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SYNTHESIS AND KINETICS OF THERMAL DEGRADATION OF POLY(2-METHOXY CYANURATE) OF 4,4'-DIHYDROXY DIPHENYL SULPHONE

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Poly(2-methoxy cyanurate) of 4,4'-dihydroxy diphenyl sulphone (PMCBS) was synthesized by interfacial polycondensation technique. PMCBS was characterized by IR and NMR, and kinetics of thermal degradation was carried out by DTA and TGA.

INTRODUCTION

Among heat-resistant polymers aromatic polyethers are of great interest. They are known for their high thermal and chemical stability, good mechanical and dielectric properties, and easy processability[1]. Mark[2] has pointed out several ways in which the melting or softening points of polymers can be raised with concomitant improvement in high temperature properties. These are stiffening the chains by the addition of ring structures or other stiff elements, cross linking the chains, and including crystallization. Sulphur containing polymers are engineering plastics with good property retention over wide temperature ranges[3]. The present paper describes the synthesis and kinetics of thermal degradation of poly(2-methoxy cyanurate) of 4,4'- dihydroxy diphenyl sulphone.

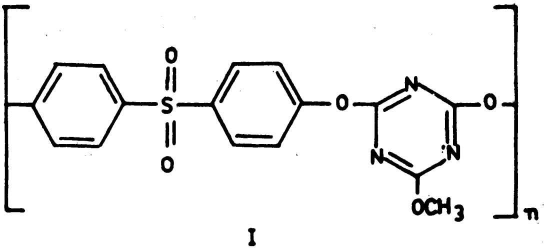
EXPERIMENTAL

Chemicals used were of laboratory grade and were purified prior to use by the methods reported in the literature[4]. 2-Methoxy-4,6- dichloro-s-triazine (MDT)[5,6] and 4,4'-dihydroxy diphenyl sulphone (Bisphenol-S)[7] were synthesized according to reported methods.

Polymer Synthesis

Bisphenol-S (0.01 mol) was dissolved in 0.02M aqueous NaOH solution (100 ml). The resultant clear solution was cooled to 10°C and cetyldimethyl benzylammonium chloride (0.25 g) was added. The contents were stirred vigorously. A solution of 0.01M MDT in 25 ml chloroform was added rapidly to the solution and stirred vigorously at 10°C for 5 hrs. The polymer was precipitated in acetone washed with water and acetone and dried. The polymer was further purified by dissolving it in chloroform and precipitating with petroleum ether (yield §*ca.* 77%).

The polymer, poly(2-methoxy cyanurate) of bisphenols-S(I) hereafter designated as PMCBS, is highly soluble in chloroform and having $[\eta] = 0.25$ dL/G at 30°C. The polymer is of low molecular weight even after changing the experimental conditions such as solvent system and temperature. The molecular weight obtained by vapor pressure osmometer is 2.7×10^3.



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(Analysis: Cald.: C, 53.78, H, 3.08, N, 11.76, S, 8.96% Found: C, 53.5, H, 2.98, N, 11.46, S, 8.42%)

RESULTS AND DISCUSSION

The characteristic IR frequencies (cm–1) of PMCBS are: 3400(–OH), 2950(C–H of –OCH3), 1360 ($\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}$, ν_{asy}), 1290 (C–O), 1255 (C–O–C, ν_{asy}), 1150 ($\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}$, ν_{sym}), besides normal modes of vibrations. The ^{1}H NMR spectrum of PMCBS revealed the following signals the signal at 3.95–4.04d is due to –OCH3 group and two multiplets at 7.29–7.40 and 7.98–8.04d are due to aromatic ring proteins. Thus the structure of PMCBS is confirmed by IR in conjunction with NMR data.

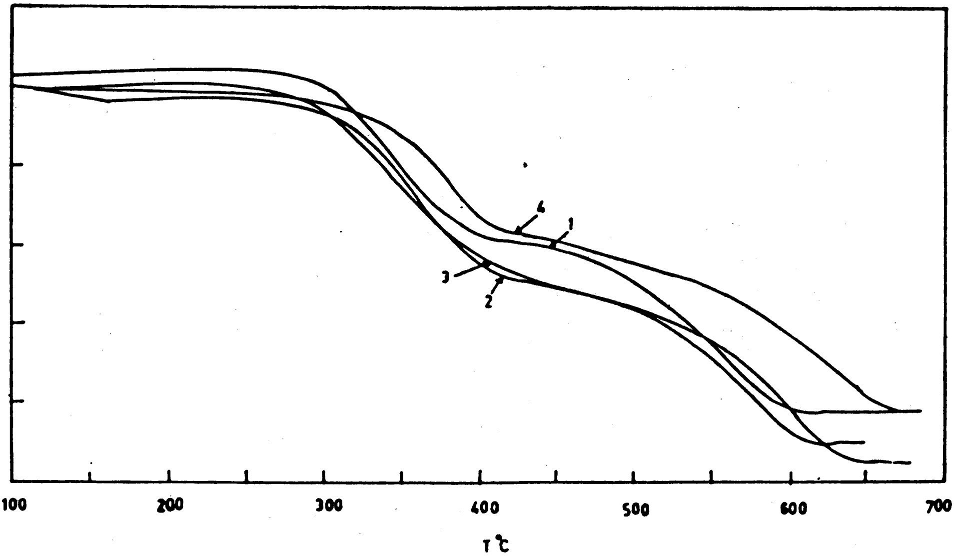

Fig. 1. TGA—thermograms of PMCBS at different heating rates: (1) 10, (2) 20, (3) 30 and (4) 40°C/min.

The DTA thermogram of PMCBS in air (40 cc/min) atmosphere at the heating rate 10°C/min showed the glass transition temperature at about 163°C and an exothermic peak at about 237°C which might be due to crystallization during heating and decomposition temperature at about 254°C. Thermogravimetric measurements for PMCBS were carriedout at different heating rates viz. 10, 20, 30 and 40°C/min in air atmosphere and shown in Fig. 1. It is observed that PMCBS is stable upto about 250-260°C in air and at high temperature polymer degrades. Thermal degradation of PMCBS is two step decomposition. The initial decomposition temperature (IDT), the temperature of maximum weight loss (T_m)and final decomposition temperature, (FDT) for both the steps are reported in Table 1.

TABLE 1

TGA DATA ON PMCBS IN AIR ATMOSPHERE

β °C/min.	IDT °K	Step I T_m, °K	FDT °K	IDT °K	Step II T_m, °K	FDT °K
10	523	623	700	700	820	883
20	513	636	700	700	846	923
30	498	638	715	715	862	950
40	510	646	720	720	873	960

Various methods for the analysis of TG data are used to evaluate kinetic parameters such as energy of activation, order of the reaction and frequency factor. Freeman-Carroll method[8] at single heating rate (10°C/min) is used to evaluate energy of activation and order of the reaction. The relation is:

$$\Delta \log \left(\frac{-dw}{dt}\right) = n \log W - \frac{E}{2.30\,3R}\Delta\left(\frac{1}{T}\right) \tag{1}$$

The symbols have their own significance. The values of E and n thus obtained graphically are reported in Table 2. The Friedman method[9] was used at two different heating rates viz.10 and 40°C/min at different degrees of conversion. The relation is:

$$\ln\left[\frac{\beta_2}{\beta_1}\left(\frac{T_1}{T_2}\right)^2\right] = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2}$$

where β_1 and β_2 are two different heating rates and T_1 and T_2 are the corresponding temperature of weight loss at constant degree of conversion. The average energy of activation obtained according to Eq. 2 for both the steps is reported in Table 2.

TABLE 2

KINETIC PARAMETERS FOR THE PMCBS

Step	Activation energy, E, Kcal			Freq. Factor A, min^{-1}	n
	Method of Friedman	Method of Ozawa	Method of Freeman-Carroll		
I	40.9	45.0	46.0	2.90×10^{15}	2.36
II	31.7	35.6	36.8	8.73×10^{8}	2.42

The method of Ozawa[10] was applied at the temperature of maximum weight loss. The relation is:

$$E = -4.35 \cdot \frac{d \log \beta}{d\left(\frac{1}{T}\right)} \tag{3}$$

where β is the heating rate. According to above Eq. (3) a plot of log β against $\frac{1}{T}$ is shown Fig. 2 for each step. From the slope the values of E was evaluated and reported in Table 2.

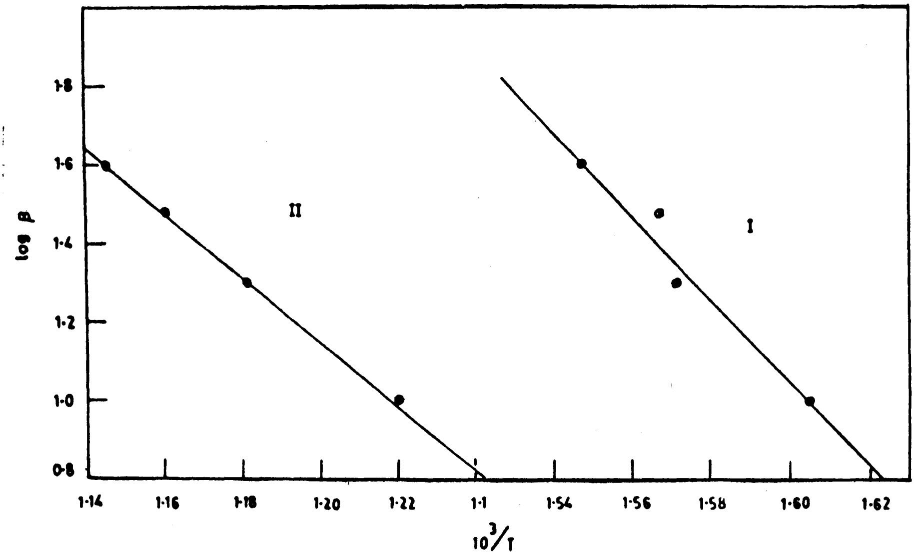

Fig. 2 A plot of log β against $\frac{1}{T}$

The values of frequency factor A is derived according to Eq. (4):

$$Ae^{-E/RT_m} = \frac{E\beta}{RT_m^2} \tag{4}$$

Where T_m is the temperature of maximum weight loss. The values of A determined according to Eq. (4) are reported in Table 2. These are 2.9 x 10^{15} and 8.73 x 10^8 min^{-1} for first and second steps, respectively. The energy of activation used in the determination of A was 46 Kcal. Thus the energies of activation for both the steps determined from various methods are in good agreement. The order of the reaction for both the steps are 2.36 and 2.43, respectively.

Polycyanurates prepared from bisphenol-A[11] and bisphenol-C[12] have high thermal stability in air *i.e.* 350°C and two step degradation. The order of the reaction for both the steps is second order. The average energies of activation for both the steps have almost the same values as PMCBS.

Thus the thermal stability can be improved by incorporating stiff elements like cardogroup (bisphenol-C) in backbone chains.[12] The kinetic parameters of PMCBS are almost identical to polycyanurates of bisphenol-A and bisphenol-C but thermal stability is low. The molecular weights and other properties of PMCBS can be improved by copolymerization with other bisphenols.

The pyrolysis process of polymers is complicated and involves a variety of reactions such as chain cleavage, rearrangement of chain segments, cross-linking, etc. In the present case pyrolysis products were not analyzed and hence it is not possible to suggest the mechanism of thermal degradation of PMCBS. From Table 2 it is clear that the pyrolysis is a second order reaction and the energy of activation is different for both the steps.

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