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## SYNTHESIS AND PROPERTIES OF POLYMERS CONTAINING S-TRIAZINE RINGS IN THE MAIN CHAIN

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*Polymers containing s-triazine rings in the main chain were synthesized by interfacial polycondensation reaction of 2,4-dichloro-6-[4'-hydroxy-1'-naphthyl]-s-triazine with various aromatic diols such as bisphenol-A (BPA), bisphenol-s (BPS), and phenolphthalein (PH) using cationic emulsifier (CTMABr) and NaOH as acid acceptor. Polymers were obtained in good yield and were characterized by solubility, intrinsic viscosity, and FT-IR spectral analysis. The relative solubilities of these polymer samples were determined in a variety of solvents. Thermal stability was studied by TGA technique.*

**Keywords:** s-Triazine, polycyanurates, synthesis, properties

### INTRODUCTION

Extensive literature exists on thermally stable polymers in which aromatic and heteroaromatic rings are linked together in the main chain [1–2]. A variety of polymers containing s-triazine nuclei in the main chain have been reported [3–11]. The choice of this heterocycle is based on its high thermal stability derived from its molecular symmetry and aromaticity.

In the present investigation, the authors describe the synthesis of 2,4 dichloro-6-[4'-hydroxy-1'-naphthyl]-s-triazine (DCHNST) and its polycondensation with different types of diols, such as BPA, BPS, and PH. A study of solubility, viscosity, IR spectra, and thermal

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behavior has been carried out in order to characterize these polymer samples.

## EXPERIMENTAL

DCHNST was synthesized by the reported method [12] and purified by crystallization from toluene (mp 225°C); BPA was crystallized from benzene (mp 156°C) BPS was synthesized by published methods [13] and was crystallized from benzene (mp 239°C). Commercially available PH (BDH) was purified by crystallization from ethanol. CTMABr (SRL) was use as received. AR grade solvents were used.

### Synthesis of Polycyanurates

A typical interfacial polycondensation is described for the formation of polycyanurate from DCHNST and BPA.

BPA (2.28 g, 0.01 mol) was dissolved in water containing equimolar amount of NaOH, in 250 ml three-necked flask equipped with a mechanical stirrer. To the resulted clear solution 0.250 of CTMABr was added. The content was stirred vigorously. A solution of DCHNST (2.92 g, 0.01 mol) in ethyl acetate was rapidly added to the aqueous solution and the emulsion was stirred vigorously for 6 h at 30°C. The polymer was precipitated from methanol. It was filtered, washed with water, and finally with methanol. The polymer was dried at 50°C under vacuum. The yield of dried polymer was 60%. Other polymers were prepared similarly.

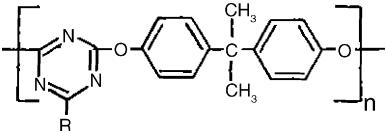
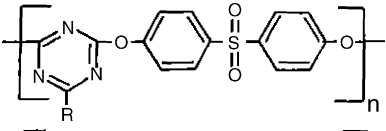
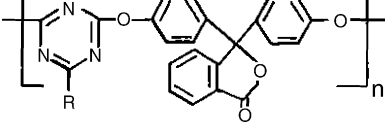
### Measurements

The FTIR spectra were recorded on “Perkin-Elmer spectrophotometer” using KBr pellet technique. Reduced viscosities of polycyanurates were determined for 1 g/dl solutions in DMF using an Ubelhode suspended level viscometer. The thermograms were obtained on a “Mettler TA 3000” system at a heating rate of 10°C/min.

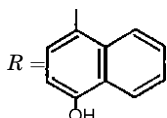
## RESULTS AND DISCUSSION

The polycyanurates obtained from different aromatic diols are highly soluble in DMF, DMAc, THF, and N-N-dimethylsulfoxide. All polycyanurates are coloured powdery substance (Table 1).

**TABLE 1** Yields and Properties of Polycyanurates Obtained from 2,4-dichloro-6-[4'-hydroxy,1'-naphthyl]-*s*-triazine and Aromatic Diols

Code	Repeat unit	Product appearance	Yield (%)	$[\eta]^*$ dl/g
PCBA		Greenish yellow	60	0.3790
PCBS		Greenish yellow	40	0.3130
PCPH		Greenish yellow	74	0.2750

\*In DMF at 30° C



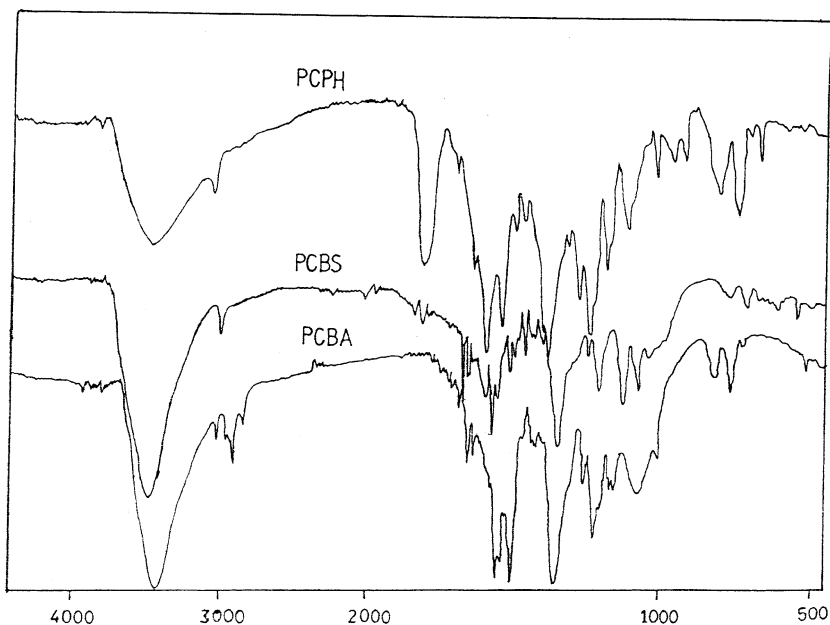
Reaction time = 6 h. Reaction temp = 30° C. Concentration of emulsifier = 0.25% wt/vol of water. Reactants = DCHNST: 0.01 mol, DIOL: 0.01 mol.

\*Examination of intrinsic viscosity values reveals that among the three polycyanurates PCBA has the highest, whereas PCPH has the lowest solution viscosity.

## IR Spectral Characteristics

Examination of Figure 1 reveals that all polymers exhibit strong or moderately strong absorption bands at frequencies around 820–788  $\text{cm}^{-1}$  and 1562–1410  $\text{cm}^{-1}$ , which may be assigned to out of plane and inplane vibrations of *s*-triazine ring, respectively. A very broad band observed in the region 1270–1200  $\text{cm}^{-1}$  is due to the presence of vibrations involving aryl-aryl ether linkage [14–16] confirming the reactions between substituted cyanuric chloride (DCHNST) and aromatic diols.

The absorption at 1170, 2840, and 2850  $\text{cm}^{-1}$  in the IR spectra (Figure 1) confirms the presence of isopropyl group in PCBS, a band at 575  $\text{cm}^{-1}$  is due to scissoring vibration of sulfone group, while two bands observed at 1160 and 1360  $\text{cm}^{-1}$  may be assigned to symmetric and asymmetric stretching vibration of sulfone group,



**FIGURE 1.** IR spectra of PCBA, PCBS, and PCPH.

respectively. In the IR spectrum of PCPH a weak band observed at  $1160\text{ cm}^{-1}$  is due to ketonic stretching vibration and a band at  $1775\text{ cm}^{-1}$  corresponds to stretching vibration of lactone ring [5,8,11].

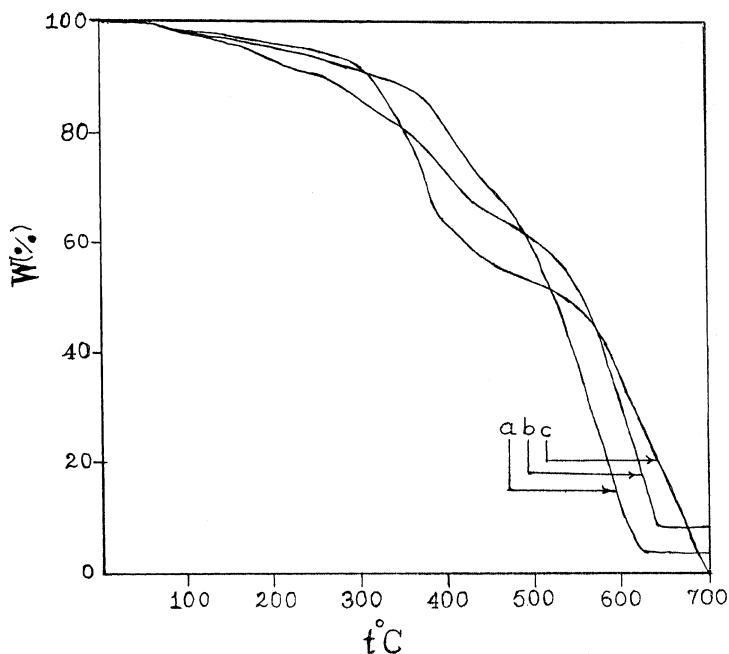
### Thermal Behavior of Polycyanurates

TGA thermograms of polycyanurates are shown in Figure 2. Table 2 shows several temperature characteristics such as  $T_i$ ,  $T_{\max}$ , and  $T_{50}$  that may be used for quantitative assessment of relative thermal stability of polycyanurates by dynamic heating. Thermal degradation of fully cured polycyanurates thermosetting materials was examined by determining the mass loss at various temperatures [17–18].

A comparison of  $T_i$  and  $T_{50}$  of polycyanurates in Table 2 indicates that PCBA has the highest thermal stability, whereas PCBS has the least thermal stability.

A comparison of thermal stability based on  $T_{\max}$  for the first step reveals that the thermal stability of the polycyanurates decrease in the following order:

$$\text{PCBA} > \text{PCPH} > \text{PCBS}.$$



**FIGURE 2.** Thermograms of (a) PCBA, (b) PCBS, and (c) PCPH.

All these temperature characteristics being single feature criteria, do not provide any certain indication of relative thermal stabilities of polycyanurates. Therefore, to obtain a semiquantitative picture of relative thermal stability, an integral procedural decomposition

**TABLE 2** Thermal Analysis Data for Polycyanurates

Polymer	$T_i$ °C	$T_{max}$ °C		$T_{50}$ °C	IPDT	Activation energy E K cal/mol	
		Step I	Step II			Step I	Step II
PCBA	360	410	520	522	570	28.41	36.75
PCBS	300	280	520	539	559	19.85	37.41
PCPH	305	380	680	545	602	25.7	42.88

$T_i$  = initial decomposition temperature;  $T_{max}$  = temperature for maximum rate of decomposition;  $T_{50}$  = half volatilization temperature; IPDT = integral procedural decomposition temperature.

temperature [19] (IPDT) is calculated for each polycyanurates and is presented in Table 2.

$$\text{IPDT} = (T_i - T_i)A^* + T_i,$$

where  $A^*$  is the fractional area under the TGA curve normalized with respect to residual weight;  $T_i$  and  $T_i$  are temperatures of completion and initiation of weight loss, respectively.

Based on IPDT values overall relative thermal stability is found to follow the order:



Attempts were made to estimate the activation energy ( $E$ ) for each polycyanurates by Broido method [20] (Table 2).

The studies reveal that the thermal stability of polycyanurates is largely depend on the type of diol involved in the polycyanurates, that is, thermal stability of polycyanurates is directly proportional to the molecular size of the aromatic diol component in the polymer chain.

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