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Synthesis and Studies of Homopolycyanurates Based on 2-Carbazol-4,6-Dichloro-s-Triazine

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Abstract—Eight homopolycyanurates have been synthesized by interfacial polycondensation of 2-carbazol-4,6-dichloro-s-triazine with 1,7-dihydroxynaphthalene, 1,4-dihydroxyanthraquinone, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,4-butanediol and 1,8-dihydroxyanthraquinone. All the homopolycyanurates synthesized were characterized for their solubility, density, viscosity, IR, NMR spectral and thermogravimetric parameters.

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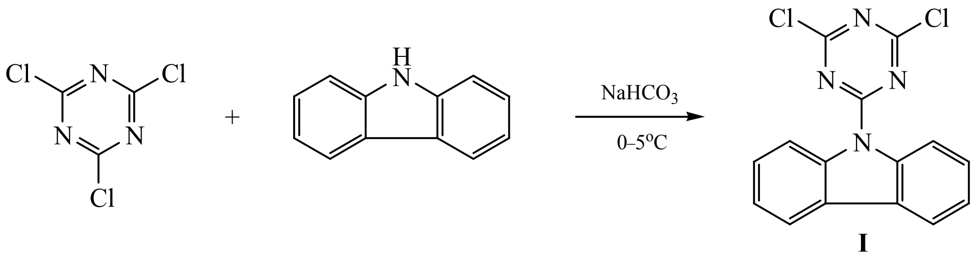
The research and development in the field of polymer are always sought with an intermediate use. Nowadays, the use of polymers rapidly increases in nearly every region of the world. Research in the area of s-triazine derivatives leading to the fundamental knowledge of novel polymers has become increasingly wide-spread in recent years. The current research and development work in this field involves studies of the ways in which polymer can be modified to make them suitable for the specific applications. Research is now focused on the materials that are not only stable but also processable and therefore usable. A typical approach in this direction is to utilize the stable ring system such as triazine and search for method to connect this nucleus with thermally stable linkage such as an ether linkage and aliphatic linkage, which imparts flexibility and solubility along with thermal stability.

A review of literature reveals that s-triazine and its derivatives have been known since 1873, but polymers with their incorporation in chain began to be extensively studied and utilized only in the late 1950's. Polymers containing s-triazine ring in the main chain have certain properties like high resistance to heat and chemical attack, good mechanical and dielectric properties and ease of process ability [1] and they are generally infusible and insoluble. Various polycyanurates are used in structural composites with glass or carbon fibers, casting resins and binders for miscellaneous organic or inorganic substrates, stabilizers for plastics or as films, fibers or lacquer components [2, 3].

Recently, various polyesters and polyamides based on s-triazine derivatives have been synthesized in our laboratory [4–7]. To continue our work, present investigation describes synthesis and studies of some novel homopolycyanurates based on s-triazine derivatives. The findings of *the present* investigation are to explore experimental conditions for the synthesis of polymers by interfacial technique and hence, to select suitable reaction conditions, to study the effect of certain specific structural features in the polymer backbone, to investigate kinetics of thermal degradation of polymers synthesized and to study the effect of chemical structure of diols on the polymers.

Homopolycyanurates were synthesized via the interfacial condensation of 2-carbazol-4,6-dichloro-s-triazine **I** with such diols as 1,7-dihydroxynaphthalene, 1,4-dihydroxyanthraquinone, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,4-butanediol and 1,8-dihydroxyanthraquinone. Synthesis of the starting 2-carbazol-4,6-dichloro-s-triazine **I** was performed in accordance with the reaction scheme (1). The following polycondensation of s-triazine **I** with 1,7-dihydroxynaphthalene (2) was used as a model reaction for the formation of linear aromatic polycyanurate via an interfacial poly-



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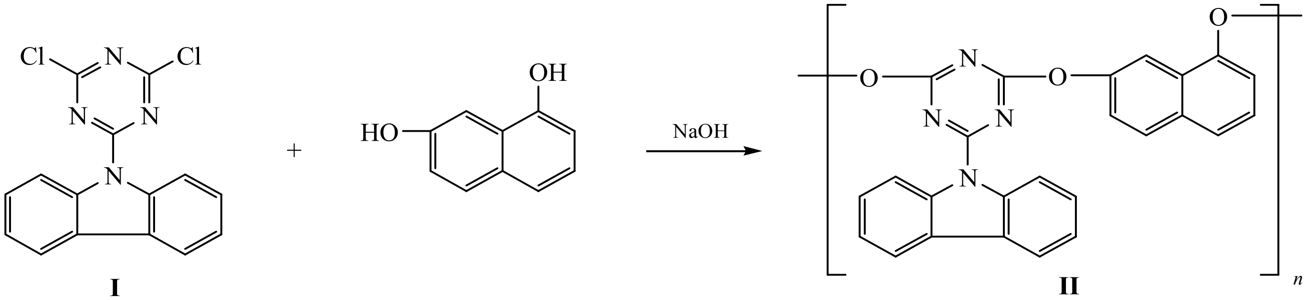

I II (2)

merization. The formation of polycyanurate is based on the Schotten–Baumann reaction, in which an acid chloride reacts with a compound containing hydrogen atom (OH, NH, SH) in the presence of aqueous alkali solution.

Using the reaction (2), we obtained homopolycyanurates **III**–**IX** starting from 1,4-dihydroxyanthraquinone, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,4-butanediol and 1,8-dihydroxyanthraquinone, respectively.

The yield of homopolycyanurates vary from 56 to 78% depending on the reactivity of diol component in the polymer chain. Highest yield (78%) was obtained for polymer based on 1,8-dihydroxyanthraquinone and lowest (56%) for polymer based on ethylene glycol.

Table 1. Yields, color and densities of polymers **II**–**IX**

Polymer	Yield, %	Color	Density, g cm^{-3}
II	76	White	1.233
III	72	Reddish brown	1.244
IV	56	Light brown	1.186
V	59	Light brown	1.209
VI	61	Light brown	1.221
VII	58	Light brown	1.195
VIII	62	Light brown	1.199
IX	78	Reddish brown	1.247

The color of the homopolycyanurates synthesized was caused by the color and stereochemistry of the diols used. The yield and color of all homopolycyanurates **II**–**IX** are summarized in Table 1. All the homopolycyanurates synthesized were characterized for their solubility, density, viscosity, IR and NMR spectral parameters.

Density of the polymers **II**–**IX** was pycnometrically determined at 25°C by the use of suspension method, which is especially suitable to powdered samples [8]. Density of the homopolycyanurates varies from 1.186 to 1.247 gm cm^{-3} and changes as follows: **IV** < **VII** < **VIII** < **V** < **VI** < **II** < **III** < **IX** (Table 1).

Solubility for all the obtained homopolycyanurates was examined in such solvents as acetone, chloroform, methylene chloride, dichloroethane, trichloroethane, tetrachloroethane, dimethyl formamide, dimethylsylfoxide and nitrobenzene. All polymers were found to be very soluble in acetone, and poorly, in dimethylsulfoxide. Note that the chlorinated solvents having solubility parameter in the range of 9.3–10.4 cal cm^{-3} are good solvents for all the polymers. Among these chlorinated solvents, chloroform is found to be best solvent. The high solubility of these polymers in chloroform is attributed to hydrogen bond donor characteristics of chloroform. Since hydrogen atom in chloroform is highly acidic, it can participate in hydrogen bonding interaction with oxygen of the ether bond. Aliphatic or aromatic hydrocarbons, alcohols and aliphatic ethers are non-solvents for the polymers. It is also observed that the solubility of the polymers

Table 2. Solubilities of homopolycyanurates **II–IX** in various solvents[a]

Solvent	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
Chloroform	±+	±+	++	++	++	++	++	±+
Dichloroethane	±+	±+	++	++	++	++	++	±+
Dichloromethane	±+	±+	++	++	++	++	++	±+
Trichloroethylene	±+	±+	++	++	++	++	++	±+
Tetrachloroethane	±+	±+	±+	±+	±+	++	++	±+
Dimethylformamide	++	++	+ +	++	++	++	++	++
Dimethylsulfoxide	–±	–±	–±	–±	–±	–±	–±	–±
Dioxane	++	++	++	++	++	++	++	++
Nitrobenzene	++	++	++	++	++	++	++	++
Chlorobenzene	++	±+	±+	±+	±+	±+	±+	±+
Cyclohexanone	±+	±+	++	++	++	±+	±+	–±
Tetrachloroethane + phenol (50:50%)	– –	–±	±±	±±	±±	–±	–±	–±

[a] The first and second symbol indicate the solubility of polymer at room temperature and 50ºC, respectively. (+) soluble, (–) insoluble, (±) partly soluble.

increase with increase in temperature. The polymers which are partly soluble at 25±3°C are dissolved at higher temperature. The data on the relative solubility of homopolycyanurates **II**–**IX** are shown in Table 2.

The IR spectra of homopolycyanurates **II–IX** exhibit characteristic absorption bands in the region of 810 cm^{-1}, which are attributed to out-of-plane and in-plane vibrations of the s-triazine ring respectively. In the IR spectra of the homopolycyanurates involving aromatic diols in their backbone there are bands in the region 780–650 cm^{-1} originating from the out-of-plane bending vibrations of C–H bonds of aromatic ring. The bands in the region 1140–980 cm^{-1} may be attributed to the vibration of aryl–ether bond and the in-plane bending vibration of aromatic C–H in homopolymers [9–13]. The homopolycyanurates involving aliphatic diols in their backbone exhibits the bands in the range of 1125–970 cm^{-1} belonging to the alkyl-ether bond. The absorption bands observed at 1330, 1340 and 1600–1590 cm^{-1} are attributed to aromatic C–N bond stretching vibrations. The bands in the region 1490–1400 cm^{-1} are attributed to the skeletal stretching vibrations of aromatic and heteroaromatic rings. The absorption bands at 2910–2820 and 3060 cm^{-1} are assigned to the saturated aliphatic C–H bond stretching vibrations.

The IR and NMR spectral parameters are listen in Tables 3, 4.

Viscosity for all the eight homopolycyanurates at various concentrations was determined at 25±0.1°C. Reduced and inherent viscosities were calculated from experimental data. Typical Huggin's and Krammer's plots were used to obtained intrinsic viscosity for each

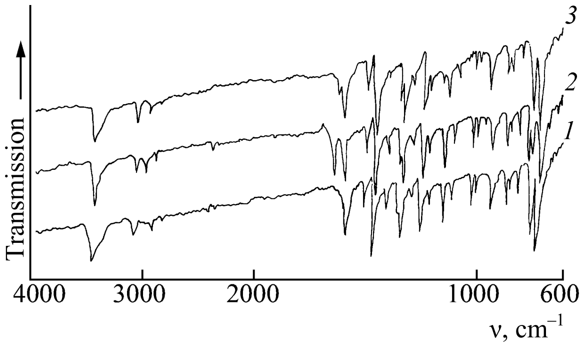

Fig. 1. IR spectra of the polymers: (*1*) **II**, (*2*) **III**, and (*3*) **IV**.

Table 3. IR spectral parameters for homopolycyanurates **II**–**IX**

Polymer	ν, cm^{-1}
II	650 w, 720 s, 780 s, 810 s, 860 s, 1000 m, 1010 s, 1110 s, 1210 s, 1230 s, 1330 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3020 w, 3440 br
III	650 w, 720 s, 760 s, 780 s, 810 s, 860 s, 980 s, 1020 m, 1080 s, 1210 s, 1230 s, 1330 s, 1590 s, 1400 m, 1450 s, 1490 s, 1630 s, 2820 w, 2910 s, 3040 w, 3100 w, 3420 br
IV	650 w, 720 s, 780 s, 810 s, 835 s, 860 s, 970 s, 1090 m, 1120 s, 1200 w, 1240 s, 1340 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3060 w, 3440 br
V	650 w, 720 s, 780 s, 810 s, 835 s, 860 s, 980 s, 1090 w, 1125 s, 1200 m, 1240 s, 1340 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3040 w, 3440 br
VI	650w, 720s, 780s, 810 s, 835s, 860s, 980s, 1040s, 1100w, 1120 m, 1190 m, 1240 s, 1260 s, 1340 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3060 w, 3440 br
VII	650 w, 720 s, 780 s, 810 s, 835 s, 860 s, 980 s, 1040 s, 1100 w, 1120 m, 1210 m, 1250 s, 1340 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3060 w, 3440 br
VIII	650 w, 720 s, 780 s, 810 s, 835 s, 860 s, 980 s, 1040 s, 1100 w, 1120 m, 1205 m, 1240 s, 1340 s, 1600 s, 1400 m, 1450 s, 1490 s, 2820 w, 2910 s, 3060 w, 3440 br
IX	650 w, 720 s, 760 m, 780 s, 810 s, 860 s, 980 s, 1010 m, 1080 s, 1120 m, 1205 w, 1240 s, 1330 s, 1590 s, 1400 m, 1450 s, 1490 s, 1630 s, 2820 m, 2910 s, 3060 w, 3410 br

of the homopolycyanurates. Viscosity of the chloroform solutions of homoplycyanurates **II**–**IX** at different concentration is shown in Table 5. Intrinsic, reduced and inherent viscosities along with Huggin's and Krammer's constants for 1% solution of all the homopolycyanurates obtained are given in Table 6. The Huggin–Krammer's plots to determine intrinsic viscosity for the polymers **II**, **III**, **V**, **VIII** are presented in Fig. 2.

By the analysis of the data from Tables 5, 6, the polymer **II** has the highest solution viscosity and hence, the highest molecular weight among all the homopolycyanurates, whereas the polymer **VII** has the lowest. The intrinsic viscosity of the homopolycyanurates follows the sequence given below: **II** > **IX** > **III** > **IV** > **V** > **VI** > **VIII** > **VII**. This may be attributed to the strength of basicity of diols. The basicity of diols and hence reactivity towards a nucleophilic substitution reaction is higher for a less acidic diols. 1,7-Dihydroxynaphthalene is less acidic and hence most reactive among all the diols used in the present investigation, while 1,2-propane is highly acidic and hence less reactive amongst the diols. Thus, the reduced viscosity values may also reflect the order of reactive reactivity in nucleophilic substitution reaction of these diols.

Table 4. NMR spectral parameters for homopolycyanurates **II**–**IX**

Polymer	Chemical shift, δ (ppm)
II	6.80–7.48 m (Ar-H)
III	7.05–7.93 m (Ar-H)
IV	4.74 s (CH_2), 6.93–7.64 m (Ar-H)
V	3.87 t (CH_2), 4.46 t (CH_2), 6.90–7.55 m (Ar-H)
VI	3.50 s (CH_2), 3.78 t (CH_2), 4.53 t (CH_2), 7.18–7.74 m (Ar-H)
VII	1.31 d (CH_3), 4.12 d (CH_2), 5.33 m (CH), 7.22–7.70 m (Ar-H)
VIII	2.18 t (CH_2), 3.76 t (CH_2), 7.12–7.63 m (Ar-H)
IX	6.93–7.57 m (Ar-H)

Table 5. Viscosity of homopolycyanurate **II** chloroform solutions at 25°C (t_0 91 s)

s, g dl^{-1}	t, s	$\eta_{rel} = t/t_0$	$\eta_{sp} = \eta_{rel}-1$	η_{sp}/c	ln (η_{rel}/c)
0.2	100.6	1.1055	0.1055	0.5275	0.5015
0.4	110.8	1.2176	0.2176	0.5440	0.4945
0.6	121.5	1.3352	0.3352	0.5586	0.4922
0.8	132.5	1.4560	0.4560	0.5700	0.4696
1.0	144.5	1.5879	0.5879	0.5879	0.4624

Table 6. Viscosities values and constants of Huggins and Kraemer equation for homopolycyanurates **II**–**IX** solutions (c 10 g dl^{-1})

Polymer	Intrinsic viscosity, η	Reduced viscosity, η_{sp}/c	Inherent viscosity, ln (η_{rel}/c)	Huggins constant, K	Kraemer constant, β
II	0.5125	0.5879	0.4624	0.2871	0.1905
III	0.4450	0.5020	0.4058	0.2879	0.1980
IV	0.4215	0.4747	0.3850	0.2994	0.2050
V	0.3795	0.4238	0.3542	0.3076	0.1756
VI	0.3550	0.3850	0.3220	0.2381	0.2619
VII	0.2800	0.3000	0.2610	0.2551	0.2420
VIII	0.3180	0.3480	0.2980	0.2967	0.1978
IX	0.4655	0.5181	0.4100	0.2423	0.2561

Thermal stability is most desirable property of the polymer. If the thermal stability of polymer is increased, it is accompanied by an increase in strength modules, rigidity and softening temperature. The thermal degradation reaction of a specific polymer depends upon a large number of variables like decomposition temperature, heating rate, rate of removal of volatile products from reaction zone, softening and melting points of the polymer, sample size and dimension, presence of oxygen in the atmosphere or absorbed in the sample or other occluded impurities, the initiator used and the mechanism of termination in the original preparation of the polymer. Therefore, thermal decomposition is carried out under inert atmosphere with carefully purified polymers in the form of finely divided powder.

Thermogravimetric curves for all the homopolycyanurates **II**–**IX** were obtained at a scan rate of 10 deg min^{-1}. The polymer **II** begins to decompose at about 230°C (Fig. 3, curve *1*). Slight initial weight loss below 230°C may be due to the presence of the absorbed moisture or associated solvent. The polymer decomposes with a rapid weight loss (47.50%) in the temperature range of 360–500°C. The maximum rate of weight loss occurs at 440°C. Beyond 530°C, the second decomposition step commences with 31.50% loss of its weight with a slower rate compared to the first step. The overall decomposition leaves about 20.75% residue. The polymer **III** exhibits two distinct steps of decomposition (Fig. 3, curve *2*). The first step is in the range of 310–500°C. The maximum rate of decomposition occurs at 400°C. The polymer loses 56.5% of its weight in this step. The second step commences in the range of 610–700°C. The maximum decomposition rate occurs at 640°C. The polymer losses 26.0% of its weight in this step and the overall decomposition leaves about 17.5% residue at the end.

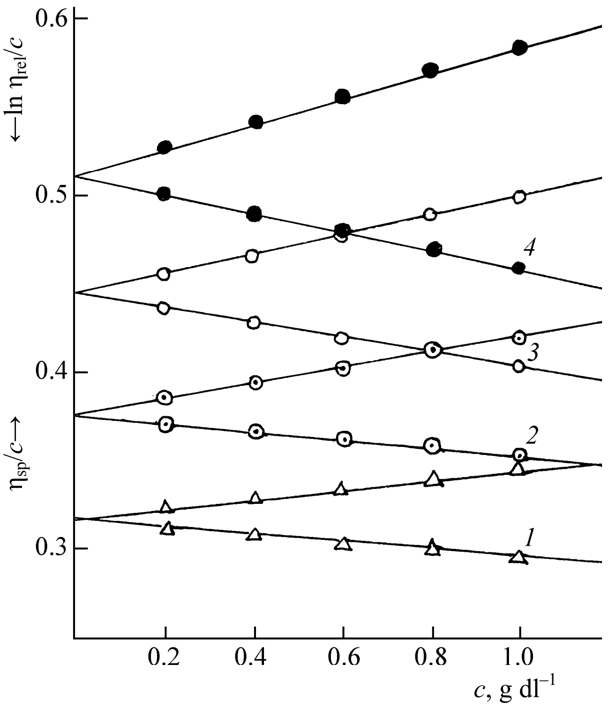

Fig. 2. Huggin's and Krammer's plots of intrinsic viscosity for the polymers: (*1*) **VIII**, (*2*) **V**, (*3*) **III**, and (*4*) **II**.

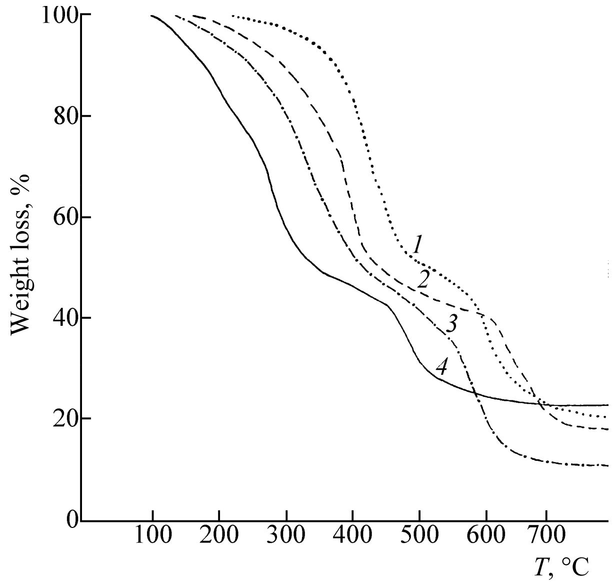

Fig. 3. Decomposition thermograms for the polymers: (*1*) **II**, (*2*) **III**, (*3*) **V**, and (*4*) **VII**.

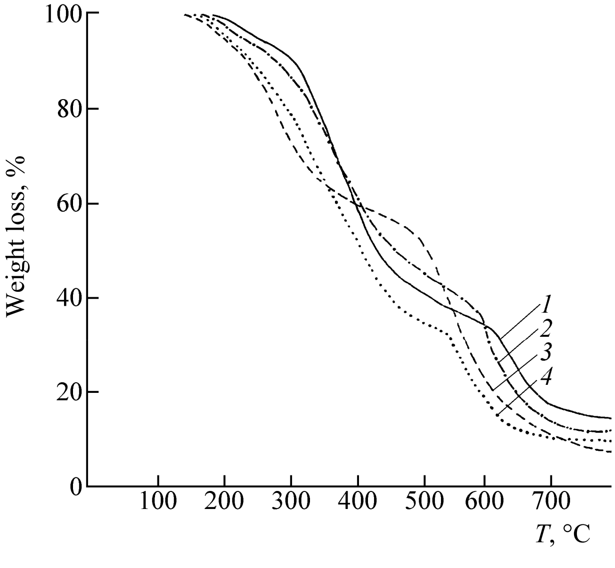

Fig. 4. Decomposition thermograms for the polymers: (*1*) **IX**, (*2*) **IV**, (*3*) **VI**, and (*4*) **VIII**.

The thermogram of **IV** exhibits two distinct steps. The decomposition starts at about 170°C with maximum decomposition rate at 370°C (Fig. 4, curve *2*). The polymer loses 54.50% of its weight up to 500°C. The second step begins at about 540–700°C, during which the polymer loses 32.75% of its weight. The maximum rate of decomposition occurs at 600°C. The overall decomposition leaves about 12.75% residue at the end.

The polycyanurate **V** loses 51.0% of its weight in the temperature range of 270–440°C with maximum rate at 340°C. The second decomposition step begins in the range of 530–640°C. The homopolymer looses 38.5% of its weight in this step (Fig. 3, curve *3*).

The thermogram of **VI** shows two distinct steps of decomposition (Fig. 4, curve *3*). The polymer begins to decompose at about 130°C. The decomposition is marked with a rapid weight loss in the range of 210–380°C, during which the polymer loses 38.0% of its weight. The maximum rate of decomposition occurs at 280°C. The second decomposition step commences with 53.5% lose of its weight, having faster rate of weight lose compared to the first step. The decomposition leaves about 8.5% weight at the end.

In the temperature range 190–360°C the polymer **VII** loses 51.5% of its weight (Fig. 3, curve *4*). The maximum rate of weight loss occurs at 290°C. Beyond 450°C the second decomposition step commences with loss of 26.0% of its weight, having low rate of weight lose compared to the first step. The maximum rate of the weight loss occurs at 490°C. The overall decomposition leaves at about 22.5% residue at the end.

The overall degradation of the polymer **VIII** comprises two steps (Fig. 4, curve *4*). The first step encompassing a temperature range of 260–510°C, involves about 63.5% of weight loss. The rate of weight loss reaches a maximum at 340°C. The second step of degradation begins at 520–620°C, which involves about 25.0% of weight loss. The maximum rate of weight loss occurs at 560°C.

Similarly, the overall thermal degradation of **IX** also involves two distinct steps (Fig. 4, curve *1*). At 300°C the first step of degradation starts and extends up to 460°C, showing about 54.0% weight loss, with a maximum rate of weight loss at 380°C. Above 590°C, the second step of decomposition begins, which involves further weight loss of 31.0% up to 700°C with a maximum rate at 640°C.

The characteristic temperature for the assessment of relative thermal stability of homopolycyanurates such as initial decomposition temperature (T_0), temperature for 10% weight loss (T_{10}), temperature for maximum decomposition rate ($T_{\max}$) and temperature for half weight loss (T_s) are represented in Table 7.

Thermal stability of homopolycyanurates **II**–**IX** was established on the basis of $T_{\max}$ values for the first step of decomposition. The thermal stability of

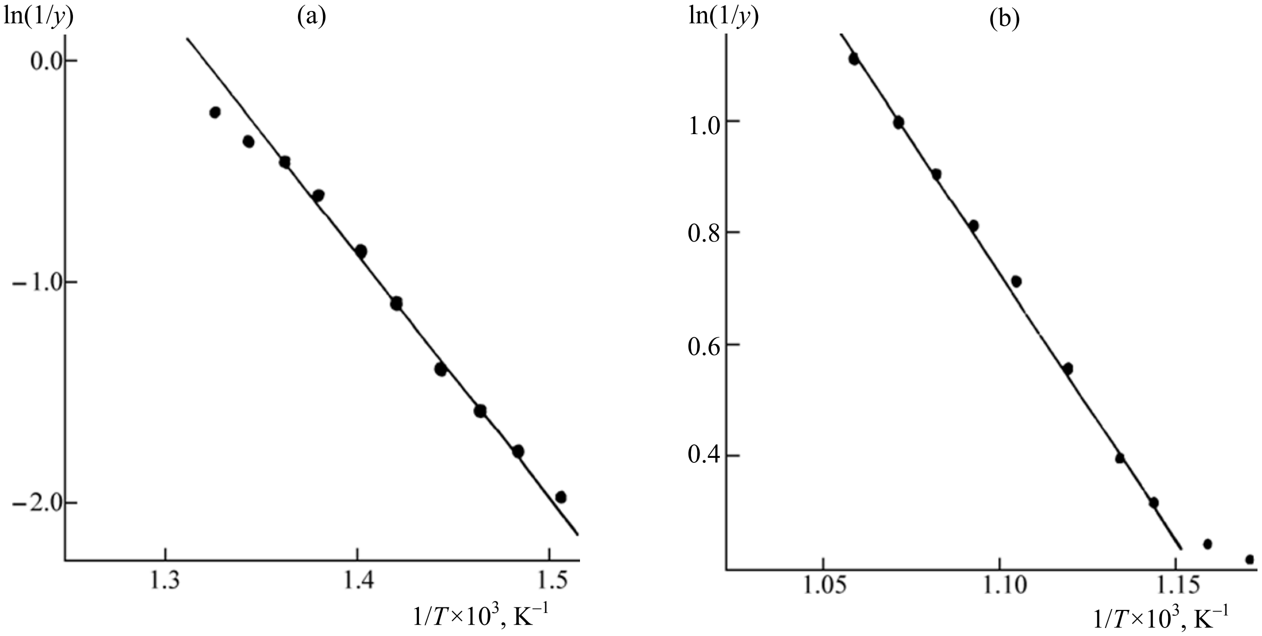

Fig. 5. Broido's plot for the thermal degradation of the polymer **II**. (a) I stage and (b) II stage.

homopolycyanurates increased in the following sequence: **VI** < **VII** < **V** ≈ **VIII** < **IV** < **IX** < **III** < **II**. This indicates that the thermal stability of the polymers increases with an increase in its molecular weight. The thermal stability based on a half weight loss temperature T_s follows somewhat different sequence. The thermal stability increase as follows: **VII** < **VIII** < **V** < **III** < **IV** < **VI** < **IX** < **II**. Thus, the homopolycyanurates **VII** derived from 1,2-propane diol is least stable while the homopolycyanurate **II** based on 1,7-dihydroxynaphthalene possess highest thermal stability.

Dynamic TGA curves obtained at a heating rate of 10 deg min^{-1} were analyzed using the graphical methods, proposed by Broido (Fig. 5) and Horowitz and Metzger (Fig. 6). A typical application of this analysis is exemplified for the polymer **II** in Tables 8, 9. The straight lines are due to the linear regression analysis of the experimental data. Since the magnitude of an apparent activation energy for the degradation reaction reflects the ease with which it can proceed, it can be used to the approximate relative ease of the polymer thermolysis, and hence their relative thermal stability.

The values of apparent activation energy corresponding to the different degradation steps evaluated by the least squares methods are presented in Table 10. Analysis of this data shows that both the methods give the comparable values. The experimental points corresponding to the initial stage (10% weight loss) of the thermal degradation tended to deviate from linearity. This deviation may be due to fact that the decomposition of solids does not obey first order kinetics in the initial stages.

Between the two methods, the Broido's method is expected to provide reliable estimates of E_a since no other temperature characteristics involves. The activation energy value for the first step varies from

Table 7. Thermogravimertic analysis data for homopolycyanurates **II**–**IX**

Polymer	T_0, °C	T_{10}, °C	T_{max}, °C		T_s, °C	Residue at 800°C, %
			stage I	stage II		
II	230	380	440	610	525	20.75
III	190	300	400	600	450	17.50
IV	170	280	370	600	475	12.75
V	140	245	340	570	420	10.50
VI	130	240	280	560	510	08.50
VII	110	200	290	490	350	22.50
VIII	150	250	340	560	415	11.50
IX	200	315	380	650	515	14.75

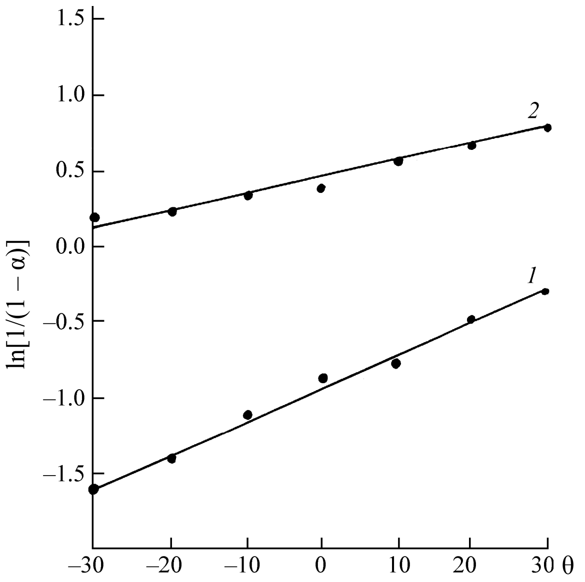

Fig. 6. Horowitz–Metzger's plot for the thermal degradation of the polymer **II**. (*1*) I stage and (*2*) II stage.

24.93 to 9.03 K cal mol^{-1} according to the Broido's method. The E_a values calculated according to the Horowitz and Metzger's method are in a good agreement with these values. The activation energy for the second step, in case the polymers **IV**–**IX** are higher than those for the first step, while in case of the compound **II** and **III** these value are lower than those for the first step of the thermal degradation. Analysis of the data of Table 10 indicates that the polymer **II** has the highest value of activation energy for the initial stage of the thermal degradation, while the polymers **IV**–**VIII** have the lower activation energies values.

Owing to the aromaticity, the homopolycyanurates derived from naphthalene diols are expected to be most thermally stable among all the homopolymers, but only homopolycyanurate **II** involving 1,7-dihydroxynaphthalene follows this assumption closely.

Further examination of the relative stability of the obtained polymers **II**, **III** and **IX** indicates that the decomposition beginning depends on the nature of the aromatic diol component of the molecular chain. Thus, the results of the qualitative and semiquantitative treating the dynamic thermogravimetric data for the obtained polymers indicates that the inclusion of bisphenol-s and symmetric dihydroxynaphthalene

Table 8. Thermogravimertic analysis data for homopolycyanurate **II** by the Broido's method (heating rate 10 deg min^{-1})

T, °C	Weight loss, %	$y = (W_t - W_\alpha)/(W_t - W_0)$	$1/y$	ln $(1/y)$	$1/T \times 10^3$, K^{-1}
I stage					
390	89.50	0.8675	1.1527	–1.9510	1.5084
400	87.50	0.8423	1.1873	–1.7623	1.4859
410	85.50	0.8170	1.2239	–1.5991	1.4641
420	83.00	0.7855	1.2731	–1.4211	1.4430
430	77.00	0.7098	1.4089	–1.0706	1.4225
440	72.50	0.6530	1.5314	–0.8529	1.4025
450	66.00	0.5710	1.7514	–0.5791	1.3831
460	63.00	0.5331	1.8757	–0.4636	1.3643
470	59.00	0.4827	2.0719	–0.3168	1.3459
480	56.50	0.4511	2.2168	–0.2281	1.3280
II stage					
580	44.00	0.2934	3.4086	0.2040	1.1723
590	43.00	0.2808	3.5618	0.2392	1.1588
600	41.00	0.2555	3.9136	0.3108	1.1455
610	39.00	0.2303	4.3425	0.3842	1.1325
620	34.50	0.1735	5.7636	0.5605	1.1198
630	31.00	0.1239	7.7317	0.7156	1.1074
640	29.00	0.1041	9.6061	0.8164	1.0953
650	27.50	0.0852	11.7407	0.9014	1.0834
660	26.00	0.0662	15.0952	0.9986	1.0718
670	24.50	0.0473	21.1333	1.1154	1.0605

Table 9. Thermogravimertic analysis data for homopolycyanurate **II** by the Horowitz–Metzger's method (heating rate 10 deg min^{-1})

T, °C	α	1 – α	1/1 – α	ln [1/(1 – α)]	θ
I stage					
410	0.1830	0.8170	1.2239	–1.5991	–30
420	0.2145	0.7855	1.2731	–1.4211	–20
430	0.2902	0.7098	1.4089	–1.0706	–10
440	0.3470	0.6530	1.5314	–0.8529	0
450	0.4290	0.5710	1.7514	–0.5791	10
460	0.4669	0.5331	1.8757	–0.4636	20
470	0.5173	0.4827	2.0719	–0.3168	30
II stage					
580	0.7066	0.2934	3.4086	0.2040	–30
590	0.7192	0.2808	3.5618	0.2392	–20
600	0.7445	0.2555	3.9136	0.3108	–10
610	0.7697	0.2303	4.3425	0.3842	0
620	0.8265	0.1735	5.7636	0.5605	10
630	0.8761	0.1239	7.7317	0.7156	20
640	0.8959	0.1041	9.6061	0.8164	30

Table 10. Kinetic parameters for thermal decomposition of homopolycyanurates **II**–**IX**

Polymer	Activation energy, E_a (kcal mol^{-1})			
	Broido's method		Horowitz–Metzger's method	
	stage I	stage II	stage I	stage II
II	24.93	18.54	25.66	19.27
III	16.63	12.29	16.16	12.13
IV	8.57	14.12	8.99	14.28
V	10.11	12.66	10.56	13.03
VI	9.75	16.44	9.76	16.27
VII	9.03	10.68	9.30	11.99
VIII	9.20	13.33	9.37	13.34
IX	14.23	15.81	13.83	15.63

fragment into a homopolymer chain is advantageous because of higher thermal stability of the polymers. In addition, such incorporation does not adversely affect the solubility of the homopolymer.

Therefore the properties of homopolycyanurates **II**–**IX** depend largely upon the structure and their preparation way. These properties are influenced by the nature of substituents on the s-triazine nucleus and also by the nature of diol component of the polymer chain.

EXPERIMENTAL

The bidistilled water was used for the solutions preparation. Chloroform (RANBAXY) was washed three times with distilled water to remove the alcohol traces following by the treating with anhydrous calcium chloride for 24 h and finally distilling. Benzene (BDH) was treated with concentrated sulfuric acid in separating funnel to remove thiophene traces and then thoroughly washed with water to remove the acid. It was then treated with anhydrous calcium chloride for 24 h and finally distilled. Other solvents such as nitrobenzene, carbon tetrachloride, petroleum ether, dimethyl formamide, acetone and methanol were all laboratory reagents and were used as received. The chemicals such as sodium hydroxide pellets and sodium bicarbonate were used as received. Cyanuric chloride (Fluka) was purified by the recrystallization from pure benzene. Ethylene glycol (Merck), diethylene glycol (Merck), triethylene glycol (Merck), 1,2-propanediol (Merck) and 1,4-butanediol (Merck) were used as received.

The density of each of the eight homopolycyanurates was determined at 25±3°C by suspending each of the homopolycyanurates in a liquid mixture of carbon tetrachloride and petroleum ether using a picnometer. This liquid system is found to be inert to all the polycyanurates since they remained in a state of suspension even for a prolonged time. The estimated accuracy of is ±0.001 g cm^{-1}.

To the solubility studying, 30–50 mg of a polymer sample was placed into a small test tube and 1 ml of solvent was added to each. The mixtures were stored at 25ºC for sometime with occasional shaking. The precipitate formation indicates dissolution. The polymer samples that swelled without dissolving at 25°C were heated to 50°C in order to affect the process of dissolution.

The infrared spectra of all the polymers were recorded on a Perkin Elmer spectrophotometer 781 from KBr pellets. A mixture of 250 mg of KBr and 1.0 mg of a polymer sample was mixed intimately and ground in mortal with glass beeds. The ground mixture was then transferred to the mould and disc was prepared by pressing it in a hydraulic press [14].

The viscosity of the dilute polymer solutions was conveniently measured using a capillary viscometer of the Ubbelohde type [15]. The NMR spectra were recorded on a Perkin-Elmer Model-32 spectrometer (300 MHz).

The thermogravimetric analysis of the polymers was carried out on a Du Pont TA 9900 system. An alumina crucible lid was used as a reference. A dried polymer sample was powdered in order to increase its surface area. The powder was poured into an alumina crucible and dispersed in order to counteract the poor thermal conductivity. All the polymers were thermo gravimetrically analyzed at the heating rate of 10 deg min^{-1}. For all these experiments small samples (5–10 mg) were used to minimize thermal gradient within the sample.

Synthesis of 2-carbazol-4,6-dichloro-s-triazine. A solution of cyanuric chloride (3.69 g, 0.02 mol) in acetone (30 ml) was added with the stirring to a cooled solution of sodium bicarbonate (2.12 g) in distilled water (80 ml). To the resulted suspension was slowly added a solution of carbazol (3.34 g, 0.02 mol) in acetone (30 m). The mixture was stirred for 2 h at 0–5°C at pH 7.0. The white product was filtered off, washed subsequently with cold water, cold dilute hydrochloric acid and finally with cold water. The product was recrystallized from chloroform. Yield 80%, mp 268°C.

This reaction is incomplete, if it is carried out in water, unless the cyanuric chloride used is in a finely divided state. The yield of the polymer is improved substantially if the cyanuric chloride is freshly precipitated by pouring acetone or dioxane solution into ice water. The use of an aqueous system allows the product to be isolated easily in higher yield [16].

Synthesis of homopolycyanurates II–IX *(general procedure).* To a stirred mixture of 1,7-dihydroxynaphthalene (1.60 g, 0.01 mol), sodium hydroxide (0.8 g, 0.02 mol), benzyl dimethyl hexadecylammonium chloride in 60 m of bidistilled water was rapidly added a solution of 3.18 g (0.01 mol) of 2-carbazol-4,6-dichloro-s-triazine in 30 ml of chloroform at 25±2°C. The emulsion was stirred vigorously for 8 h at 25±2°C. Then the organic layer was separated, washed with water and poured into methanol excess. The formed polymer precipitates was filtered off, washed thoroughly with water and methanol. Yield ~76%.

The polycyanurates of 1,4-dihydroxyanthraquinone, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,4-butanediol and 1,8-dihydroxyanthraquinone were synthesized similarly.

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