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Synthesis and Physico-Chemical Properties of Homopolycyanurates Based on s-triazine Ring

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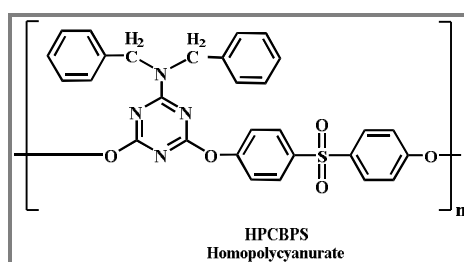
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ABSTRACT

Various homopolycyanurates were synthesised by polycondensation of the diacid chloride of *N,N*-Dibenzyl-4,6-dichloro-1,3,5-triazin-2-amine with different diols such as: Bisphenol-A [BPA], Bisphenol-C [BPC], Bisphenol-S [BPS], Ethylene glycol [EG], Triethylene glycol [TEG], Propylene glycol [PG], Catechol [C], Resorcinol [R], Hydroquinone [Hq] and Phenolphthalein [Ph]. All the synthesized polycyanurates were characterized by solubility, density, viscosity measurements, IR spectra, NMR spectra and thermo gravimetric analysis [TGA]. The densities of homopolycyanurates are measured pycnometrically, the highest density is 1.798 g cm^{-3} is found for HPCBPS while lowest density is 1.322 g cm^{-3} found for HPCDM13PD. Most of the homopolycyanurates are found to stable more than 350°C temperature thus it can be used for high temperature applications.

Graphical Abstract



Keywords: Homopolycyanurates, Polycondensation.

INTRODUCTION

Polymer chemistry is just known to the scientists before World War II and is a leading achievement of chemistry. “Polymer” is not an ordinary word but these polymers are chemically big molecules, the

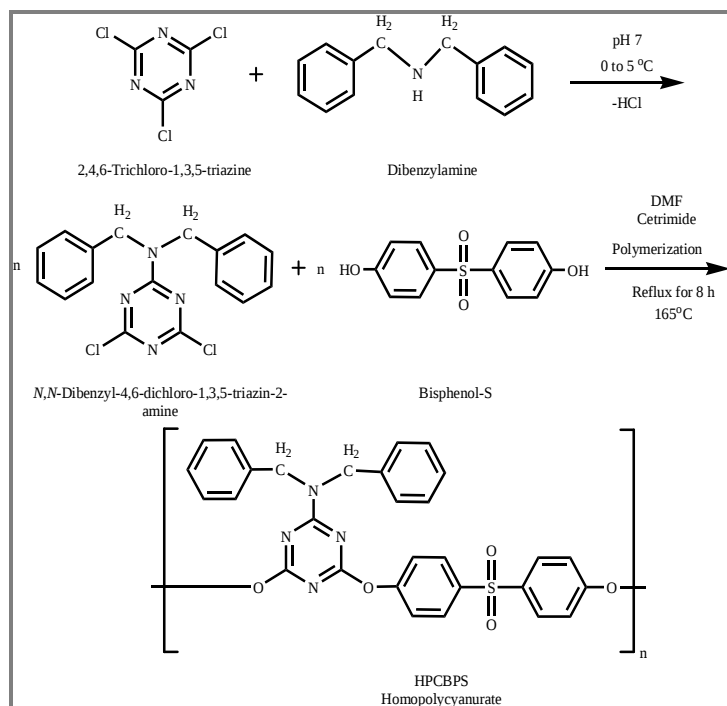
materials that constitute most of our natural and synthetic environment. ranges of deformability and durability, which can be exploited by careful design. The world would have appeared totally different without artificial fibers, plastics, elastomers, etc., and as cheaper, better and stronger synthetic materials are developed, their use will undoubtedly increase further [1]. Shortage of natural fibers like cotton, jute wool led to the discovery of synthetic fibers. Researchers have laid foundation in the laboratories to develop the manmade fibers [2-5].

The approaches that have been employed to improve the processability of these polymers [6], includes the introduction of flexible linkages [7-9], asymmetric units [10], bulky pendant groups [11-14] and kinked or non-coplanar structures [15-18] into the polymer chain. These modifications lower the melting temperature and lead to soluble and amorphous polymers. Aromatic polyesters containing s-triazine ring in main chain are known for their excellent high temperature properties and several commercially available high performance engineering plastic materials [19-21].

As the work reported in the present research work is synthesis and characterization of new high performance polyesters and polyamides with s-triazine backbone. Various homopolycyanurates and copolycyanurates were synthesized from *N,N*-Dibenzyl-4,6-dichloro-1,3,5-triazin-2-amine by polycondensation with different diols and diamines.

MATERIALS AND METHODS

Step-1 Synthesis of *N,N*-Dibenzyl-4,6-dichloro-1,3,5-triazin-2-amine (Monomer): A solution of cyanuric chloride (18.44 g, 0.1 mol) in acetone (60 mL) was added with stirring to a cold solution (0-5°C) of sodium bicarbonate (8.4 g, 0.1 mol) in 100 mL of 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 dibenzylamine (19.7 mL, 0.1 mol) in 10 mL acetone was added drop by drop to the cold slurry of cyanuric chloride with continuous stirring, maintaining 7.0 pH throughout the experiment. After addition was completed, the reaction mixture was stirred for three hours at 0-5°C. The white colored product was filtered and washed several times with cold water, finally recrystallized from ethanol and dried in a vacuum desiccator. Yield 75% and m.p. 155-158°C.



Scheme 1. Synthesis of homopolycyanurates.

Step-II Synthesis of homopolycyanurates from monomer and various diols: *N,N*-Dibenzyl-4,6-dichloro-1,3,5-triazin-2-amine (3.45 g, 0.01 mol) in minimum quantity of DMF (10 mL) was heated to about 150°C, cetrimide (0.25 g) as an initiator and bisphenol-S (2.50 g, 0.01 mol) were added. Triethylamine in catalytic amount was added as a neutralizer. The reaction temperature was raised to 165°C and refluxed for 8 h. The reaction mixture was cooled and poured with constant stirring in 250 mL of ice-cold water. The solid was filtered, washed with hot water and finally with methanol to remove unreacted monomer and dried. Yield is around 70.0 %, m. p. 230-234°C (Scheme 1).

The other homopolycyanurates were synthesized from monomer and various diols such as bisphenol-C, 1,4-Dihydroxy Naphthalene, 1,8-Dihydroxy Naphthalene, 1,5-Dihydroxy Naphthalene, Propane-1,2-diol, Propylene-1,3-diol, Butane-1,4-diol, 2,2-dimethyl propane-1,3-diol and Pentane-1,5-diol by the similar method as shown above.

Method of Characterization: Several solvents reported in table 1 were tested for this purpose. Examination of the information shows that the methylated solvents are good solvents for all the homopolycyanurate. It is also noticed that solubility increases with the temperature and those polymers that have partial solubility at 25±3°C are dissolved at higher temperatures. Homopolycyanurate are soluble in polar aprotic solvents like DMF and DMAc. Aliphatic or aromatic halogenated solvents are non-solvents for polycyanurates.

Table 1. Solubility of Homopolycyanurates in various solvents

Solvent	I	II	III	IV	V	VI	VII	VIII	IX	X
HPCBPS	- $\pm$	--	--	--	--	++	++	++	++	--
HPCBPC	--	--	--	--	--	++	++	$\pm$ +	- $\pm$	--
HPC13DHN	--	--	--	--	--	++	++	++	$\pm$ +	- $\pm$
HPC14DHN	--	--	--	--	--	$\pm$ +	$\pm$ +	$\pm$ +	- $\pm$	--
HPC15DHN	- $\pm$	--	--	--	--	++	++	$\pm$ +	$\pm$ +	- $\pm$
HPC12PD	- $\pm$	--	--	--	--	$\pm$ +	$\pm$ +	- $\pm$	- $\pm$	--
HPC13PD	- $\pm$	--	--	--	--	++	++	- $\pm$	- $\pm$	--
HPC14BD	- $\pm$	--	--	--	--	++	++	$\pm$ +	- $\pm$	--
HPCDM13PD	--	--	--	--	--	++	++	$\pm$ +	$\pm$ +	- $\pm$
HPCDEG	--	--	--	--	--	$\pm$ +	$\pm$ +	$\pm$ +	- $\pm$	--

+ indicate soluble, - indicate insoluble and $\pm$ indicate partly soluble.

Where, the first and second symbol indicates the solubility of homopolycyanurates at room temperature and at 50°C respectively.

Solvent: (I) Acetone (II) Benzene (III) Chlorobenzene (IV) Chloroform (V) Carbon tetrachloride (VI) Dimethylacetamide (VII) Dimethylformamide (VIII) Ethyl acetate (IX) 1,4-Dioxane (X) Methanol.

Density measurement: Density of a polymer is usually determined pyknometrically in a liquid inert to the polymer. The density of each of the polycyanurates was determined at 25±3°C by suspending each of the polycyanurates in a liquid mixture of carbon tetrachloride and methanol and subsequently measuring the density of the liquid mixture by a pycnometer. Measured data are present in table 2. This liquid system found to be inert to all polycyanurates since they remained in a state of suspension even for a prolonged time. Estimated accuracy of density is $\pm 0.001 \text{ g cm}^{-3}$.

The sequence of density of polycyanurates is as follow: HPCBPS > HPCBPC > HPC13PD > HPC14BD > HPC15DHN > HPC13DHN > HPC14DHN > HPC12PD > HPCDEG > HPCDM13PD.

Viscosity measurements: Dilute solution viscosity measurements were carried out using Ubbelohde suspended level viscometer. The polycyanurate sample solutions were prepared in DMF and were filtered through G-3 sintered glass funnel prior to flow time measurements.

Table 2. Density of Homopolycyanurates

Polycyanurate code	Density (g/cm ³)	% Yield
HPCBPS	1.798	70
HPCBPC	1.751	72
HPC13DHN	1.580	66
HPC14DHN	1.460	63
HPC15DHN	1.598	60
HPC12PD	1.448	61
HPC13PD	1.676	69
HPC14BD	1.634	70
HPCDM13PD	1.322	68
HPCDEG	1.333	70

Intrinsic, reduced and inherent viscosity for all the polycyanurates at various concentrations were determined at $25 \pm 3^\circ\text{C}$ temperature. The relative (η_{rel}) and specific (η_{sp}) viscosities were calculated $\eta_{\text{rel}} = t/t_0$ and $\eta_{\text{sp}} = \eta - \eta_0 / \eta_0 = \eta_{\text{rel}} - 1$. Reduced and Inherent viscosities were then calculated from experimental data.

The intrinsic viscosity of the polycyanurates follows the sequence is: HPC12PD < HPC13PD < HPC14BD < HPCBPS < HPCDM13PD < HPC15PD < HPC13DHN < HPC15DHN < HPC14DHN < HPCBPC

Table 3. Solution viscosity of polycyanurate HPCBPS

Conc. g dL ⁻¹	Flow Time (t second)	$\eta_{\text{rel}} = t/t_0$	$\eta_{\text{sp}} = \eta_{\text{rel}} - 1$	$\eta_{\text{red}} = \eta_{\text{sp}}/C$
0.2	185	1.119	0.119	0.598
0.4	207	1.252	0.252	0.632
0.6	229	1.384	0.384	0.641
0.8	257	1.554	0.554	0.693
1.0	282	1.699	0.699	0.699

Solvent: Dimethylformamide (DMF), $t_0 = 166$ second

The values of Huggins and Kraemer coefficients are adequate to evaluate the solvent quality. Experimental results indicate that the values are lower than 0.5 are obtaining from dilute polymer solution in good solvents. Higher the affinity between polymer and solution lower the value of K.

Table 4. Huggins and Kraemer coefficients for Homopolycyanurate

Polycyanurate Code	$[\eta]$	$[\eta_{\text{sp}}/C]$ (dl/g)	$[(\ln \eta_{\text{rel}})/C]$ (dl/g)	Huggins Slope	Kraemer Slope	Huggins constant K_H	Kraemer constant K_K	$K = K_H + K_K$
HPCBPA	0.69	0.821	0.655	0.067	0.099	0.203	0.281	0.484
HPCBPS	0.41	0.457	0.214	0.065	0.035	0.334	0.360	0.694
HPC14AQ	0.21	0.648	0.490	0.089	0.071	0.321	0.172	0.493
HPC18AQ	0.43	0.678	0.455	0.079	0.078	0.223	0.234	0.457
HPCPh	0.55	0.831	0.399	0.064	0.056	0.249	0.173	0.422
HPCR	0.45	0.565	0.289	0.074	0.045	0.298	0.280	0.578
HPCC	0.46	0.612	0.395	0.058	0.030	0.378	0.134	0.512
HPCHQ	0.37	0.569	0.312	0.086	0.029	0.348	0.185	0.569
HPCEG	0.39	0.427	0.198	0.066	0.049	0.384	0.226	0.610
HPCDEG	0.40	0.346	0.795	0.097	0.064	0.432	0.171	0.603

*Concentration of all homopolycyanurates solution is 1 g dL⁻¹ and DMF as solvent.

IR Spectroscopy: An invaluable tool in organic structure determination and verification involves the class of electromagnetic radiation with frequencies between 4000 and 400 cm⁻¹ (wave numbers). The category of electromagnetic radiation is termed infrared (IR) radiation and its application to organic chemistry known as IR spectroscopy.

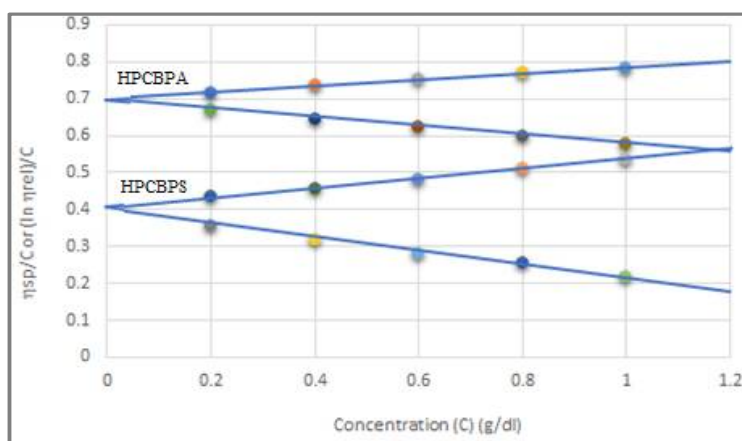


Figure 1. Huggins and Kraemer plots for intrinsic viscosity.

^1H NMR Spectroscopy: High-resolution ^1H NMR is one of the most powerful techniques for the structure determination. Advance-II (Bruker) high-resolution (400 MHz) ^1H NMR spectra of representative polycyanurates samples were scanned in DMSO-d_6 solvent using TMS as an internal reference.

RESULTS AND DISCUSSION

IR spectral data of HPCBPC: 1301.99 cm^{-1} of C-N stretching vibration of amine, 1367.58 cm^{-1} of C-N stretching vibration s-triazine, 1429.30 cm^{-1} of C=C stretching vibration of aromatic ring, 1566.25 cm^{-1} of C-N stretching vibration, 1747.38 cm^{-1} of C-O stretching vibration, 3527.50 of N-H stretching vibration of secondary amine (Figure 2).

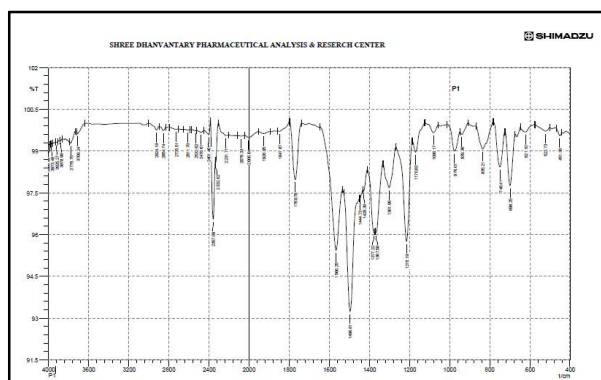


Figure 2. IR Spectrum of HPCBPC.

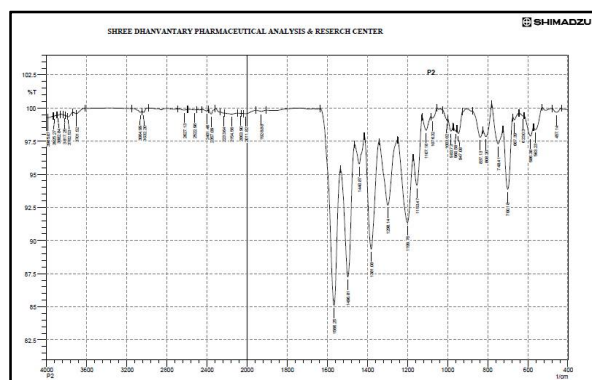
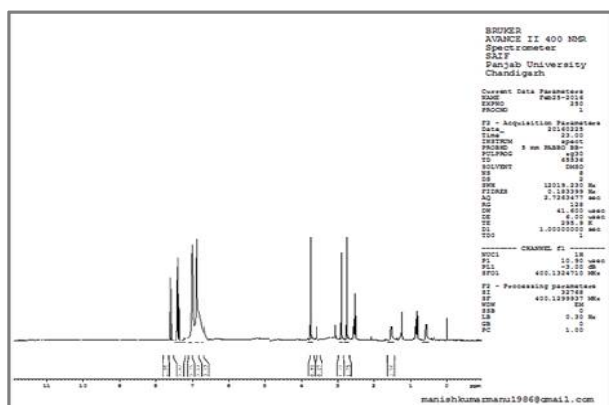
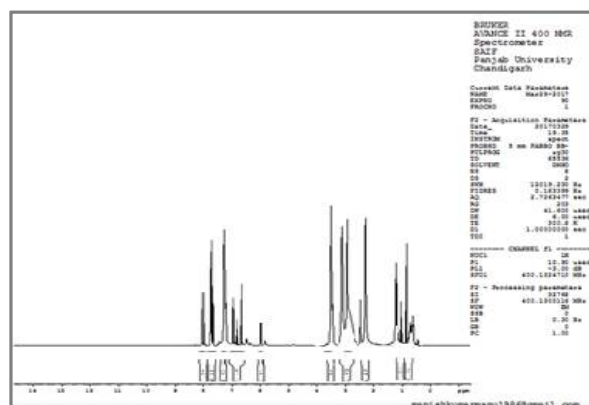


Figure 3. IR Spectrum of HPC13PD.

IR Spectral data of HPC13PD: 837.13 cm^{-1} of Out of plane vibration of s-triazine ring, 1381.08 cm^{-1} C-N Stretching vibration s-triazine, 1440.87 cm^{-1} of C=C stretching vibration of aromatic ring, 1496.81 cm^{-1} of C-H bending vibration of $-\text{CH}_2-$ group, 1735.16 cm^{-1} of C-O stretching vibration, 3032.20 cm^{-1} of C-H stretching vibration of $-\text{CH}_2-$ group, 3284.40 cm^{-1} of N-H stretching vibration (Figure 3).

^1H NMR Spectral data of HPCBPC: 1.5δ ppm (M) of $-\text{CH}_2-$ group of cyclohexane, 2.0 - 2.5δ ppm (M)- CH_2- linkage, 6.7 - 7.5δ ppm (M) of aromatic ring proton (Figure 4).

^1H NMR spectral data of HPC13PD: 1.7 - 2.2δ ppm (M) $-\text{CH}_2$ group of propane diol, 7.2 - 7.8δ ppm (M) $-\text{CH}$ group of aromatic ring (Figure 5).

Figure 4. ^1H NMR Spectrum of HPCBPC.Figure 5. ^1H NMR spectrum of HPC13PD.

Thermogravimetric analysis: The polymeric materials are subjected to high temperature during process and use; therefore, it is necessary for polymeric material to have certain degree of thermal stability. Thermal analysis is used to identify the degree of curing and to study the kinetics of degradation reactions. Such investigations assist in establishing criteria for the selection of materials in specialty applications.

Different workers define thermal stability in many different qualitative and arbitrary ways. Reich and Levi described arbitrary methods for the assessment of thermal stability of polymers from TG traces by the visual observation of thermograms. Several temperature characteristics used for the qualitative assessment of relative thermal stability of polymers are initial temperature (T_0), temperature for 10% weight loss (T_{10}), temperature for maximum rate of decomposition ($T_{\max}$) and half volatilization temperature (T_s). These parameters have proved very useful to appraise, at least qualitatively, thermal stability of the polymer. These characteristic data are presented in table 5.

For half volatilization temperature, the thermal stability of polymer is as follow: REBPS-I > REBPA-I > REHQ-I.

Table 5. Temperature ($^{\circ}\text{C}$) characteristics of polycyanurates

Polymer	T_0	T_{10}	$T_{\max}$	T_s
HPCBPC	94	137	212	343
HPC13PD	87	123	234	234
HPCDEG	113	110	321	321

T_0 = Initial temperature, T_{10} = Temperature for 10% weight loss, $T_{\max}$ = Temperature for maximum rate of decomposition, T_s = Half volatilization temperature.

Thermal stability of the polycyanurates can also be established based on $T_{\max}$ for the first step of decomposition. The thermal stability of polycyanurates decreases in the following order. T_{10} data obtained from their respective thermograms of the polycyanurates also follows below order. HPCBPC > HPC13PD > HPCDEG.

Degradation data of the thermograms states that HPCBPC is more stable than propyl linkage of HPC13PD, propyl linkage HPC13PD of is more stable than diethylene glycol linkage of HPCDEG.

Thermogram of HPCBPC: The thermal degradation of HPCBPC is shown in figure 6. The polymer begins to decompose at about 71°C . However, the small initial weight loss may be due to presence of small amount of solvent or absorbed moisture. Maximum degradation is extended up to 791°C . The maximum rate of weight loss occurs at 250°C . At 791°C about 7 % residue left out.

Thermogram of HPC13PD: The thermal degradation of HPC13PD is shown in figure 7. The polymer begins to decompose at about 81°C. However, the small initial weight loss may be due to presence of small amount of solvent or absorbed moisture. Maximum degradation is extended up to 795°C. The maximum rate of weight loss occurs at 180 °C. At 795°C, about 21 % residue left out.

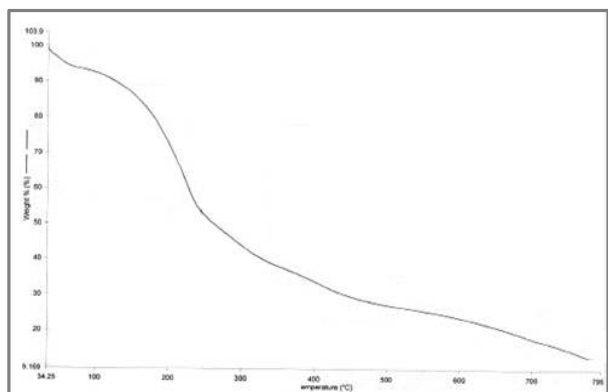


Figure 6. Thermogram of HPCBPC.

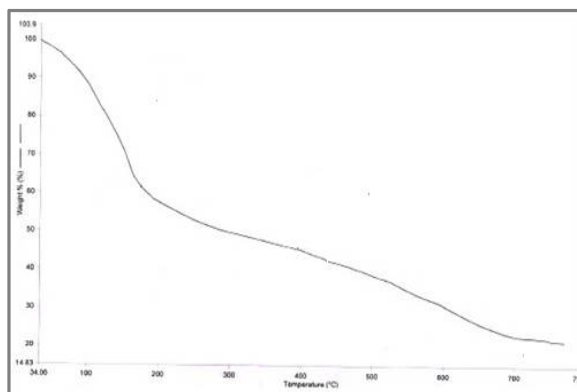


Figure 7. Thermogram of HPC13PD.

Thermogram of HPCDEG: The thermal degradation of HPCDEG is shown in figure 8. The degradation starts around 200°C and proceeds up to 791°C involving 80% weight loss with a maximum rate at 270°C and 25 % residue left out.

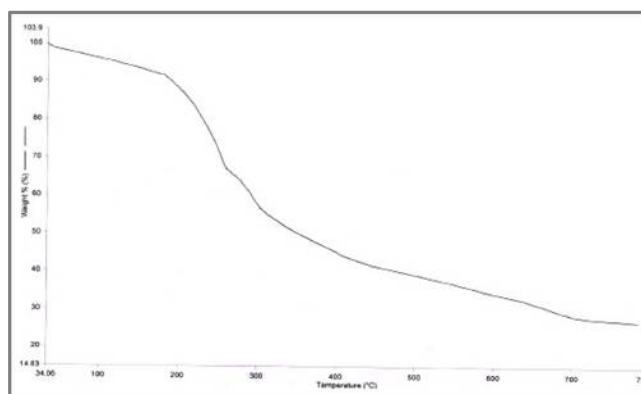


Figure 8. Thermogram of HPCDEG.

APPLICATION

Some of the synthesized homopolycyanurates are soluble in some common solvents, thus they can be reuse. The synthesized homopolycyanurates are found to be stable more than 350°C temperature thus it can be used for high temperature applications.

CONCLUSION

Methylated solvents are found to be good solvents for all the homopolycyanurates. It is also noticed that solubility increases with temperature and those homopolycyanurates that have partial solubility at 25°C get dissolved at higher temperature. All the polyesters are soluble in polar aprotic solvents like DMF and DMSO. DMF is found to be best solvent for all the polycyanurates. The density of homopolycyanurates is measured pycnometrically, the highest density is 1.798 g cm⁻³ is found for HPCBPS while lowest density is 1.322 g cm⁻³ found for HPCDM13PD. Intrinsic viscosity, reduced viscosity and inherent viscosity for all the homopolycyanurates at various concentrations were

determined by using Huggins and Kraemer method at $25\pm 1^\circ\text{C}$ temperature. The homopolycyanurates are found to stable more than 350°C temperature thus it can be used for high temperature applications.

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