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SYNTHESIS AND PROPERTIES OF SOME POLYCYANURATES

ABSTRACT

Seven polycyanurates were synthesized by stirred interfacial polycondensation of 2-phenylthioureido-4,6-dichloro-s-triazine with each of the aromatic diols, bisphenol-A, bisphenol-C, phenolphthalein, 1,5-dihydro-xynaphthalene, resorcinol, catechol and hydroquinone. The polycyanurates, obtained in 50-69% yield, possessed reduced viscosities in the range 0.1-0.19 dl/g and were soluble in chlorinated solvents such as chloroform, dichloroethane etc. The polycyanurates were characterized by IR spectra. The density and thermal stability of each of the polycyanurates derived from bisphenol-A was found to possess greater thermal stability than the others.

Keywords:-

Bisphenol -A (BPA), phenolphthalein (Ph), resorcinol(R) and catechol(C).

1.INTRODUCTION:-

Thermo-responsive shape memory polymers (SMPs) have the capability for changing their shapes from a temporary shape to a permanent shape upon application of an external thermal stimulus [1, 2]. It evinces great interest due to the adaptability for shape change when temperature switches from below to above the transition temperature. They provide great potential for application in self-deployable structures for space applications [3,4], micron-sized actuators [5], orthodontic applications, medical treatment [6] etc. The recent SMPs can be classified into two main categories. One is a polymer network, including covalently cross-linked and physically cross-linked amorphous or crystalline copolymers [7-9] and the other is a polymer blend. Polymer blends offer a much simpler way to fabricate SMPs. The shape memory polymer blends described in literatures usually consist of an amorphous polymer and a crystalline polymer such that and the two components be melt-miscible, like polyvinylidene fluoride/poly(methyl methacrylate), polyvinylidene fluoride/polyvinyl acetate and polylactic acid/polyvinyl acetate, etc [10]. Shape memory thermoset blends have rarely been reported. Xie et al. studied the shape memory properties of epoxy resins and aliphatic amine. They tuned glass transition temperatures of epoxy resins by varying the crosslink density of the systems [11]. Merline et al. synthesized shape memory oxazolidinone polymer by reacting isocyanate with hydroxy-telechelic poly (tetramethyleneoxide) and an epoxy resin. The modulus ratio and shape recovery increased with increase in the oxazolidinone-content in the polymer [12]. Tong et al. reported the shape memory cyanate ester synthesized from polyols and diols in presence of metal catalyst. The obtained glass transition temperature was greater than 150 °C [13]. Apart from the above, there are good numbers of reports on shape memory epoxy resin systems [14-18]. It can be seen that majority of them are patented. There are a few reports on cyanate ester based shape memory polymer for space deployable application [13, 19, 20].

In the present investigation, polycyanurates synthesized interfacial polycondensation of 2-phenyl thioureido-4,6-dichloro-s-triazine (PTUDCT) with each of several aromatic diols viz. Bisphenol-A(BPA), bisphenol-C(BPC), phenolphthalein(Ph), 1,5-dihydroxy naphthalene(DN-1,5),resorcinol, catechol and hydroquinone are reported. The polycyanurates have been characterized by viscosity, solubility, UV and IR spectroscopy and thermogravimetry.

2. EXPERIMENTAL PROCEDURES:

Material:

PTUDCT was synthesized by the reported method [21] and purified by crystallization from ethanol (M.P.1720). BPA was synthesized by crystallized from benzene (M.P.1560). BPC was synthesized by published method and was crystallized from benzene (M.P.1870) commercially available phenolphthalein, DN-1,5 (Sisco Lab) were purified by crystallization. Benzyl dimethyl hexadecylammonium chloride (BDMHDAC) (BDH) was used as received. AR grade solvents were used.

Synthesis of polycyanurates :-

A typical of interfacial polycondensation is given below for the formation of polycyanurates of BPA.

A solution of (2.28 g,0.01 mole) of bisphenol-A (0.8 g, 0.02 mole) of sodium hydroxide and 0.125 g of cetyltrimethylammonium bromide (CTMABr) in 50 ml of double distilled water was stirred vigorously at 250 C in a 250 ml three necked flask equipped with mechanical stirrer. A solution of (2.86 g, 0.02 mole) of 2-phenyl thioureido-4,6-dichloro-s-triazine in (25 ml) chloroform was rapidly added to the aqueous solution and the emulsion was stirred vigorously for 5 hours at 250 C. The organic layer containing the polymer was isolated and washed with water; polymer was precipitated from methanol. It was filtered, washed with water with methanol, and finally dried. The yield of the dried polymer was 65 %. The polymer was further purified by dissolving in chloroform followed reprecipitation from petroleum ether. A solution of the polymer in chloroform (1 g/dl) had a reduced viscosity of 0.204. Other polycyanurates (see Table 1), were prepared by this procedure.

Characterization methods :

Reduced viscosities of polycyanurates were determined for 1 g/dl solution in dimethyl formamide at room temperature using an Ubblohd suspended level viscometer. The densities of polycyanurates were determined using suspension method [22]. The liquid system used was carbon tetrachloride and petroleum ether. IR spectra of the polycyanurates were recorded on a Perkin-Elmer IR spectrophotometer using a KBr pellet technique. Thermo gravimetric analysis (TGA) of the polycyanurates was performed using a Mettler TA 3000 system at a heating rate 100 /min in air.

3.RESULTS AND DISCUSSION :

Several characteristic of polycyanurates are now reported (Table-1).The interfacial system involved a good solvent (chloroform). Polycyanurates formation was formed to be possible only with the use of cationic emulsifier. Both surfactant and catalytic function could be combined through the use of cationic surfactants which as quaternary ammonium compounds, could aid in transfer of monomer between phases [23]. Cation emulsifier has been exclusively used for synthesis of polycyanurates.

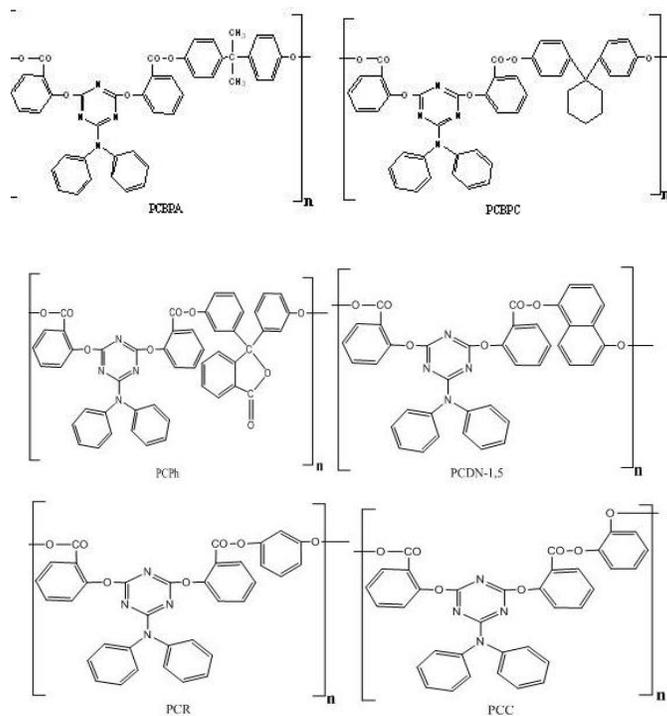
Examination of reduced viscosity values reveals that, among polycyanurates PCBPA has the highest where as PCPh has the lowest solution viscosity. BPA is the least acidic and hence most reactive towards nucleophilic displacement reaction and hence leads to the formation of polycyanurates of a comparatively higher molecular weight. Among the polymers of resorcinol, Catechol and hydroquinone, catechol seems to be more reactive probably because of its greater symmetry.

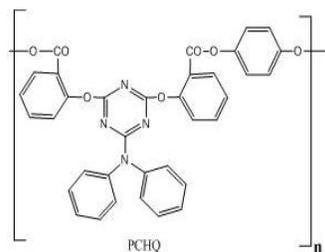
TABLE-1

Aromatic diols	Polymer Code	Yield %	η_{sp}/c_2 (ml/g)	D (g/cm ³)	V1 (A0)3	d(calc) (g/cm ³)
Bisphenol-A	PCBPA	65	0.218	1.318	399.6	1.300
Bisphenol-C	PCBPC	57.8	0.2154	1.301	438.6	1.290
Phenolphthalein	PCPh	50	0.080	1.374	456.2	1.362
1,5-dihydroxy naphthalene	PCDN-1,5	69	0.176	1.396	318.4	1.390
Resorcinol	PCR	49	0.147	1.343	287.6	1.388
Catechol	PCC	55	0.172	1.364	287.6	1.388
Hydroquinone	PCHQ	62.8	0.164	1.352	287.6	1.388

ELEMENTAL ANALYSIS :-

No	Code	Molecular Formula	M.W.	C		H		N	
				Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
1.	PCBPA	C ₄₄ H ₃₂ O ₇ N ₄	728	72.52	72.56	4.39	4.41	7.69	7.72
2.	PCBPC	C ₄₉ H ₃₀ O ₉ N ₄	818	71.88	71.85	3.67	3.69	6.84	6.88
3.	PCPh	C ₄₉ H ₃₀ O ₉ N ₄	818	71.88	71.85	3.67	3.69	6.84	6.88
4.	PCDN-1,5	C ₃₉ H ₂₄ O ₇ N ₄	660	70.91	70.88	3.64	3.68	8.48	8.50
5.	PCR	C ₃₅ H ₂₂ O ₇ N ₄	660	68.85	68.90	3.61	3.54	9.18	9.16
6.	PCC	C ₃₅ H ₂₂ O ₇ N ₄	610	68.85	68.89	3.61	3.66	9.18	9.22
7.	PCHQ	C ₃₅ H ₂₂ O ₇ N ₄	610	68.85	68.92	3.61	3.59	9.18	9.23





IR and NMR :-

1. PCBPA :-550(S),C-C deformation vibration of Propyl ring, 620-750(S,M,W), Out-of-plane bending vibrations of C-H bonds of aromatic ring, 805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring,1070-1120(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1720(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1170(S), C-C skeletal vibrations of propyl group,1205-1260(S,M), vibration of aryl-ether linkage, 1315-1570,(m,s) , aromatic C-N stretching vibrations,1410-1610(s,m,w) , skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,2855-2920(w,m), saturated C-H bending vibrations,3010-3070(w). aromatic C-H stretching vibrations,3440(vb), stretching vibrations of -OH group.

1H-NMR: δ ppm :- 1.687(s,6H,-CH₃),7.05-7.289(m,26H, Ar-H).

1. PCPBC :- 620-750(S,M,W), Out-of-plane bending vibrations of C-H bonds of aromatic ring, 805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring,940-980(s,m), C-C deformation vibration of cyclohexane ring,1050-1120(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1710(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1260-1290(S,M), vibration of aryl-ether linkage, 1310-1570,(m,s) , aromatic C-N stretching vibrations,1410-1605(s,m,w), skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,2870-2920(w,m), saturated C-H bending vibrations,3040-3060(w). aromatic C-H stretching vibrations,3440(vb), stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.15-7.80(m,25H, Ar-H),3.69-3.75(t,10H,cyclohexane ring)

1. PCPh :-610-760(S,M,W), Out-of-plane bending vibrations of C-H bonds of aromatic ring, 805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring,1010-1105(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1710(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1170(S), C-C skeletal vibrations of propyl group,1205-1260(S,M), vibration of aryl-ether linkage, 1315-1570,(m,s) , aromatic C-N stretching vibrations,140-1610(s,m,w) , skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,2855-2920(w,m), saturated C-H bending vibrations,3010-3070(w). aromatic C-H stretching vibrations,3440(vb), stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.05-7.89(m,30H, Ar-H).

1. PCDN-1,5 :- 620-760(S,M,W), Out-of-plane bending vibrations of C-H bonds of aromatic ring, 805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring,1010-1105(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1725(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1260 (m), vibration of aryl-ether linkage, 1310(m) , aromatic C-N stretching vibrations,1440-1660(s,m,w) , skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,2855-2920(w,m), saturated C-H bending vibrations,3040(w). aromatic C-H stretching vibrations,3440(vb), stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.11-7.75(m,23H, Ar-H).

1. PCR :- 640-740(W,S), Out-of-plane bending vibrations of C-H bonds of aromatic ring,805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring, 1030-1105(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1715(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1260-1280(M,W),vibrations of propyl group, 1310(M),aromatic C-N stretching vibrations,2855-2920(W,M), saturated C-H bending vibrations,1420-1505(S,W), skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,3050(W), aromatic C-H stretching vibrations, 3440(v.b) stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.25-7.81(m,22H, Ar-H).

1. PCC :-640-750(W,S), Out-of-plane bending vibrations of C-H bonds of aromatic ring,805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring, 1010-1105(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1720(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1260-1280(M,W),vibrations of propyl group, 1315(M),aromatic C-N stretching vibrations,2855-2920(W,M), saturated C-H bending vibrations,1410-1510(S,W), skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,3050(W), aromatic C-H stretching vibrations, 3440(v.b) stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.35-7.71(m,22H, Ar-H).

1. PCHQ :- 650-750(W,S), Out-of-plane bending vibrations of C-H bonds of aromatic ring,805(S), Out -of-plane vibration of s-Triazine ring, 840(S) C-H bending vibration of aromatic ring, 1015-1105(S,W), vibration of aryl ether linkage and in-plane bending vibrations of aromatic C-H, 1715(S) , C=O stretching vibrations of aromatic and α - β unsaturated ring, 1250(m),vibrations of propyl group, 1315(m),aromatic C-N stretching vibrations,2855-2920(w,m), saturated C-H bending vibrations,1410-1505(s,w), skeletal ring stretching vibrations of aromatic and hetero aromatic ring system,3040(W), aromatic C-H stretching vibrations, 3440(v.b) stretching vibrations of -OH group.

1H-NMR: δ ppm :- 7.30-7.69(m,21H, Ar-H).

Densities of Polycyanurates:

Densities of polycyanurates determined at 250 by suspending each of the polycyanurates in a mixture of carbon tetrachloride and petroleum ether and subsequently measuring the density of the liquid mixture by a pycnometer are also presented in Table-1. Densities, Calculated theoretically on the basis of structural concept proposed by Slonimskii et al. [23] are also presented, an average value of 0.684 for packing coefficient, K was used for this calculation: K was approximated from the slope of a line best fitting the curve.

d-M/NA $\sum \Delta V_i$ volume increments, ΔV_i , of relevant atomic groups making up the polycyanurates repeat unit have been calculated by us and used by calculate intrinsic volume. Comparison of experimental and calculated densities shows a good correlation.

Infrared Spectral Characteristic :

The IR spectra of this polycyanurates exhibit the following common characteristic absorption frequencies (cm⁻¹) at 810-820 and 1580-1430

attributable to out-of-plane and in-plane vibration of s-triazine ring, respectively. At 1295-1240 attributed to vibration involving aryl ether linkage [23]. In addition, the spectra exhibits a few absorption frequencies based on which these polycyanurates can be distinguished from the one another. These frequencies (cm⁻¹) are: 420,550 (C-C deformation vibrations of propyl link), 1170 (C-C skeletal vibrations of propyl link), 1380 (due to C-CH₃ deformation of propyl group) for PCBPA; 535-940-980 (all C-C deformation vibrations of cyclohexane ring) for PCBPC 1775 (C-O stretching of lactones group PCPh).

Thermal characteristics of polycyanurates :

TGA thermograms of polycyanurates are shown in fig.1. Several temperature characteristic such as T₀ (initial decomposition temperature), T₁₀ (temperature for 10 % wt. Loss), T_{max} (temperature for maximum rate of decomposition) and T_s (half volatilization point temperature), which may be used for qualitative assessment of relative thermal stabilities of polycyanurates are presented in table-2. With dynamic heating, T₀ and T₁₀, the greater the heat stability of a given polymer. Comparison of T₀ and/or T₁₀ for polycyanurates indicates that the thermal stabilities of PCBPA and PCBPC are quite similar and that PCC, PCHQ, PCR, PCPh and PCDN-1,5 follow the former in decreasing order of thermal stability. The thermal stability of isomeric polycyanurates (PCR, PCC, PCHQ) is also similar.

A comparison of thermal stability based on T_{max} for the first step also reveals the similar order i.e. the thermal stability of the polycyanurates is the following order.

PCBPA ~ PABPC > PCC ~ PCR ~ PCHQ > PCPh > PCDN-1,5

Based on half volatilization point temperature (T_s) PCBPA seems to exhibit highest thermal stability and PCPh, PCBPC, PCR, PCHQ, PCC and PCDN-1,5 seems to be in the order of decreasing thermal stability.

These studies reveal that the thermal stability of polycyanurates are significantly related to the aromatic diol component of the molecular chain and that polycyanurates of enhanced stability may be derived from aromatic diols of the type HO-Ph-X-Ph-OH where X = C(CH₃)₂ and cyclohexyl.

TABLE-2
Temperature (°C) characteristic of polycyanurates

Polymer	T _{max}					
	T ₀	T ₁₀	Step-1	Step-2	T _s	Residue at 7000 C
PCBPA	360	425	430	595	505	7.0
PCBPC	380	405	415	540	480	11.0
PCPh	230	295	290	545	485	12.0
PCDN-1,5	170	230	250	435	295	34.0
PCR	350	370	405	580	455	14.0
PCC	355	375	410	560	435	18.0
PCHQ	350	375	400	595	440	15.0

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