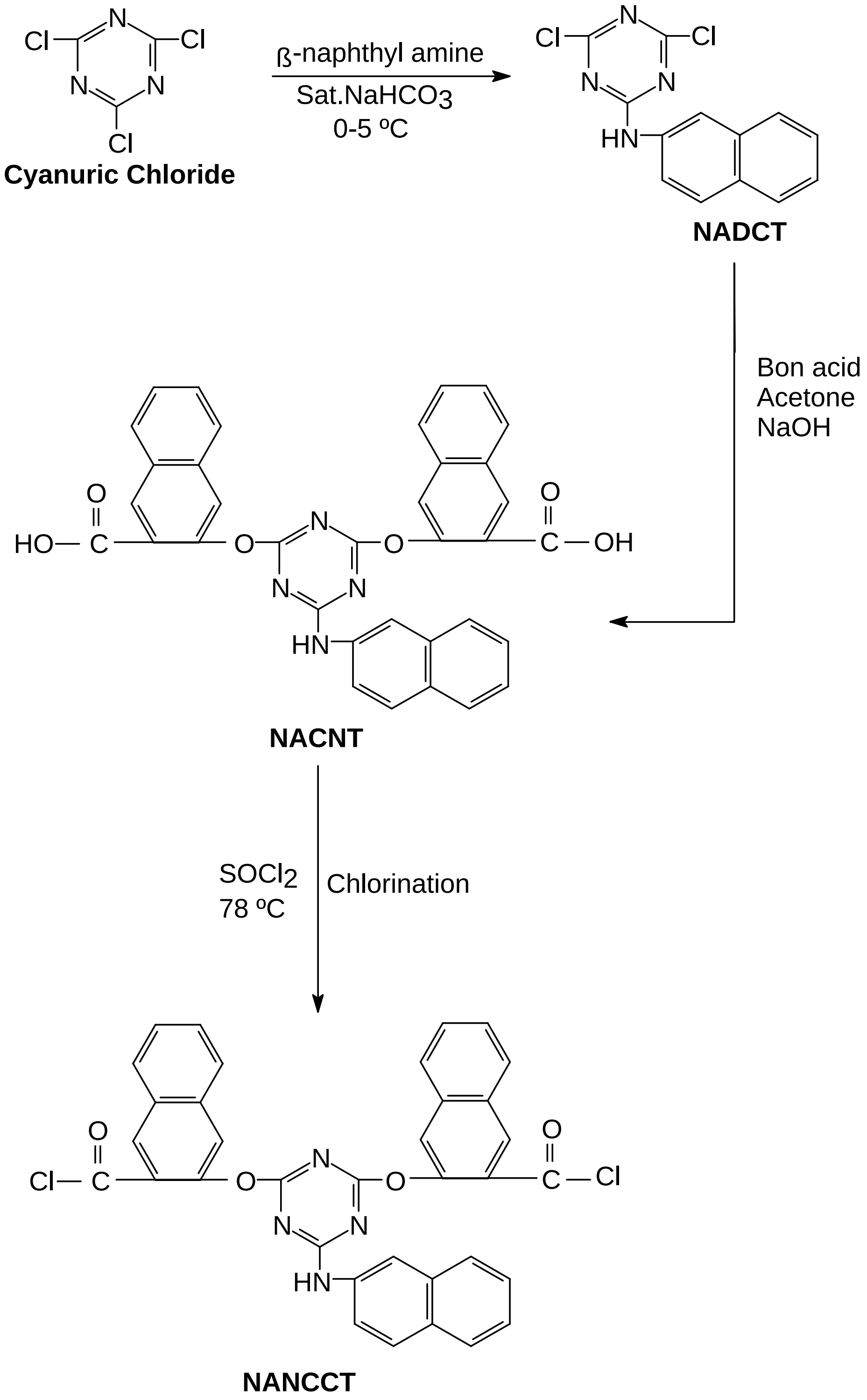


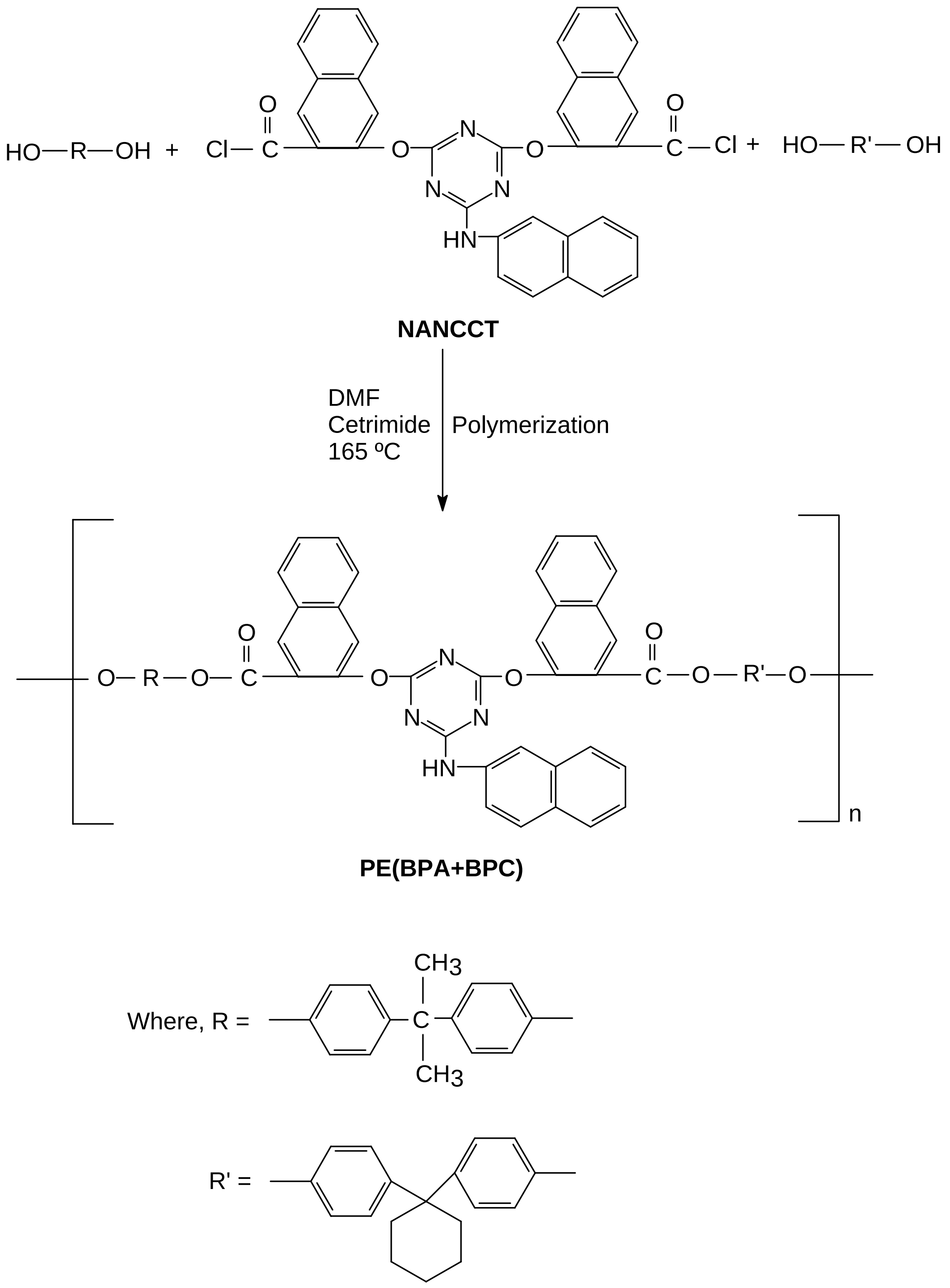
Figure 1 — IR spectra of copolyersters

Table III — Temperature characteristics of various copolyesters

Polymer code	T_0°C	T_{10}°C	T_{max}°C		T_S°C	E_A(Kcal/mol)	
			Step-I	Step-II		Step-I	Step-II
PE(BPA+1,4 - DHA)	240	282	310	-	670	13.12	-
PE(BPA+1,5 - DHN)	220	275	300	-	622	13.12	-
PE(BPA+BPC)	200	258	285	620	524	11.47	15.10
PE(BPA+Hq)	258	295	320	-	464	14.43	-
PE(BPA+Ph)	263	301	325	-	501	16.00	-
PE(Ph+1,4 - DHA)	245	286	336	-	484	15.20	-
PE(Ph+C)	265	284	314	-	446	15.95	-
PE(Ph+R)	260	290	314	644	450	5.07	5.05



Scheme I — Reaction scheme for synthesis for monomer



Scheme II – Reaction scheme for synthesis of copolyesters

The other copolyesters from NANCCT and various diols such as [BPA+Hq], {BPA+Ph], [BPA+1,5-DHN], [BPA+1,4-DHA], [BPA+C], [BPA+R], [Ph+C], [Ph+R] and [Ph+1,4 DHA] were synthesized by similar methods as mentioned earlier.

Conclusion

Introduction of *s*-triazine rings and the flexibilizing linkages into the backbone of wholly aromatic copolyesters affords soluble polymers with high thermal stability. Thus, these polymers can be

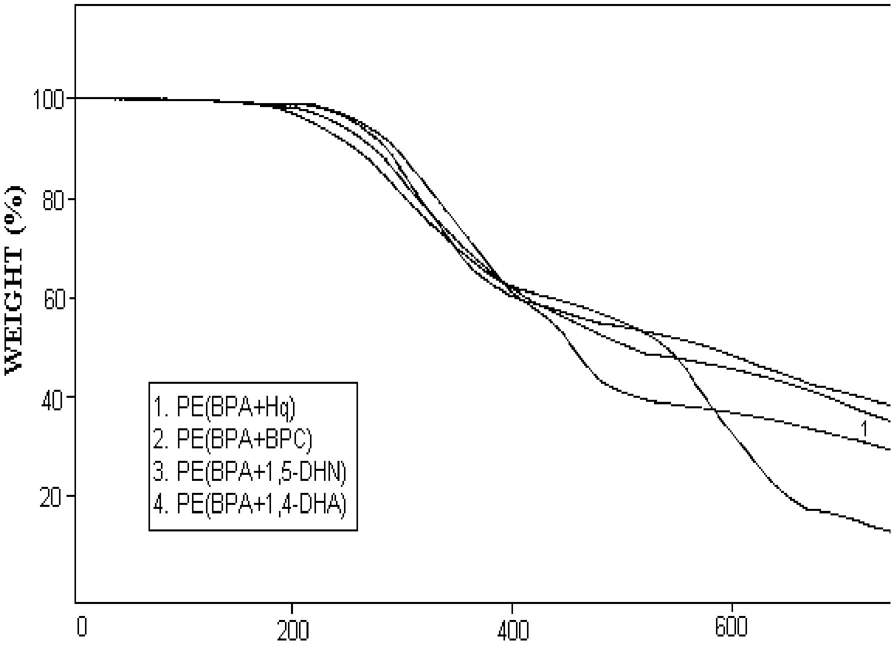


Figure 2 — Thermograms of copolyesters

considered as promising, processable, high-temperature resistant polymeric materials.

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