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SYNTHESIS AND CHARACTERIZATION OF POLY (2-METHOXY-CYANURATE) OF BISPHENOL-A AND BISPHENOL-F

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ABSTRACT

Synthesis and characterization of thermally stable polycyanurate is being reported here. The polycyanurate is a copolymer obtained by interfacial polycondensation of bisphenol-A, bisphenol-F and 2-methoxy-4,6-dichloro-s-triazine. The copolymer obtained is characterized by various means. Spectroscopic characterization includes IR and NMR. Solution study includes the determination of intrinsic viscosities in solvents such as chloroform, dichloroethane, dioxane and nitroethane. Molecular weights and polydispersity were determined by gel permeation chromatography method. Mechanical properties were determined by Instron tensile tester. Thermal properties and kinetic parameters like activation energy and order of reaction were also determined. All the experimental observations support the formation of a thermally stable copolymer having good solubility, mechanical properties and rigidity.

INTRODUCTION

Thermal stability of polymeric materials find use particularly in aerospace and instruments where failure of most of the plastics and polymeric materials is observed due to degradation and/or softening. A typical approach to this problem is to utilize stable nuclei such as s-triazine and search for methods to connect the nuclei by thermally stable linkages. Polycyanurates are known for their stability because of the s-triazine moiety in the main chain structure.

However they are generally insoluble and infusible, hence are non-processible [1-3]. Nakamura et al. [4] synthesized various polycyanurates using different bisphenols by interfacial polycondensation method in presence of cationic emulsifier, and in different solvents. Recently various workers [5-7] have synthesized poly (2-methoxycyanurate) of bisphenol-A, poly (2-methoxycyanurate) of bisphenol-C (PMCBC), poly (2-methoxycyanurate) of bisphenol-F (PMCBF) and investigated some aspects of solution properties and physical properties. These polymers are found to be soluble only in chloroform and this may be due to regular arrangement of monomeric units in macromolecular chains. With a view of destroying the regular arrangement of monomeric units in homopolymer chains, it is aimed to synthesize and to study the change in properties of polycyanurate of mixed bisphenols.

The present paper reports the synthesis of poly (2-methoxycyanurate) of bisphenol-A and bisphenol-F (PMCBFA) obtained by interfacial polycondensation of equimolar mixture of bisphenol-A and bisphenol-F, and 2-methoxy-4,6-dichloro-s-triazine. The polymer was characterized by IR, NMR, viscosity, and GPC. Mechanical and thermal properties of the polymer were also studied.

EXPERIMENTAL

Materials

Various monomers required for polymerization reaction were prepared and/or purified as follows. 4,4'-dihydroxydiphenyl methane (bisphenol-F) was synthesized as reported before [8]. Repeated crystallization from hot water and finally from benzene yield pure white product having m.p. 162-163°C. 4,4'-dihydroxydiphenyl propane (bisphenol-A) was obtained commercially. It was crystallized from benzene having m.p. 156°C.

2-Methoxy-4,6-dichloro-s-triazine (MDT) was synthesized according to the method reported elsewhere [9]. The solid product was recrystallized from petroleum ether, m.p. 88-90°C.

Synthesis

Interfacial polycondensation of 2-methoxy-4,6-dichloro-s-triazine with bisphenol-A and bisphenol-F was carried out as follows. Polymerization reaction conditions were optimized by varying the proportion of emulsifier, monomer, solvents and stirring rate to give high molecular weight and a better yield. In a typical reaction, solution of 0.025 moles of bisphenol-A, 0.025 moles of bisphenol-F, 0.1 moles of NaOH and 0.125 gm of emulsifier (cetyl dimethyl benzyl ammonium chloride) in water was stirred vigorously. To the emulsified mixture, 0.05 moles of MDT in $CHCl_3$ was added. The resulting mixture was

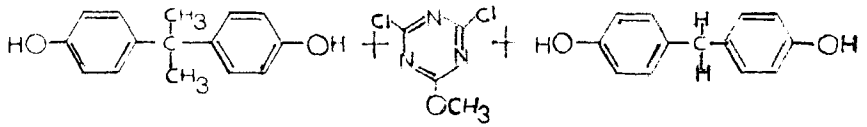
stirred for 5 hr. at 8-10°C. After the reaction period was over, the solution was poured into methanol, resulting in the precipitation of the polymer in the fibrous form. The polymer was washed thoroughly with water, then with methanol and finally dried at 50°C.

Characterization

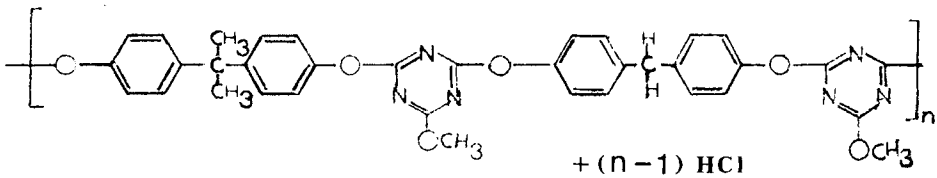
IR spectra of polymer PMCBFA, in form of film was recorded on Shimadzu 408 spectrophotometer. NMR of polymer in $CDCl_3$ was recorded on Perkin Elmer (R-32), 90 MHz Spectrometer. The intrinsic viscosities of polymer were determined in chloroform, dichloroethane, dioxane and nitroethane at 30°C using an Ubbelohde Viscometer. The weight - and number- average molecular weights of the polymer were determined by gel permeation chromatography technique with columns of pore size 10^3, 10^4, 10^5 and 10^6 Å using $CHCl_3$ as effluent with flow rate of 2 ml/min. The instrument was calibrated using standard polystyrene samples of known molecular weights under the same conditions.

The ultimate mechanical properties of PMCBFA i.e. tensile strength, modulus and % elongation at break were determined from stress-strain data measured at room temperature by means of Instron tensile tester with a cross head speed of 0.2 cm/min. Specimens were 5 cm in length and 1.0 cm wide dumbbells.

The glass transition temperature was determined on DSC Du Pont 9000 differential scanning calorimeter. Measurements on 2.64 mg samples were carried out from 25°C to 500°C in air at a scanning rate of 40°C/min. Thermograms were recorded on Shimadzu TG-30 instrument at three different heating rates in air.



(i) NaOH
(ii) Cationic emulsifier
(iii) $CHCl_3$-H_2O interface



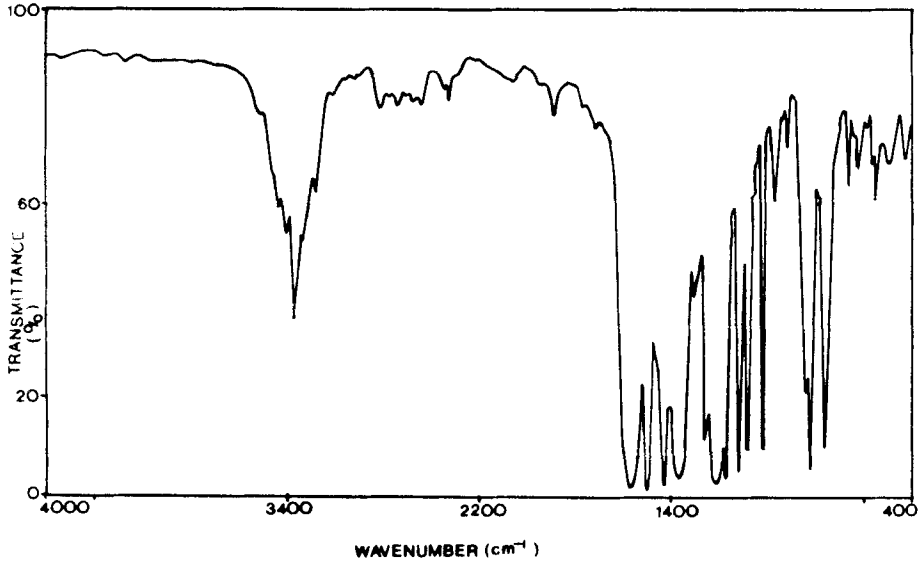


Fig. 1 : IR spectra of PMCBFA film.

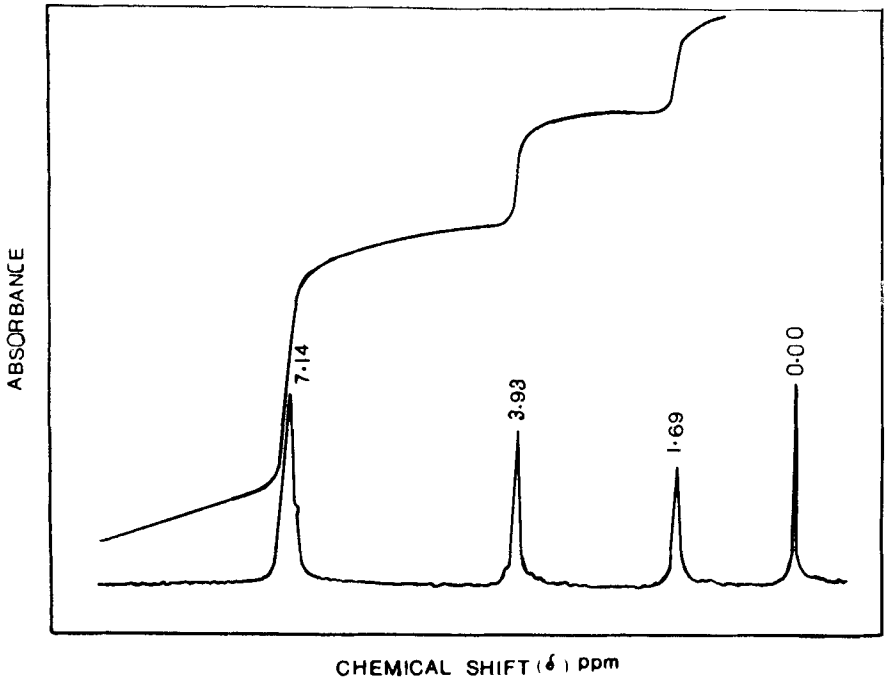


Fig. 2 : NMR spectra of PMCBFA.

Table - 1

Positions and peak heights of different protons of PMCBFA

Chemical shift δ (ppm)	Integral peak height (mm)	Average number of moles of protons	Assignment
1.7	24	$a_c \times 6$	Six protons of isopropyl group of bisphenol-A*
3.9	33	$6 + 2(2 - a_c)$	Methoxy protons of MDT and methylene protons of bisphenol-F*
7.15	65	$a_c + 8(2 - a_c)$	Aromatic protons of bisphenol-A and bisphenol-F

* Assuming 'a_c' moles of bisphenol-A moiety and $(2 - a_c)$ moles of bisphenol-F moiety per 2 moles of MDT of polymer chain.

RESULTS AND DISCUSSION

IR spectra of polymer PMCBFA is shown in Fig. 1. Absorptions at 1176cm^{-1} and in the range of 1202-1229cm^{-1} indicate the presence of ether linkage formed on polymerization. Other characteristic absorption bands due to respective functional groups of monomeric units can also be seen in the below figure.

From NMR we have ascertained the composition of the copolymer as has been done before [10-12]. Fig. 2 shows NMR spectra of PMCBFA The position and peak heights for different protons are compiled in Table-1. Quantitative information about the polymer having bisphenol-A and bisphenol-F in 1:1 mole ratio can be obtained as explained below. Any unit segment of PMCBFA polymer will contain in average, 2 moles of methoxy cyanuric chloride and 2 moles of bisphenol-A and bisphenol-F together. Suppose a_c moles of bisphenol-A is present in these two moles of bisphenols, then there will be $2-a_c$ moles of bisphenol-F. Total number of protons present in the unit segment will be 6 (from two moles of MDT) + 6 a_c (from a_c moles of bisphenol-A) + 2 $(2-a_c)$ from $(2-a_c)$ moles of bisphenol-F. Thus total $6 + 6a_c + 2(2-a_c) = 10 + 4a_c$ protons are responsible for total integral height of 57mm. Therefore $57/10 + 4a_c$ mm integral height is due

Table - 2

Intrinsic viscosities, $\bar{M}_w$ and $\bar{M}_n$ of PMCBFA at 30°C

Solvent	$[\eta]$	$\bar{M}_w.10^5$	$\bar{M}_n.10^5$	$\bar{M}_w/\bar{M}_n$
Chloroform	0.90	1.71	1.09	1.56
1,2-Dichloroethane	0.83			
Dioxane	0.67			
Nitroethane	0.45			

to one proton. a_c moles of bisphenol-A have $6a_c$ protons and responsible integral height of 24 mm.

$$\left(\frac{57}{10 + 4a_c}\right) 6a_c = 24$$

$$\therefore \quad a_c \simeq 1$$

Therefore unit segment of PMCBFA contains 1 mole of bisphenol-A and 1 mole of bisphenol-F. Thus NMR with IR analysis confirm the proposed structure of polymer PMCBFA.

Intrinsic viscosities $[\eta]$ of PMCBFA in different solvents at 30°C alongwith the number and weight average molecular weights obtained by GPC method are shown in Table-2. Results show that chloroform is the best solvent for the polymer as $[\eta]$ is the highest in chloroform at given temperature. Molecular weight of the polymer lies in the range of most of commercially important thermoplastics. The thermograms (TGA) of PMCBFA at different heating rates in air are shown in Fig.3.

The activation energy and rate of reactions were determined according to Freeman and Anderson method [13,14]. The activation energy and the order of reaction (Table-3) reflect that the first stage degradation is probably due to random chain scission reaction, which is induced by oxygen present in air.

Higher stability due to resonance present in PMCBFA results in

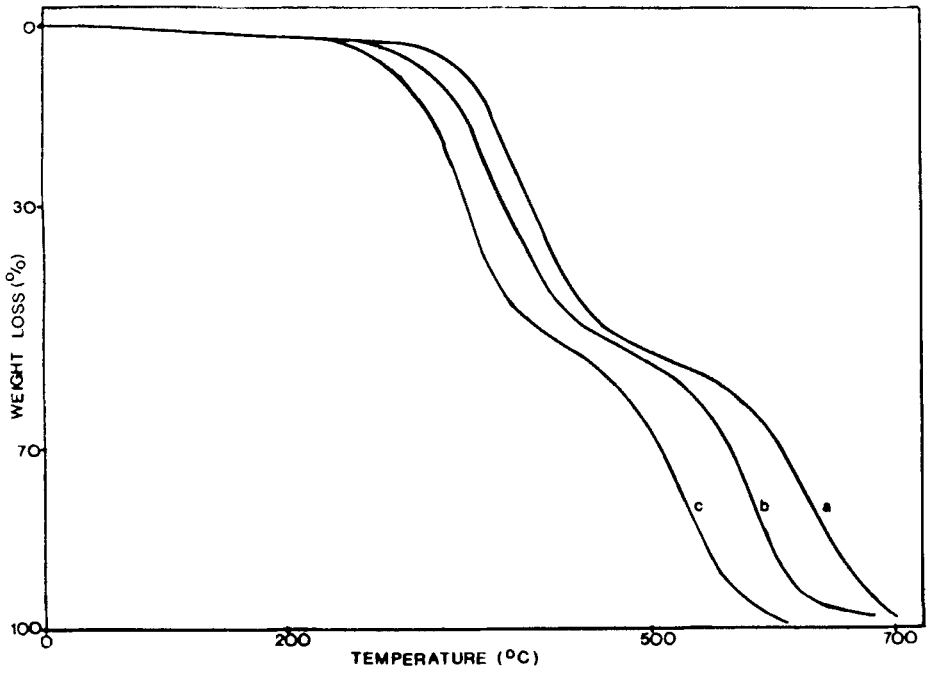


Fig. 3 : TGA of PMCBFA in air at three different heating rates
(a) 10°C/min (b) 20°C/min (c) 50°C/min

higher activation energy values. Initial site for oxygen attack is likely to be isopropylene or methylene linkage [15]. After hydrogen abstraction from either of the groups, respective unstable radicals could rearrange to a stable radical as follows:

R. radical

$$\sim\!\!\sim OC_6H_4 - C(CH_3) - C_6H_4O\sim\!\!\sim \quad \longleftrightarrow$$
$$\dot{C}H_2 \qquad\qquad OC_6H_4 - \dot{C}(CH_3)CH_2 - C_6H_4O$$

R'. radical

$$\sim\!\!\sim OC_6H_4 - \dot{C}H - C_6H_4O\sim\!\!\sim \qquad \text{..... (2)}$$

$$R.\ (R.') + O_2 \longrightarrow R\ OO.(R'OO.) \qquad \text{..... (3)}$$

$$ROO.(R'OO.) + \text{Polymer} \longrightarrow ROOH\ (R'OOH) + R''. \qquad \text{..... (4)}$$

Table - 3

Mechanical and thermal properties of PMCBFA

Polymer	PMCBA	PMCBF	PMCBFA
Solvent	Chloroform	Chloroform	Chloroform 1,2 Dichloroethane dioxane nitroethane
Tensile strength ($kg\ cm^{-2}$)	-	-	875
Modulus Kg/cm^2	-	-	2.4×10^4
Elongation at break %	-	-	4.0
Glass Transition Temp. (°C)	165	160	156
Decomposition Temp. (°C)	350	350	350

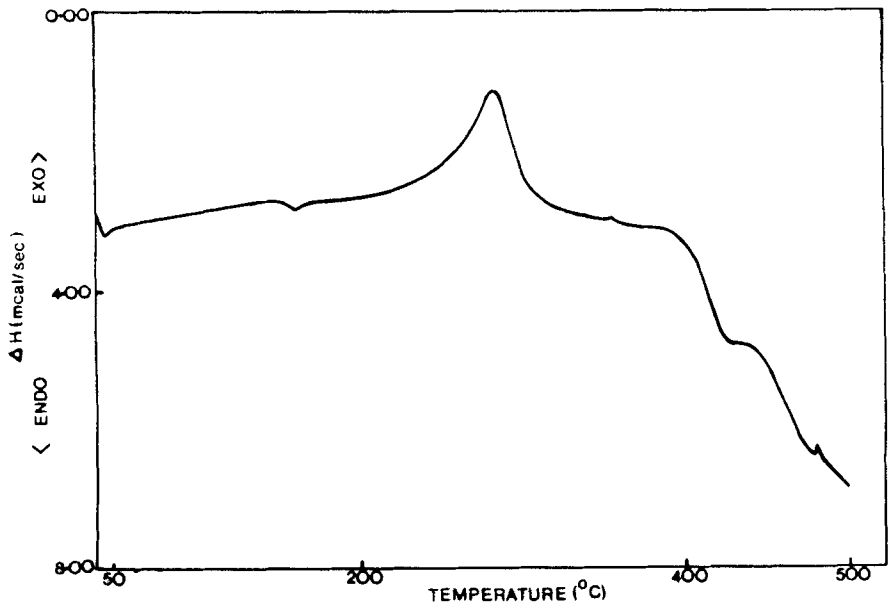


Fig. 4 : DSC of PMCBFA in air.

Table - 4

Kinetic parameters of PMCBFA obtained from TGA thermograms

Heating rate (°C/min)	1st transition		2nd transition	
	Activation energy, E (Kcals)	Order (n)	Activation energy, E (Kcals)	Order (n)
10	47.0	1.0	38.0	0.8
20	46.1	1.1	36.8	0.7
50	42.2	1.4	38.8	1.1

These peroxides decompose homolytically to give .OH and RO. (R'O.).

$$\text{Polymer} + \text{.OH} \longrightarrow \text{R''.} + H_2O \quad \ldots\ldots (5)$$

$$\text{Polymer} + \text{RO.(R'O.)} \longrightarrow \text{R''.} + \text{ROH (R'OH)} \quad \ldots\ldots (6)$$

The second stage having lower activation energy (Table-3) is probably due to thermal decomposition of lower molecular weight compounds formed during first stage decomposition (i.e. chain scission). DSC curve of PMCBFA is shown in Fig.4.

The mechanical properties of PMCBFA, solubility and thermal properties of PMCBA, PMCBF and PMCBFA are listed in Table-4. The tensile strength and high modulus value of PMCBFA clearly indicate that polymer possesses good mechanical properties and high rigidity which are required for applications like films and sheets. The thermograms show that decomposition begins around 350°C. The weight loss is less than 50% even at 500°C, indicating good thermal stability. Comparison of the results shown in Table-4 shows that PMCBFA has got better choice for various solvents than PMCBA and PMCBF. Other thermal characteristics of PMCBFA are similar to PMCBA and PMCBF. Thus the present polymer has excellent solubility and hence processibility without affecting the thermal properties.

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