

Engineering polyamide materials: s-triazine framework with specialized bulky side chains for advanced applications

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ABSTRACT

The focus of this study is on the synthesis of organic fluorescent and thermally stable polyamides using an s-triazine frame. Coumarin and n-phenyl anthranilic acid have been utilized as bulky pendent groups in the synthesis of the monomer, resulting in polyamides with two groups that enhance stability and fluorescence. The synthesized polyamides have been characterized using a variety of techniques. The thermal stability of the polyamides has been studied using thermogravimetric analysis. These polyamides offer appealing features such as fluorescence and enhanced thermal stability, making them significant for a wide range of applications, including biosensors, clean energy technologies, and explosive sensing.

Keywords: Biosensors, coumarin, polyamides, polycondensation, s-triazine, thermogravimetric analysis

INTRODUCTION

Polyamides are an important type of polymer that is widely utilized in various industries for their exceptional mechanical qualities, high glass transition temperatures, and thermal and chemical durability [1-5]. The demand for heat-resistant materials has led to extensive research on thermally stable polymer systems, with aromatic polyamides garnering global attention for their unique properties [6]. Recently, there has been a growing focus on developing polyamides with enhanced properties, leading to the incorporation of s-triazine-heterocyclic compounds and derivatives into polyamides. These compounds, such as the six-membered heterocyclic compound s-triazine, have exceptional heat resistance and stability [7-10]. Heterocyclic polyamides containing the s-triazine moiety have been widely applied in various fields, including construction, transportation, consumer products, industrial machinery, aircraft, electronics, packaging, and more [11-12].

Newly developed fluorescent polyamides boast a unique blend of high-performance features achieved by bonding between s-triazine and coumarin rings [13-15]. Coumarin was selected as the photosensitive group due to its proven ability to cause a simple $[2\pi+2\pi]$ photodimerization of reactive C=C double bonds in various polymer thin films when exposed

to wavelengths above 300 nm [16-20]. Numerous fields have found uses for these fluorescent-thermally stable polyamides, including biological imaging [22], explosive sensing, pH/temperature monitoring, clean energy technologies [21], ultra-sensitive molecular diagnosis [22], and novel light-emitting nanodevices [23]. Among other applications, they can be used in fluorescent imaging, drug delivery, fluorescent chemosensors, smart polymer machines, biological detection schemes, and fluorescent molecular thermometers.

Many research groups have synthesized and studied polymers from coumarin and s-triazine. Three-armed star-shaped polymer has been synthesized by using the ATRP method from the chlorine ends of the initiator containing triazole coumarin groups. The resulting polymers are used as materials in electronic applications [24]. Feng *et al.*, [25] have synthesized three s-triazine-based functional monomers with thermopolymerizable propargyl-ether units. These monomers may be thermally cured to generate cross-linked networks. The synthesized polymers demonstrated good thermal stability and are used in variable fields.

The various experimental evidence provides strong support for the current work, which focuses on synthesizing and characterizing a new type of thermally stable polyamides. These polyamides boast exceptionally high performance and fluorescent

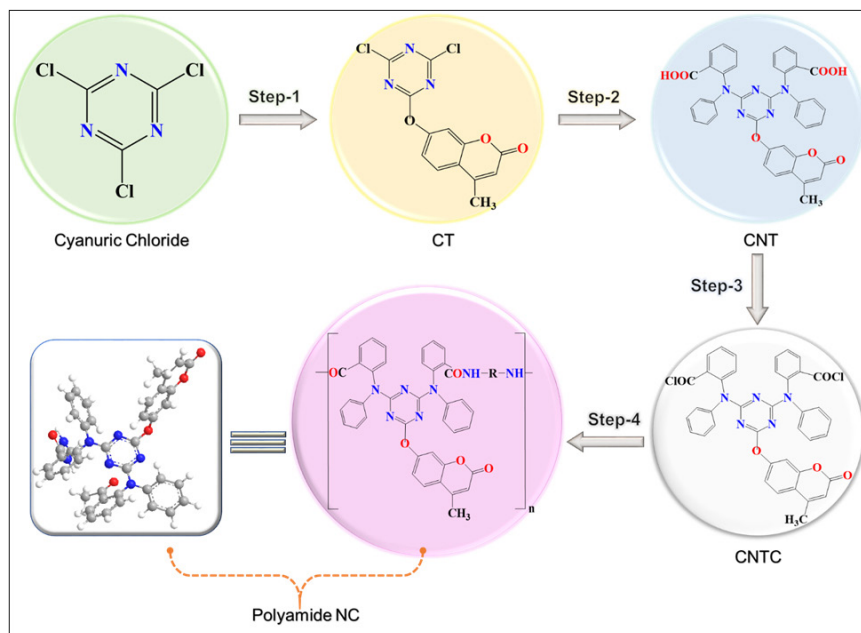
properties, thanks to the incorporation of the s-triazine ring and coumarin ring as the primary moiety. The current study involves the synthesis and characterization of fluorescent-thermally stable polyamides, using 7-hydroxy 4-methyl coumarin, n-phenyl anthranilic acid, cyanuric chloride, and several commercial diamines.

EXPERIMENTAL

In the preparation of the solutions, freshly distilled water was employed. Chemicals such as sodium bicarbonate, sodium hydroxide, thionyl chloride, and cetrimide were used directly.

Merck provided the following solvents: dimethylformamide (DMF), carbon tetrachloride (CT), chloroform, methanol, ethanol, acetone, benzene, n-butanol, ethyl acetate, amyl acetate, isoamyl acetate, and dimethyl sulfoxide (DMSO). Recrystallization of cyanuric chloride was performed using benzene. Ethylene diamine, o-phenylene diamine, diaminodiphenyl sulfone, diaminodiphenyl methane, and p-phenylene diamine were purified.

Polyamide synthesis is given in a schematic manner in which monomer synthesis is explained by steps 1-3 and then polyamide synthesis is described by step 4.



Schematic way for synthesis of Polyamides (NC) via polycondensation

Monomer synthesis: 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(n-phenyl anthranilic chloride) s-triazine

Step-1: Synthesis of 2-(7-hydroxy 4-methyl coumarino)-4,6-dichloro-s-triazine [CT]: Sodium bicarbonate (10.6 g) was dissolved in 100 mL of distilled water and then cooled to a temperature range of 0 - 5 °C. In a separate step, a slurry of cyanuric chloride (18.44 g, 0.1 mol) in 60 mL acetone was created. The sodium bicarbonate solution was added to the cyanuric chloride slurry in a 250 mL three-necked flask equipped with a mechanical stirrer while maintaining a temperature range of 0 - 5 °C. Next, a solution of 7-hydroxy 4-methyl coumarin (17.60 g, 0.1 mol) was added to the cooled cyanuric chloride slurry, and the mixture was stirred for 2 h at the same temperature range. The resulting off-white product was filtered, recrystallized, and dried in vacuum desiccators, yielding 78% of the product with a melting point (M.P) of 120 °C.

Step-2: Synthesis of 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(n-phenyl anthranilic acid) s-triazine [CNT]: 2-(7-hydroxy 4-methyl coumarino)-4,6-dichloro-s-triazine (32.40 g, 0.1 mol) which was

synthesized in step-1 was taken in 40 mL acetone, combined with NaOH (16 g, 0.4 mol) and N-phenyl anthranilic acid (42.64 g, 0.2 mol) in double distilled water (80 mL). The reaction mixture was stirred for 2 h at room temperature and 2 h at 80 °C. The solid was separated, washed with hot water, and dried in a vacuum at 100 °C, producing an 80% yield. Finally, the product was recrystallized from acetone and had a melting point of 189 °C.

Step-3: Synthesis of 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(n-phenyl anthranilic chloride) s-triazine [CNTC]: In a dry round bottom flask, 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(n-phenyl anthranilic acid) s-triazine [CNT] (6.77 g, 0.1 mol) was combined with thionyl chloride (11.9 mL, 0.1 mol) and refluxed at 78 °C for 2 h. Once the reaction was complete, excess thionyl chloride was distilled and the dry product was collected, yielding approximately 82% of the product. The final product was recrystallized using dimethylformamide and had a melting point of 267 °C.

Step-4: Synthesis of polyamides NC-11 to NC-15 via polycondensation: To synthesis of NC-11 to NC-

15 polyamides, in a round bottom flask, approximately 10 mL of DMF was added to 2-(7-hydroxy-4-methylcoumarino)-4,6-bis-(n-phenylanthranil chloride) s-triazine [CNTC] (0.01 mol) and stirred. The mixture was then heated to 150 °C after adding the initiator cetrimide (0.25 g). Various diamine (0.02 mol) was used to synthesize polyamides via polycondensation and HCl was eliminated. Then, the reaction temperature was increased to 160 - 180 °C and heated for 7 h. The reaction mixture was cooled and poured into 250 mL of ice-cooled water with constant stirring. The solid was filtered, washed with hot water, and dried. Different polyamides were synthesized using various diamines and 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(n-phenyl anthranil chloride s-triazine [CNTC]) with a similar method. Ethylene diamine, 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl sulfone, o-phenylene diamine, and p-phenylene diamine were used to synthesize NC-11 to NC-15 polyamides, respectively.

RESULTS AND DISCUSSIONS

Properties of polyamides: Polyamides that contain coumarin and n-phenyl anthranilic acid, along with various diamines, exhibit dark colors. Table 1 displays the colors of these polyamides, which correspond to the specific diamines used. Generally, polyamides based on coumarin and n-phenyl anthranilic acid are dark in color. However, those containing ethylene diamine, o-phenylene diamine, and p-phenylene diamine are dark, while those containing diaminodiphenyl methane and diaminodiphenyl sulfone are grey.

Table 1. Colour of polyamides [NC]

Polyamide	Diamine	Colour
NC-11	Ethylene diamine	Dark
NC-12	o-Phenylene diamine	Grey
NC-13	Diaminodiphenyl sulfone	Grey
NC-14	Diaminodiphenyl methane	Dark
NC-15	p-Phenylene diamine	Dark

Solubility: The solubility of various polyamides which were formed from coumarin and n-phenyl anthranilic acid as a main moiety has been examined in different solvents at both room temperature and 50 °C, and the results are presented in Table 2. Interestingly, the polyamides were found to be insoluble in aliphatic chlorinated solvents such as chloroform and carbon tetrachloride, as well as in halogenated and non-halogenated aromatic solvents like chlorobenzene and benzene. However, the polyamides exhibited partial solubility in solvents such as acetone, methanol, ethanol, THF, n-butanol, isopropyl alcohol, and ether, while showing full solubility in dimethyl formamide, dimethyl sulfoxide, and ethyl acetate. Please note that the solubility of each polyamide in a respective solvent is indicated by the symbols ++, ± ±, and - - in Table 2.

The ++ symbol indicates the polyamide is completely soluble in the respective solvent and the - symbol indicates insolubility and the ± ± symbol illustrates polyamide is partly soluble in the respective solvent.

Table 2. Relative solubility of polyamides in polar and non-polar solvents [NC]

Solvent	NC-11	NC-12	NC-13	NC-14	NC-15
DMF	++	++	++	++	++
DMSO	++	++	++	++	++
Chloroform	--	--	--	--	--
CCl ₄	--	--	--	--	--
Acetone	± ±	± ±	± ±	± ±	± ±
Benzene	--	--	--	--	--
Cl-Benzene	--	--	--	--	--
Methanol	± ±	± ±	± ±	± ±	± ±
Ethanol	± ±	± ±	± ±	± ±	± ±
THF	± ±	± ±	± ±	± ±	± ±
n-Butanol	± ±	± ±	± ±	± ±	± ±
IPA	± ±	± ±	± ±	± ±	± ±
Ether	± ±	± ±	± ±	± ±	± ±
Ethyl acetate	++	++	++	++	++

Viscosity: Vasava *et al.*, [26] have synthesized s-triazine-based polymers and evaluated Intrinsic, reduced, and inherent viscosities along with Huggins and Kraemer's constants for 1% solution. In which, inherent viscosity is in the range of 0.397 - 0.541 g/dL. In the present investigation, to measure the viscosity of polyamides, solutions were prepared in DMF and filtered through a G-3 sintered glass funnel before measuring flow time. The solvent's flow time (t_0) was 72 seconds, and an Ubbelohde suspended level viscometer was used to measure viscosity for diluted solutions. NC-11 to NC-15 polyamides were examined at various concentrations, and relative viscosities (η_{rel}), specific (η_{sp}) viscosities, reduced viscosities, and inherent viscosities were calculated. The results were tabulated in Table 3, and it was found that NC-12, which contains diamino diphenyl methane as diamine, had the highest solution viscosity. The range of inherent viscosity was 0.417 - 0.50 g/dL. Intrinsic viscosity followed the sequence NC-15 < NC-14 < NC-13 < NC-11 < NC-12. Polyamides that contain bulky aromatic side chains showed high intrinsic as well as inherent viscosity. Huggins's and Kraemer's plots were used to obtain intrinsic viscosity for each

Table 3. Specific (η_{sp}) viscosity, reduced viscosity, and Inherent viscosity values of Huggins's (K') and Kraemer's constants (K'') for NC-11 to NC-15 polyamides

Polyamide	$[\eta]$	η_{sp} / C	$\ln \eta_{rel} / C$	K'	K''
NC-11	0.510	0.600	0.470	0.346	0.153
NC-12	0.580	0.650	0.500	0.208	0.238
NC-13	0.485	0.558	0.443	0.310	0.178
NC-14	0.470	0.520	0.418	0.227	0.236
NC-15	0.469	0.518	0.417	0.218	0.237

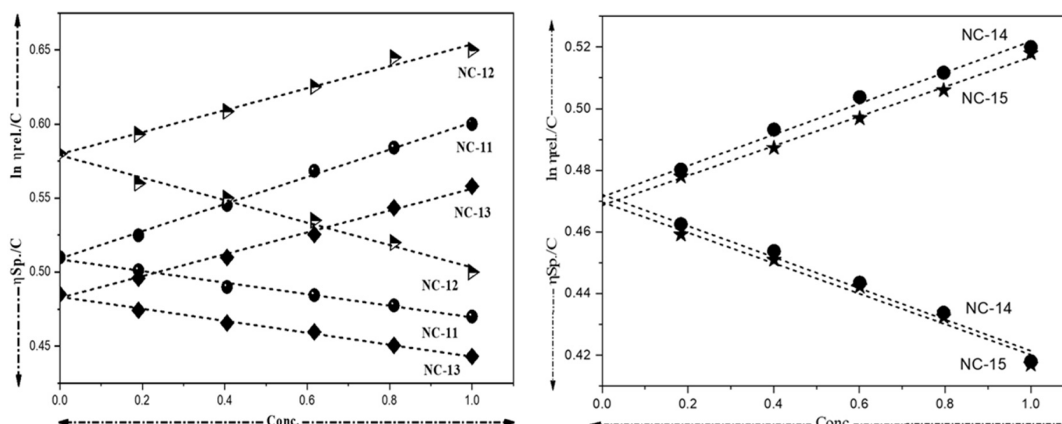


Fig. 1. Typical Huggins and Kraemer plots for intrinsic viscosity of [NC]

of the polyamides [NC], and the results for intrinsic, reduced, and inherent viscosities, along with Huggin's and Kraemer's constants for 1% solution, are shown in Fig. 1.

IR spectra: The analysis of infrared absorption frequencies is a crucial aspect of the study of polyamides. In this regard, Table 4 reveals the details of infrared absorption frequencies of NC-11, NC-12, NC-14, and NC-15 for various functional groups. Analyzing the IR spectrum, it has been found that polyamides showed strong or moderately strong absorption at frequencies of 835 - 839 cm^{-1} and 1487 - 1491 cm^{-1} , which can be predicted to out-of-plane and in-plane vibrations of the s-triazine ring, respectively. Additionally, the vibration of the amide group is seen at 3310 - 3312 cm^{-1} , while

C-N stretching vibration is assigned to 1272 - 1275 cm^{-1} . Furthermore, Ar-O-Ar asymmetric and symmetric vibrations appear at 1134 - 1136 cm^{-1} and 1102-1104 cm^{-1} , respectively, with Ar (C=C) stretching vibration at 1662 - 1665 cm^{-1} and C-O-C (sym) stretching vibration at 1059-1072 cm^{-1} .

Fig. 2 illustrates the IR study of polyamide NC-13, which reveals C-N stretching vibration at 1275 cm^{-1} , >C=O stretching vibration at 1665 cm^{-1} , Ar-O-Ar asymmetric at 1179 cm^{-1} , and Ar-O-Ar symmetric at 1136 cm^{-1} . Notably, out-of-plane and in-plane vibrations of the s-triazine ring appear at 839.08 cm^{-1} and 1491 cm^{-1} , respectively, while N-H stretching vibration of the -CONH group is seen at 3310 cm^{-1} , and C-H stretching vibration of CH_3 appears at 2923 cm^{-1} .

Table 4. IR absorption frequencies of NC-11 to NC-14 polyamides

Polyamide (cm^{-1})	>C-N	>C=O Coumarin	Ar-O-Ar		s-triazine		>N=H (CONH)
			(sym)	(asym)	Out plane	In plane	
NC - 11	1272	1666	1158	1135	824	1487	3312
NC - 12	1272	1665	1160	1135	820	1486	3310
NC - 13	1271	1654	1160	1136	822	1489	3313
NC - 14	1273	1666	1159	1144	823	1484	3308

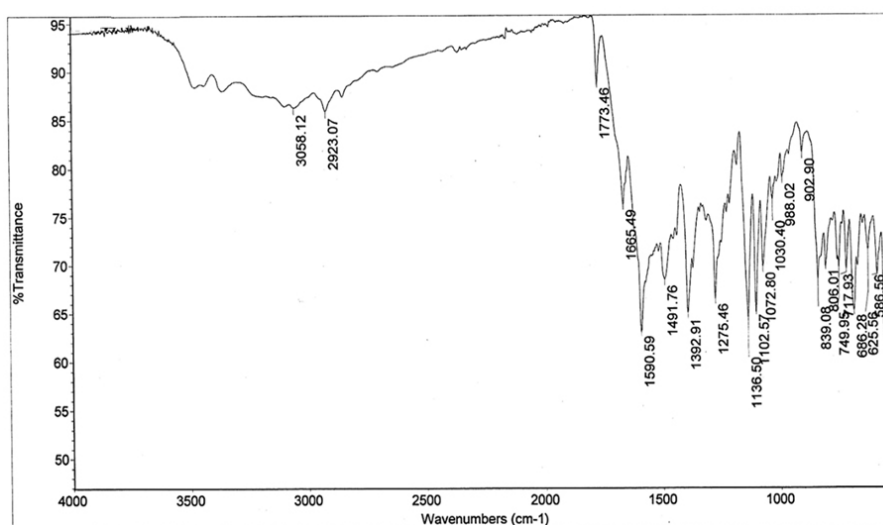
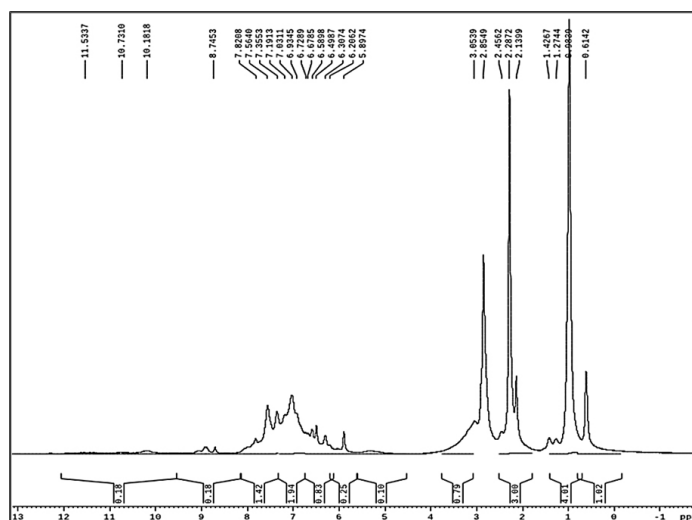


Fig. 2. IR spectra of NC-13

Fig. 3. ¹H-NMR spectra of NC-11

¹H-NMR spectra: The structural characteristics of polyamide NC-11 were examined through a study of its ¹H-NMR spectra. The study was conducted at 400 MHz in DMSO, using TMS as an internal reference. The results are presented in Fig. 3. The ¹H NMR spectra revealed the presence of multiple signals of aromatic protons at 6.20 - 7.82δ, a doublet at 8.74δ indicative of the -NH group of -CONH-, and a singlet at 1.27δ ppm, indicating the presence of -CH₃ group of coumarin. Table 5 shows the chemical shifts of tested NC-12, NC-14, and NC-15 polyamides.

Table 5. ¹H-NMR characteristic of NC-12 to NC-14 polyamides

Chemical shift (δ ppm)	NC-12	NC-13	NC-14
Ar-H Protons (m)	6.20 - 7.82	6.12 - 7.78	6.10 - 7.57
>CH ₃ - group (s) coumarin	1.21	1.21	1.18
-NH- group of amide linkage (d)	8.93	8.70	8.91

Thermogravimetric analysis: Thermal degradation characteristics and kinetic parameters of polyamides based on coumarin and n-phenyl anthranilic acid have been evaluated through thermogravimetric analysis. A qualitative assessment of the thermal stability of some of the polyamides has been attempted based on the visual thermograms obtained, with T₀ and T₁₀ serving as some of the main criteria for thermal stability. The heat stability of polyamides is directly proportional to the values of T₀ and T₁₀.

Table 6. Thermal characteristics of polyamides NC-11 to NC-15 for 10% weight loss and 50% weight loss

Polyamide	T ₀ (°C)	T ₁₀ (°C)	T _{max}		T _s (°C)
			Step - 1	Step - 2	
NC-11	115.35	225.35	305.35	485.35	415.35
NC-12	128.30	238.30	318.30	498.30	388.30
NC-13	176.25	286.25	296.25	496.25	386.25
NC-14	187.27	267.27	287.27	487.27	387.27
NC-15	125.32	225.32	285.32	485.32	375.25

TGA curves have been obtained for polyamides at a scan rate of 10 °C/min. Table 6 describes the thermal characteristics of NC-11 to NC-15, while Table 6 provides an evaluation of the activation energy E_a for all synthesized polyamides using the Broido method and Horowitz-Metzger method from the TGA graph. The thermal properties of NC-14 were examined through TGA under a nitrogen atmosphere, with a heating rate of 100 °C/min. The 10% weight loss temperature and 50% weight loss temperature of the aromatic polyamide in nitrogen were recorded at 267 °C and 567 °C, respectively. Fig. 4 shows the TGA thermogram of NC-14 polyamide, which exhibited high thermal stability.

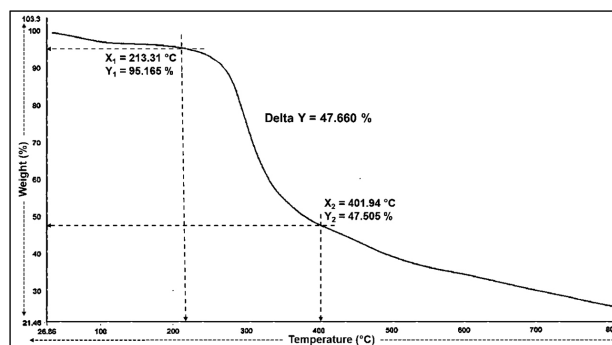


Fig. 4. TGA of NC-14

Many research groups have synthesized various thermally stable polyamides and evaluated thermal stability by thermogravimetric analysis. Tamboli *et al.*, [4] have reported thermally stable polyamides which exhibited T₀ and T₁₀ values in the range 250 - 280 °C and 270 - 296 °C, respectively. In line, it is concluded that in the present research, synthesized polyamides showed good thermal stability, which will be applicable in various fields such as automotive components, aerospace applications, etc. Linear deterioration analysis was conducted on the experimental data to obtain the values of apparent activation energy corresponding to the degradation steps involved.

The calculated energy of activation (E_a) values for all polyamides [NC] are presented in Table 7. An examination of the energy of activation E_a reveals that both the Broido method and Horowitz-Metzger method yield analogous values for E_a .

Table 7. Calculated activation energy from Broido and Horowitz and Metzger method for NC-11 to NC-15 [27]

Polyamide	Broido		Horowitz-Metzger	
	E_a (K.Cal/mol)	T_s	E_a (K.Cal/mol)	
NC-11	14.22	598	14.32	
NC-12	12.27	618	12.35	
NC-13	15.21	623	15.23	
NC-14	15.00	608	15.42	
NC-15	13.36	608	13.40	

Using the Broido method, the activation energy E_a value for NC-11 is 14.22, NC-12 is 12.27, NC-13 is 15.21, NC-14 is 15.00, and NC-15 is 13.36. Meanwhile, using the Horowitz and Metzger method, the activation energy E_a value for NC-11 is 14.32, NC-12 is 12.35, NC-13 is 15.23, NC-14 is 15.42, and NC-15 is 13.40. Overall, the results of this study provide valuable insights into the thermal stability and degradation characteristics of polyamides based on coumarin and n-phenyl anthranilic acid.

Fluorescence spectra: Polyamides NC-14 were synthesized using 7-hydroxy 4-methyl coumarin, n-phenyl anthranilic acid, and diamino diphenyl methane as an aromatic diamine. Fig. 5 showcases their fluorescence spectrum.

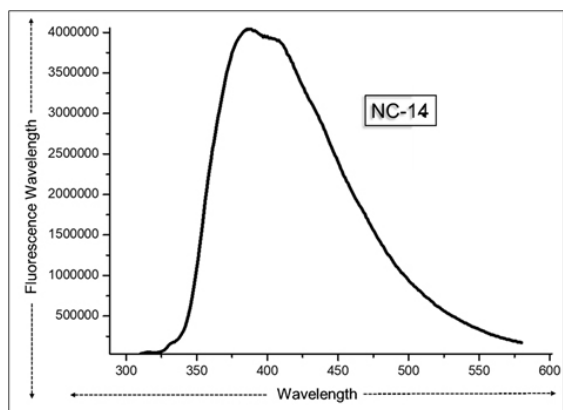


Fig. 5. Fluorescence spectrum of NC-14

To obtain the emission spectra, polyamide NC-14 was dissolved in DMSO-D6 and excited at 300 nm. NC-14 showed broad emission between 350 - 500 nm, with the emission peak located at 400 nm. The resulting polyamide showed the emission peak in the visible region therefore NC-14 polyamide is a fluorescent polyamide.

CONCLUSIONS

A new type of polyamide has been successfully synthesized through polymerization at an elevated temperature. This process involved the polycondensation of monomers that contained an s-triazine ring with n-phenyl anthranilic acid and 7-hydroxy 4 methyl coumarin with various types of diamines. Compared with the above literature survey, it is concluded that the resulting polyamides have exceptional thermal stability and exhibit good fluorescence, making them ideal for a wide range of applications. These synthetic polyamides can be utilized for innovative light-emitting nanodevices, ultrasensitive molecular diagnosis, fluorescent probes, enhanced bioimaging, biological imaging, drug delivery, automotive components, aerospace Applications, and chemosensors.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- Liou G.S., Yen H.J. (2012) Polyimides in polymer science: A comprehensive reference, **5**, Elsevier, 497-535. <https://doi.org/10.1016/B978-0-444-53349-4.00149-7>
- Der-Jang L., Kung-Li W., Ying-Chi H., Kueir-Rarn L., Juin-Yih L., Chang-Sik H. (2012) Advanced polyimide materials: Syntheses, physical properties and applications. *Progress in Polymer Science*, **37**, 907-974. <https://doi.org/10.1016/j.progpolymsci.2012.02.005>
- Bazzar M., Ghaemy M., Alizadeh R. (2012) Novel fluorescent light-emitting polymer composites bearing 1,2,4-triazole and quinoxaline moieties: Reinforcement and thermal stabilization with silicon carbide nanoparticles by epoxide functionalization. *Polymer Degradation and Stability*, **97**, 1690-1703. <https://doi.org/10.1016/j.polymdegradstab.2012.06.018>
- Tamboli A.B., Kalshetti B.S., Ghodke S.D., Diwate A.V., Maldar N.N. (2020) Synthesis and characterization of semi-aromatic polyamides containing heterocyclic 1,3,5 s-triazine and methylene spacer group for thermally stable and colloidal property. *Designed Monomers and Polymers*, **23**(1), 93-105. <https://doi.org/10.1080/15685551.2020.1795435>
- Guipeng Y., Cheng L., Jinyan W., Xiuping L., Xigao J. (2010) Heat-resistant aromatic s-triazine-containing ring-chain polymers based on bis(ether nitrile)s: Synthesis and properties. *Polymer*

- Degradation and Stability*, **95**, 2445-2452. <https://doi.org/10.1016/j.polymdegradstab.2010.08.011>
6. Mallakpour S., Rafiee Z. (2007) Preparation and characterization of new photoactive polyamides containing 4-(4-dimethylaminophenyl) urazole units. *Journal of Applied Polymer Science*, **103**, 947-954. <https://doi.org/10.1002/app.25258>
 7. Sagar A.D., Shingte R.D., Wadgaonkar P.P., Salunkhe M.M. (2001) Polyamides containing s-triazine rings and fluorene "cardo" groups: Synthesis and characterization. *European Polymer Journal*, **37**, 1493-1498. [https://doi.org/10.1016/S0014-3057\(00\)00194-4](https://doi.org/10.1016/S0014-3057(00)00194-4)
 8. Mishra N., Vasava D. (2020) Recent developments in s-triazine holding phosphorus and nitrogen flame-retardant materials. *Journal of Fire Sciences*, **38**(6), 1-22. <https://doi.org/10.1177/0734904120952347>
 9. Gu L., Chen G., Yao Y. (2014) Two novel phosphorus-nitrogen-containing halogen-free flame retardants of high performance for epoxy resin. *Polym. Degrad. Stab.*, **108**, 68-75. <https://doi.org/10.1016/j.polymdegradstab.2014.05.030>
 10. Prokhorov A.M., Prokhorova P.E. (2015) Triazines and tetrazines. *Prog. Heterocycl. Chem.*, **27**, 451-464. <https://doi.org/10.1016/B978-0-08-100024-3.00014-3>
 11. Modh J.V., Patel S.K. (2020) Synthesis, characterization and study of fluorescent-high performance polyesters. *Rasayan Journal of Chemistry*, **13**(3), 1458-1471. <https://doi.org/10.31788/RJC.2020.1335683>
 12. Yu C.M., Wu Y.L., Zeng F., Li X.Z., Shi J.B., et al. (2013) Hyperbranched polyester-based fluorescent probe for histone deacetylase via aggregation-induced emission. *Biomacromolecules*, **14**, 4507-4514. <https://doi.org/10.1021/bm401548u>
 13. Halim M.A. (2013) Harnessing sun's energy with quantum dots based next-generation solar cell. *Nanomaterials*, **3**, 22-47. <https://doi.org/10.3390/nano3010022>
 14. Jeong J.W., Kwon Y., Han Y.S., Park L.S. (2005) Electroluminescent property and photolithographic process of photosensitive random copolymers. *Mol. Cryst. Liq. Cryst.*, **443**, 59-68. <https://doi.org/10.5402/2012/352759>
 15. Trenor S.R., Shultz A.R., Love B.J., Long T.E. (2004) Coumarins in polymers: from light harvesting to photo-cross-linkable tissue scaffolds. *Chemical Reviews*, **104**, 3059-3077. <https://doi.org/10.1021/cr030037c>
 16. Wagner B.D. (2009) The use of coumarins as environmentally sensitive fluorescent probes of heterogeneous inclusion systems. *Molecules*, **14**(1) 210-237. <https://doi.org/10.3390/molecules14010210>
 17. Nechifor M. (2009) Synthesis and properties of some aromatic polyamides with coumarin chromophores. *Reactive & Functional Polymers*, **69**, 27-35. <https://doi.org/10.1016/j.reactfunctpolym.2008.10.006>
 18. Cao D., Liu Z., Verwilt P., Koo S., Jangjili P., et al. (2019) Coumarin-based small-molecule fluorescent chemosensors. *Chemical Review*, **119**, 10403-10519. <https://doi.org/10.1021/acs.chemrev.9b00145>
 19. Defize T., Thomassin J.M., Ottevaere H., Malherbe C., Eppe G., et al. (2019) Photo-cross-linkable coumarin-based poly(ϵ -caprolactone) for light-controlled design and reconfiguration of shape-memory polymer networks. *Macromolecules*, **52**, 444-456. <https://doi.org/10.1021/acs.macromol.8b02188>
 20. Modh J.V. (2023) Synthetic protocols and significance of heterocyclic fluorescent reinforcing polymers: A comprehensive review. *Journal of Advanced Scientific Research*, **14**, 9-39. <https://doi.org/10.55218/JASR.202314202>
 21. Gindre D., Liopoulos K., Krupka O., Evrard M., Champigny E., et al. (2016) Coumarin-containing polymers for high density non-linear optical data storage. *Molecules*, **21**(2), 147. <https://doi.org/10.3390/molecules21020147>
 22. Zhang L.Z., Li Y., Liang Z.X., Yu Q.S., Cai Z.G. (1999) New cross-linked polymer systems with high and stable optical nonlinearity. *React. Funct. Polym.*, **40**, 255-262. [https://doi.org/10.1016/S1381-5148\(98\)00048-0](https://doi.org/10.1016/S1381-5148(98)00048-0)
 23. Mizoguchi K., Hasegawa E. (1996) Polymers for advanced technologies, photoactive polymers applied to advanced microelectronic devices. *Polym. Adv. Technol.*, **7**, 471-477. [https://doi.org/10.1002/\(SICI\)1099-1581\(199605\)7:5/6<471::AID-PAT534>3.3.CO;2-I](https://doi.org/10.1002/(SICI)1099-1581(199605)7:5/6<471::AID-PAT534>3.3.CO;2-I)
 24. Biryani F. (2020) Triazole-coumarin centered star-shaped polymer: Structural characterizations and electrical properties of graphene composites. *Journal of Molecular Structure*, **1222**, 128926. <https://doi.org/10.1016/j.molstruc.2020.128926>
 25. Zhou J., Wang J., Jin K., Sun J., Fang Q. (2016) s-Triazine-based functional monomers with thermocrosslinkable propargyl units: Synthesis and conversion to the heat-resistant polymers. *Polymer*, **102**, 301-307. <https://doi.org/10.1016/j.polymer.2016.09.027>
 26. Nizama S.K., Mishra N., Vasava D., Patel S.K. (2021) Hetero-aromatic-fluorescent polyesters: Synthesis, characterization and physical study. *Journal of Advance Scientific Research*, **12**, 146-153.
 27. Vasava D.V., Patel S.K. (2016) Synthesis, characterization and study of thermally stable fluorescent polyesters. *Int. Lett. Chem. Phys. Astron.*, **70**, 48-62. <https://doi.org/10.18052/www.scipress.com/ILCPA.70.48>