Copolycyanurates from 2-(N-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-triazine: Synthesis and Characterization

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A B S T R A C T

Various copolyamides were synthesized using high temperature polycondensation technique from 2-(N-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-triazine [EAPCCT] and various mixtures of diamines such as; (p-phenylene diamine [PPDA]+4,4'-diaminodiphenylamide [DADPA]), (PPDA+4,4'-diaminodiphenylsulphonamide [DADPSA]), (ethylene diamine [EDA]+DADPA), (EDA+DADPSA), (EDA+1,4-diamino toluene [DAT]) etc. They were characterized by density and viscosity measurements, FTIR and NMR spectroscopy, techniques solubility tests and thermogravimetric analysis method. Density of different copolyamides was in the range of 1.155-1.232 g/cm^3. Reduced viscosity was in the range of 0.430-0.386 g/dL that indicates the fairly higher molecular weight range of the synthesized polymers, which is required for the polymer to possess reasonably good mechanical and thermal properties. All the polymers synthesized showed moderate to high thermal stability required to be categorized as high performance materials.

Key Words:

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INTRODUCTION

Extensive literature exists on thermally stable polymers in which aromatic and heteroarmatic rings are linked together in the main chain [1,2]. Aramides (aromatic polyamides) are well known as high-performance materials with useful properties, such as outstanding thermal stability, good chemical resistance and excellent mechanical properties [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 of the properties essential for successful fabrication into useful forms. Many researchers have tackled these inherent problems over the few decades by modifying the monomers structures [5,6].

The promising approach for modifying the properties of polyamides is the introduction of aromatic pendent groups [7] or heterocyclic rings [8] into the polyamide backbone, which imparts good solubility and thermal stability. As an approach to improve the stability and processibility of heterocyclic polymers while maintaining the thermal stability, a number of published reports have described the synthesis and properties of polycyanurates and copoly-cyanurates [9-13].

The polymers containing the s-triazine moiety in their backbone are unique in the sense that they exhibit an unusual combination of properties such as high softening temperature and thermal stability together with solubility.

These properties are influenced by the nature of substituents on the s-triazine nucleus and also by the nature of the diamine component in the polymer chain. There are many reports about synthesis and characterization of polyamides containing s-triazine nuclei in the main chain [14-18].

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 [19].

The present investigation describes the synthesis and characterization of several copolyamides synthesized by high temperature polycondensation of 2-(N-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-tri-azine [EAPCCT] with each of several mixture of diamines such as; (PPDA+DADPA), (PPDA+DADPSA), (PPDA+DADPS), (PPDA+DADPM), (EDA+DADPA), (EDA+DADPS), (EDA+DADPSA), (EDA+DAT), and (EDA+DADPM). All the copolyamides were characterized by viscosity and density measurements, IR and NMR spectroscopy and thermogravimetric analysis (TGA) techniques.

EXPERIMENTAL

Materials

Dimethyl formamide, methanol, sodium hydroxide, thionyl chloride and other common chemicals used were laboratory grade reagents. Cyanuric chloride (Fluka) was purified by recrystallization from pure benzene (m.p.146 °C). N-ethyl aniline (Merck) was used as received. The diamines such as; 4,4'-diamino diphenylsulphone [Cibatul, Atul (Gujarat), India], 4,4'-diaminodiphenylmethane [Cibatul, Atul (Gujarat), India], 4,4'-diaminodiphenyl (Merck), 2,4-diamino toluene (Merck), o-phenylene diamine (Merck), m-phenylene diamine (Merck), p-phenylene diamine (Merck), ethylene diamine (Merck) of purity better than 99% were used as received. Diaminodiphenyl-amide (DADPA) (m.p. 204°C) was synthesized by published method [20]. 4,4'-diaminodiphenyl-sulphonamide (DADPSA) was synthesized from acetanilide by published method [21] and purified by crystallization from alcohol and water (m.p. 137°C).

Synthesis of Monomer 2-(N-ethyl anilino)-4,6-bis (phenoxy-2-carbonyl chloride)-s-triazine [EAPCCT]

EAPCCT was synthesized by the reported method [22]. The yield was 90%. It was recrystallized from benzene, m.p. 198°C.

Synthesis of Copolyamides

A high temperature polycondensation is exemplified below for the synthesis of polyamide from 2-(N-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-tria-zine [EAPCCT] and equimolar mixture of diamines; (p-phenylene diamine [PPDA]+4,4'-diamino-diphenylamide [DADPA]). Reaction scheme for polymerization reaction is given in Scheme I.

A mixture of EAPCCT (5.09 g, 0.01 mol), p-phenylene diamine [PPDA] (1.08 g, 0.01 mol), 4,4'-diaminodiphenylamide [DADPA] (2.27 g, 0.01 mol), triethylamine (5 mL) and minimum quantity of DMF (approx 10 mL) was placed in a three necked flask equipped with a mechanical stirrer and drying tube. The reaction mixture was heated with stirring at 165°C for 8 h. At the initial stage of the reaction, the evolution of hydrogen chloride gas was rapid and later on it slowed down. The evolved HCl gas was absorbed by triethylamine, which was of basic nature.
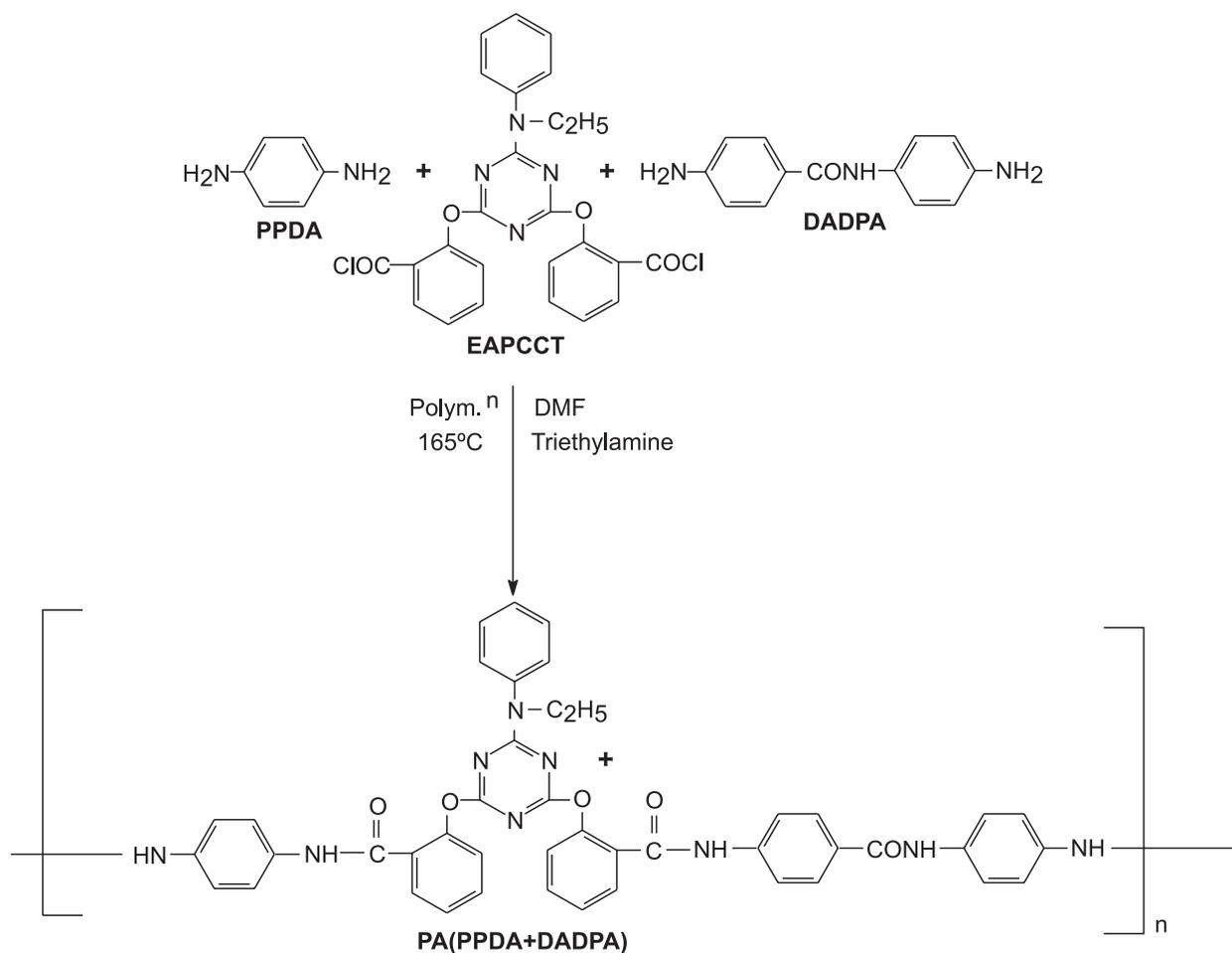
Scheme 1. Reaction scheme for synthesis of copolyamide.

The polymer obtained was filtered, thoroughly washed with hot methanol and hot acetone. Finally, the polymer was dried in a vacuum oven at 80°C over night. The yield of polymer was 90%.

The other copolyamides from 2-(*N*-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-triazine [EAPCCT] and various diamine mixtures such as; (EDA+DADPA), (PPDA+DADPSA), (PPDA+ DADPS), (PPDA+DADPM), (EDA+DADPS), (EDA+DADPSA), (EDA+DADPA), (EDA+DAT), (EDA+DADPM) were synthesized by the similar method shown as above. The structures of some copolyamides are given in Scheme II.

RESULT AND DISCUSSION

s-Triazine ring containing diacyl chloride was

synthesized by the route shown in Scheme I. 2-(*N*-ethyl-anilino)-4,6-dichloro-s-triazine (EADCT) readily underwent nucleophilic displacement of chloride ions by phenolate anion formed from salicylic acid to yield the corresponding diacid EACPT. The copolyamides obtained from different mixtures of aromatic diamines are highly soluble in polar aprotic solvents like *N*-methyl-2-pyrolidone (NMP), *N,N′*-dimethyl formamide (DMF), *N,N′*-dimethyl acetamide (DMA) and dimethylsulphoxide (DMSO).

All the copolyamides are powdery substance. The reduced viscosity of the polymer solution $(1~\mathrm{gdL^{-1}})$ in dimethylformamide is used as a criterion of the quality of the polymer formed in a given set of reaction conditions. The trend in viscosity reflects relative reactivities of the diamines used.

The polymers have reasonably high molecular weights and tough films could be cast form

Mixture of diamines	Structure of repeating unit of copolyamide
PA(PPDA+DADPSA)	
PA(PPDA+DADPM)	
PA(EDA+DADPA)	
PA(EDA+DADPS)	
PA(EDA+DADPM)	

Scheme II. Structures of some copolyamides.

dimethylacetamide solution of copolyamides.

Viscosity Measurements
Dilute solution viscosity measurements were carried out using Ubbelohde suspended level kinemetic viscometer. The polymer solutions were prepared in DMF and were filtered through G-3 sintered prior to flow time measurements. Intrinsic, reduced, and inherent viscosities for all the copolyamides at various concentrations were determined at $25\pm0.1°C$. Typical Huggin's and Krammer's plots were used to obtain intrinsic viscosity for each of the copolyamides. Reduced viscosity of copolyamides is shown in Table 1. Copolyamide PA(PPDA+DADPSA) has the highest whereas PA(EDA+DAT) has the lowest solution viscosity. The overall results for viscosity of copolyamides reveal that all the synthesized polymers are of reasonably higher molecular weight required to possess good mechanical and thermal properties.

Density Measurements
Density of each copolyamide was determined at $25\pm1°C$ using the suspension method [23]. The liquid system CCl_4 and petroleum ether was found to be inert to all the copolyamides. The density of the copolyamides varies from 1.232-1.155 g/cm^3, which is shown in Table 1. PA(PPDA+DADPSA) displays the highest density, while the lowest is shown by PA(EDA+DAT). Thus the order of the results of

density measurements matches with the results of the viscosity measurements, which proves that as viscosity increases, the molecular weight of the polymer increases and thus the density of the polymer. The density of copolyamides varies with the different chemical properties of diamine used. Though PA(PPDA+DADPSA) shows highest density value than other copolyamides, this value is less than the value for the homopolyamide PADADPSA (1.237 g/cm^3). This may be due to the fact that the structure of copolyamide is not so compact as in hompolyamide PADADPSA due to the interaction of other diamine.

The density of the copolyamides decreases in the following order: PA(PPDA+DADPSA) > PA(PPDA + DADPS) > PA(PPDA+DADPM) > PA(PPDA +DADPA) > PA(PPDA+DADP) > PA(EDA+DADPSA) > PA(EDA+ DADPS) > PA(EDA+DADPA) > PA(EDA+DADPM) > PA(EDA+DAT)

FTIR Measurements
The IR spectra of the copolyamides exhibits the several characteristic absorption frequencies (cm^{-1}) which have been shown in Figures 1 and 2.

The band observed around 3340-3445 cm^{-1} is attributed to N-H stretching vibration of secondary amide. A broad band, maximum around 3350-3385 cm^{-1} is probably due to O-H stretching vibration (hydrogen bonded) of end –CONH group of

Table 1. Physical characteristics of copolyamides.

| Polymer	Colour	Yield (%)	Density (g/cm^3)	Reduced viscosity $n_{sp/c}$ (dL/g)
PA(PPDA+DADPSA)	Black	95	1.232	0.6957
PA(PPDA+DADPA)	Black	90	1.198	0.6609
PA(PPDA+DADPS)	Black	90	1.217	0.6348
PA(PPDA+DADPM)	Gray	85	1.210	0.6174
PA(PPDA+DADP)	Brown	80	1.193	0.6000
PA(EDA+DADPA)	Reddish Brown	90	1.178	0.5565
PA(EDA+DADPSA)	Brown	80	1.191	0.5826
PA(EDA+DADPS)	Black	85	1.180	0.5478
PA(EDA+DADPM)	Reddish Brown	95	1.172	0.5217
PA(EDA+DAT)	Black	80	1.155	0.4957
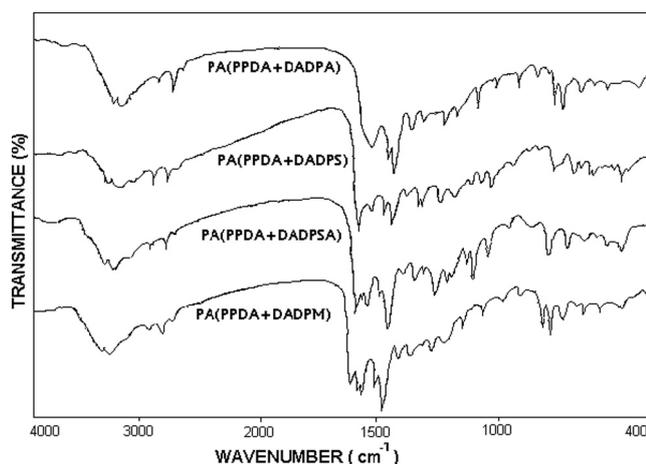
Figure 1. IR Spectra of copolyamides.

copolyamides [24]. The presence of two bands due to stretching and bending vibration of amide-I and amide-II bands is anticipated in the region of 1620-1660 cm^{-1} and 1540-1560 cm^{-1}, respectively, depends upon the structure. The strong band is observed in the region 1400-1500 cm^{-1} is attributed to the skeletal and ring vibration of aromatic and heteroaromatic rings. The bands at 3060-3080 cm^{-1} are attributed to aromatic C-H stretching [25,26]. The strong band observed around 800-840 cm^{-1} is due to the out of plane vibration of s-triazine ring.

The presence of s-triazine ring is further supported by the appearance of a band at 1445-1515 cm^{-1}, which is due to the in plane bending vibration of s-triazine ring. The band at 1400 cm^{-1} is attributed to C-N stretching vibrations of amide group. The bands at 1020 and 1240-1260 cm^{-1} may be attributed to

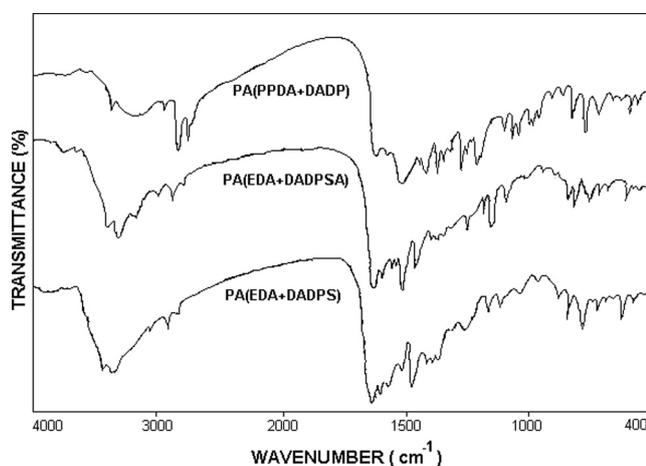symmetric and asymmetric vibration of aryl-ether linkage, respectively.

The IR spectra of the copolyamides exhibit two distinct bands at 1145 cm^{-1} (symmetric) and 1315 cm^{-1} (asymmetric) for PA(PPDA+DADPS) and bands at 1150 cm^{-1} (symmetric) and 1340 cm^{-1} (asymmetric) for PA(EDA+DADPS), confirming the presence of -SO$_2$ group due to DADPS. The IR spectra of the copolyamides exhibit two distinct bands at 1180 cm^{-1} (symmetric) and 1370 cm^{-1} (asymmetric) for PA(PPDA+DADPSA) and PA(EDA+DADPSA) confirming the presence of –SO$_2$NH group due to DADPSA. The IR spectra of the copolyamides containing EDA, exhibit bands at 535, 557, and 584 cm^{-1} confirming the presence of aliphatic chain due to EDA.

NMR Spectral Characteristics
High resolution (300MHz) NMR spectrum of the solution of copolyamide sample of PA(PPDA+DADPS) was measured in deuterated dimethylsulphoxide using TMS as an internal reference is shown in Figure 3 and the assignments of the chemical shifts are summarized in Table 2.

PA(PPDA+DADPS)
The ^{1}H NMR spectra of PA(PPDA+DADPS) shows chemical shift δ at 6.81-7.98 ppm may be due to the presence of aromatic protons. 3 H due to methyl group and 2 H due to –CH$_2$ group of ethyl appear around 1.07 and 3.85 ppm, respectively. 1 H due to –NH of amide group appears around 10.26 ppm [16].

Thermogravimetric Analysis
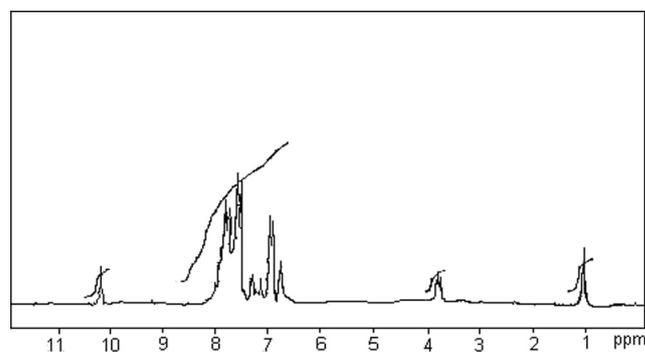Thermograms for copolyamides were obtained at the

Figure 2. IR Spectra of copolyamides.

Figure 3. NMR Spectrum of PA(PPDA+DADPS).

Table 2. Characteristic data of the 300 MHz spectrum of copolyamide PA(PPDA+DADPS).

Chemical Shift δ (ppm)	Assignment
6.81-7.98 (m)	Aromatic protons (Ar-H)
1.07 (t)	Methyl protons of -CH_2CH_3 group
3.85 (q)	Methylene protons of -CH_2CH_3 group
10. 26(s)	Amide proton of -CONH

scan rate of $10°Cmin^{-1}$. Thermograms of some copolyamides are shown in Figure 4. These methods can broadly be classified as qualitative and semiquantitative. The relative thermal stability such as initial decomposition temperature T_0, temperature T_{10} for 10% weight loss, temperature T_{max} for maximum rate of decomposition, temperature T_s for half volatilization, are presented in Table 3. The higher the value of T_{10} the greater is the thermal stability of polymer [27]. Comparison of T_{10} for all the copolyamides synthesized indicates the following decreasing order of thermal stability: PA(EDA+ DADPS) > PA(PPDA+DADPSA) > PA(EDA+ DADPA) > PA(EDA+DADPM) > PA(PPDA+ DADPM) > PA(PPDA+DADPA) > PA(EDA+ DADPS) > PA(PPDA+DADPS).

Though PA(EDA+DADPM) is of lower viscosity and lower density and hence of lower molecular weight, it possesses comparatively higher thermal stability, which implies the disproportionality in relation between molecular weight and thermal stability [28].

A single heating rate method has been employed for the treatment of TGA data, to evaluate activation energy (E_a) for each step of thermal decomposition of polyamides. Values of activation energy (E_a) were calculated according to the methods of Broido [29].

These studies reveal that, the thermal stabilities of copolyamides are significantly related to the aromatic diamine component in the molecular chain. They are directly proportional to the molecular size of the diamine component.

CONCLUSION

Introduction of s-triazine rings and the flexibilizing linkages into the backbone of wholly aromatic copolyamides affords soluble polymers with high thermal stability. Thus, these polymers can be considered as promising, processable, high-temperature resistant polymeric materials.

Table 3. Thermal characteristics of copolyamides.

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
PA(PPDA+DADPSA)	195	315	320	635	680	7.28	9.77
PA(PPDA+DADPA)	175	265	350	670	720	12.34	10.50
PA(PPDA+DADPS)	160	225	300	-	385	10.50	-
PA(PPDA+DADPM)	180	275	510	-	675	13.08	-
PA(EDA+DADPA)	190	310	410	700	645	9.50	20.32
PA(EDA+DADPS)	185	320	360	750	760	6.60	22.84
PA(EDA+DADPSA)	180	255	355	-	565	7.26	-
PA(EDA+DADPM)	185	300	370	-	380	7.15	-
PA(EDA+DAT)	190	275	360	-	570	6.95	-
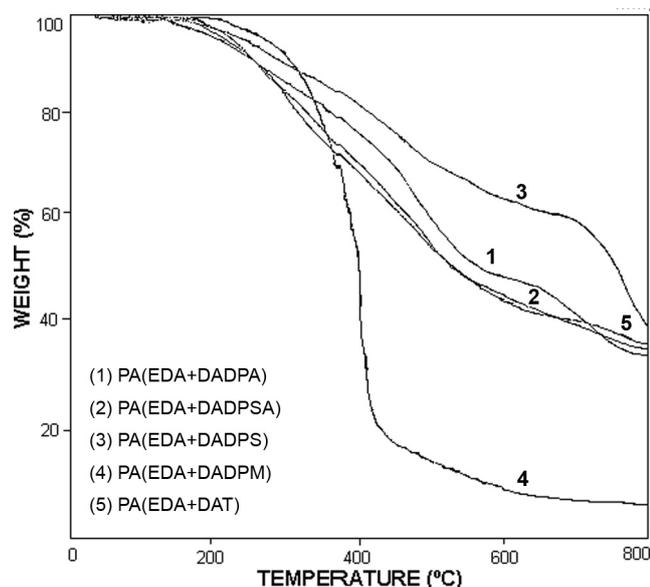
Figure 4. Thermograms of copolyamides.

ACKNOWLEDGEMENT

SYMBOLS AND ABBREVIATIONS

EADCT   2-(N-ethyl anilino)-4,6-dichloro-s-triazine

EACPT   2-(N-ethyl anilino)-4, 6-Bis (carbo-2-phe-noxy)-s-triazine

EAPCCT   2-(N-ethyl anilino)-4, 6-bis (phenoxy-2-carbonyl chloride)-s-triazine

PA(PPDA+DADPA)

    Copolyamide of (PPDA+DADPA)

PA(EDA+DADPSA)

    Copolyamide of (EDA+DADPSA)

η_{sp}/c Reduced viscosity

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

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