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Arylidene polymers.
Part 21. Thermal decomposition parameters of new diarylidenecycloalkanone organophosphorus polymers

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Abstract

A study of the non-isothermal decomposition of new aromatic polyphosphates (**I**–**V**) based on diarylidenecycloalkanone moieties has been carried out using TGA measurements at atmopsheric pressure. Analysis of non-isothermal TG and DTG curves of these polyphosphate esters indicated that their decompositions proceed in three stages. Kinetic parameters such as activation energy (E_a), pre-exponential factor (A) and entropy of activation (ΔS^*) for the whole samples at different decomposition stages are determined. The data showed that the thermal stability of polymers **I**–**III** decreases with increasing ring size of the diarylidenecycloalkanone moieties.

The effect of the presence of $-OCH_3$ groups upon the thermal properties of polymers is also discussed.

INTRODUCTION

In recent communications, our work has focused on the synthesis and characterization of a new class of polymers containing diarylidenecycloalkanone moieties [1–16] which possess interesting electrical [8, 13], morphological [4, 6, 10], optical [14] and thermal properties [3, 12, 15].

Polyphosphate esters are an important class of organophosphorus polymers, used as flame-retardant materials and possessing attractive plasticizing properties [17].

A survey of the literature reveals that thermogravimetry is a widely used technique for polymer characterization, particularly additive and degradation kinetics [18, 19]. In the present work, we describe the thermogravimetry and kinetic analysis of non-isothermal decomposition for new synthesized organophosphorus diarylidenecycloalkanone polyesters [16]. In

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addition, the effect of both the ring size of the diarylidenecycloalkanones and the presence of a $-OCH_3$ substituent group upon the thermal properties of the polyphosphates is determined and discussed.

EXPERIMENTAL

The polymer under investigation was prepared as described recently [16]. Dynamic thermogravimetric analysis was carried out using a Sartorius Electrobalance. Samples (100 mg) were placed in a Pyrex basket suspended from the arm of the balance by means of a Pyrex wire. The measurements were obtained between 25 and 450°C with a heating rate of 7°C min^{-1} under air temperature.

RESULTS AND DISCUSSION

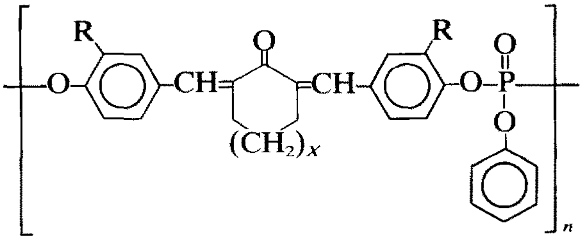
Dynamic thermogravimetry is a continuous process which involves the measurement of sample weight while the reaction temperature is changed by means of a programmed rate of heating.

The determination of the thermal behaviour and kinetic parameters of the new synthesized organophosphorus polyesters which possess an interesting plasticizing property, provides important additional information for their use and applications as new materials.

The polymer samples under investigation are based on the macromolecular structures shown in Scheme 1.

Figures 1–4 show TG and DTG curves for the polymers **I**, **II** and **III**. These curves indicate that the polymers decompose in three stages: ionic cleavage of a P–O bond, in agreement with the results of Kricheldorf and Koziel [20]; oxidative degradation of the olefenic –C=C– bonds; decomposition of the aromatic residues with simultaneous scission of different kinds of covalent linkages, such as C–O, C–H and C–C bonds, up to the formation of phosphorus oxide and char as end product.

The TG curves in Fig. 5 indicate that polymers **IV** and **V** have similar pyrolysis patterns, with less well defined stages than those in Fig. 1. This indicates that all the stages in the polymers in Fig. 5 overlap into a very



Scheme 1. Macromolecular structures. **I**: $X = 0$, R is H; **II**: $X = 1$, R is H; **III**: $X = 2$, R is H; **IV**: $X = 0$, R is OCH_3; **V**: $X = 1$, R is OCH_3.

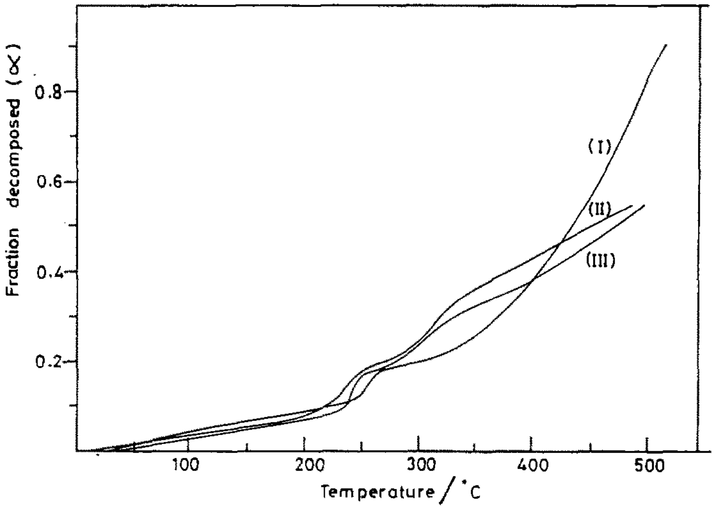


Fig. 1. TG curves for polymers **I**, **II** and **III**.

rapid stage, whereas the well-defined stages are predicted from the DTG curves in Figs. 6 and 7.

From Fig. 1 and Table 1, it can be seen that the thermal stability of the polymers is in the order **I** > **II** > **III**, i.e. the polymer containing the 2-oxo-1,3-cyclopentanediylidene moiety is more thermally stable than those containing the 2-oxo-1,3-cyclohexanediylidene and 2-oxo-1.3-cycloheptanediylidene moieties. This stability can be attributed to the more rigid structure in polymer **I** due to the cyclopentanone moiety, compared with the structures of polymers **II** and **III** which contain the cyclohexanone and cycloheptanone moieties [21], respectively.

Figure 5 and Table 1 reveal that the thermal stability of the polymers are

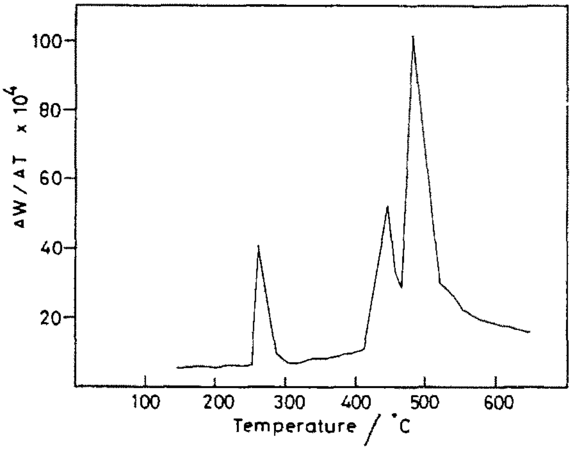


Fig. 2. DTG curve for the decomposition of polymer **I**.

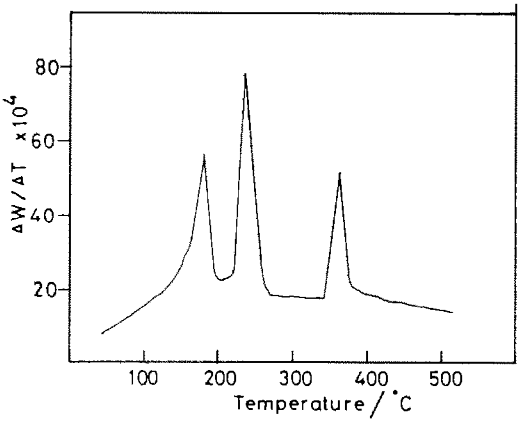


Fig. 3. DTG curve for the decomposition of polymer **II**.

in the order **IV** > **I** and **V** > **II**. The greater relative stability of polymers **IV** and **V** compared to **I** and **II**, respectively, is due to the presence of a $-OCH_3$ donor group which increases the stability of $-C=C-$ towards oxidation in the thermolysis stage [21].

The following equation was used to evaluate the kinetic parameters from non-isothermal TG curves [22, 23]

$$\ln \alpha - 2\ln T = \ln \frac{AR}{E_a\beta} - E_a/RT$$

where α is the fraction of solid decomposed after time t, β is the heating rate, and the other terms have their usual significance.

Plots of $\ln \alpha - 2\ln T$ against $1/T$ for the samples are shown in Figs. 8–12.

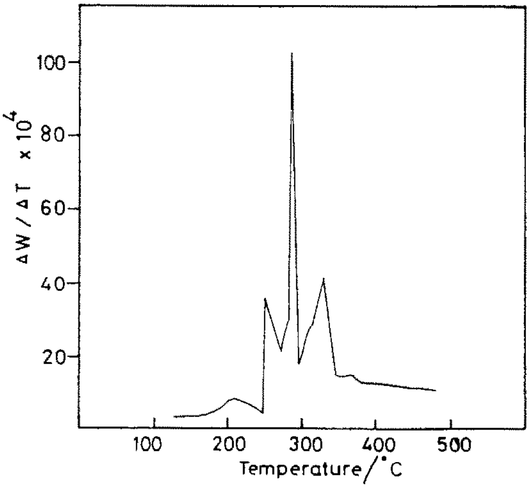


Fig. 4. DTG curve for the decomposition of polymer **III**.

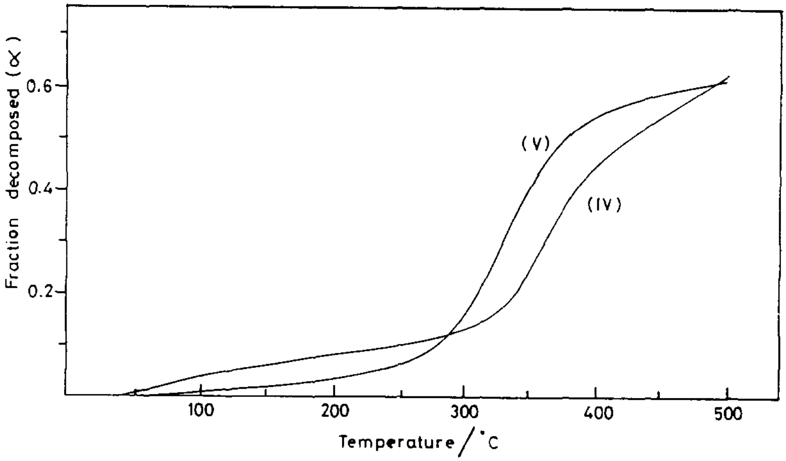


Fig. 5. TG curves for polymers **IV** and **V**.

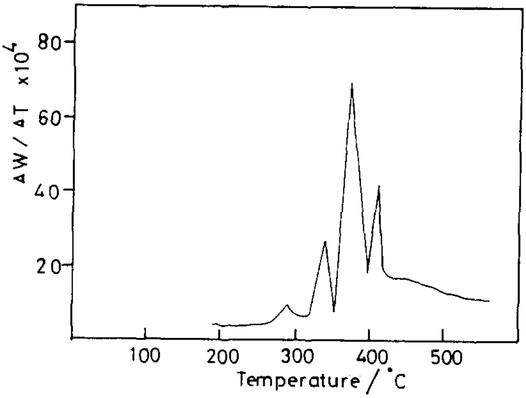


Fig. 6. DTG curve for the decomposition of polymer **IV**.

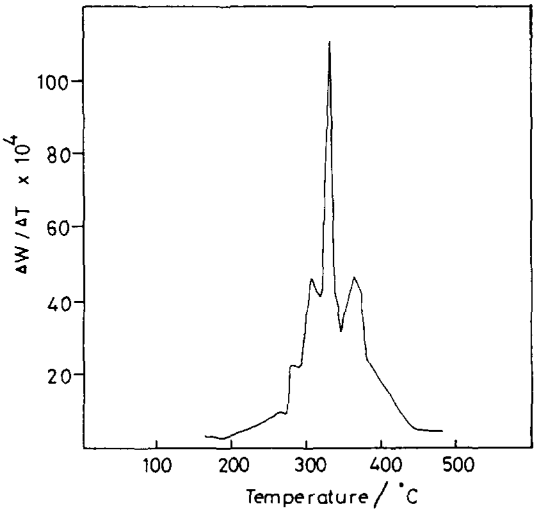


Fig. 7. DTG curve for the decomposition of polymer **V**.

TABLE 1

Temperature (°C) corresponding to various α values of the polymers

Polymer	Temperature (°C) for various α values			
	0.1	0.2	0.3	0.4
I	248	308	470	390
II	242	284	335	380
III	230	274	320	345
IV	302	248	369	390
V	294	314	333	353

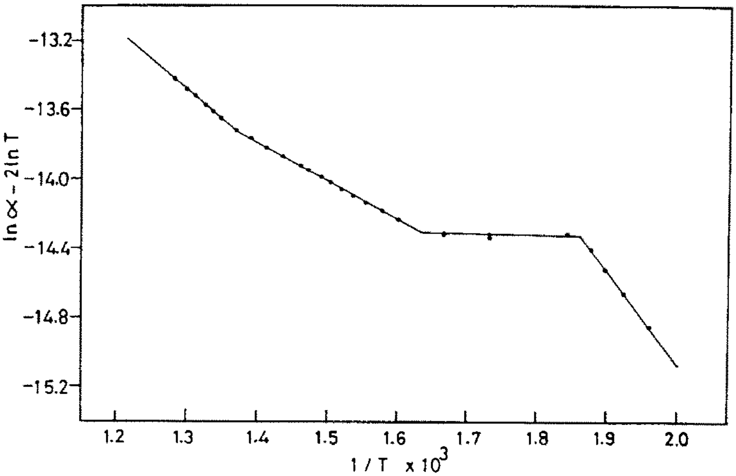


Fig. 8. Plot of ln $\alpha - 2\ln T$ vs. $1/T$ for the thermal decomposition of polymer **I**.

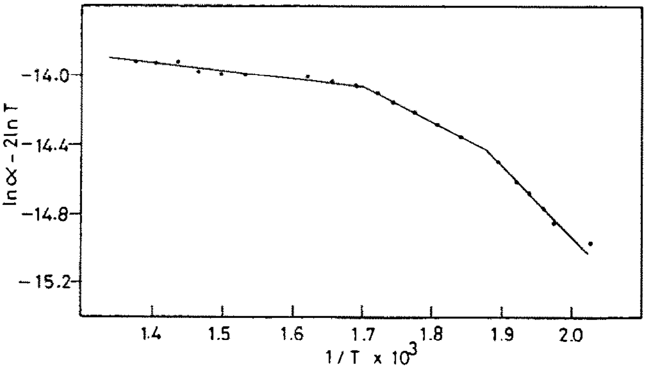


Fig. 9. Plot of ln $\alpha - 2\ln T$ vs. $1/T$ for the thermal decomposition of polymer **II**.

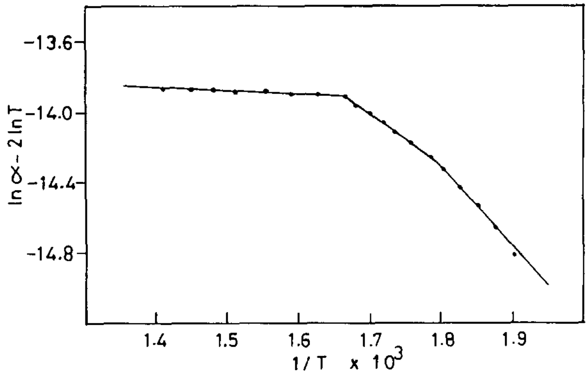


Fig. 10. Plot of ln α − 2ln T vs. 1/T for the thermal decomposition of polymer **III**.

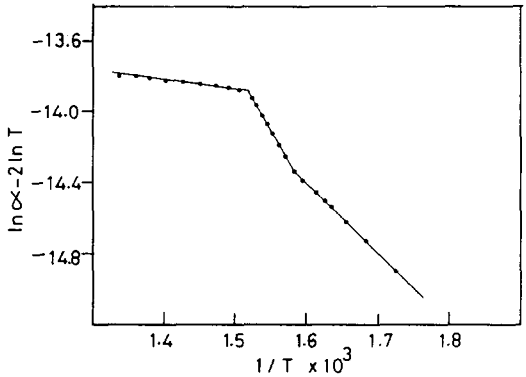


Fig. 11. Plot of ln α − 2ln T vs. 1/T for the thermal decomposition of polymer **IV**.

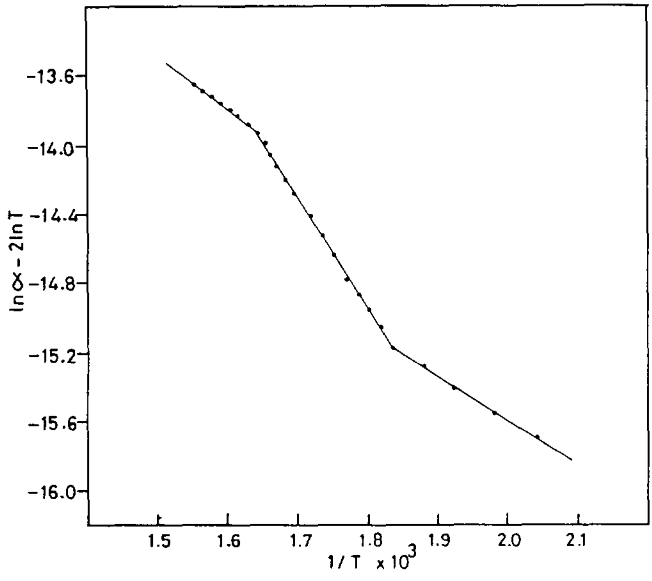


Fig. 12. Plot of ln α − 2ln T vs. 1/T for the thermal decomposition of polymer **V**.

TABLE 2

Kinetic parameters of the polymers

Polymer	Range/°C	E/kJ mol^{-1}	A/s^{-1}	ΔS/J K^{-1} mol^{-1}
I	245–270	44.18	7.6	−0.54
	350–455	18.35	6.1×10^{-3}	−0.69
	460–500	28.3	5.4×10^{-2}	−0.64
II	235–260	37.62	8.1×10^{-1}	−0.56
	280–315	19.65	7.2×10^{-3}	−0.65
	320–500	3.97	9.7×10^{-5}	−0.74
III	225–255	36.12	9.7×10^{-1}	−0.55
	295–330	22.24	4.0×10^{-2}	−0.61
	340–435	1.76	3.2×10^{-5}	−0.74
IV	320–360	32.69	1.4×10^{-1}	−0.55
	365–385	58.52	37.8	−0.45
	390–485	4.51	1.4×10^{-4}	−0.67
V	220–285	18.81	84.5	−0.42
	285–330	51.83	30.9	−0.44
	335–375	20.0	3.3×10^{-2}	−0.56

A good linear correlation is shown, composed of three separate straight lines, indicating that there are three reactions involved in the decomposition processes, as mentioned above. The activation energies for each were calculated from the corresponding slopes, A was obtained from the intercept, and the entropy of activation $\Delta S^\star$ was determined from the equation [23]

$$A = \frac{KI}{h}\exp(\Delta S^\star/R)$$

where K is Boltzmann's constant, h is Planck's constant and T the peak temperature obtained from the DTG curves of Figs. 2–4, 6 and 7. The kinetic data for the non-isothermal decomposition and the temperature range in which each decomposition step occurs are summarized in Table 2.

REFERENCES

1 M.A. Abd-Alla, M.M. Kandeel, K.I. Aly and A.S. Hammam, J. Macromol. Sci. Chem., A27 (1990) 523.
2 M.A. Abd-Alla and Kamal I. Aly, High Perform. Polym., 2 (1990) 181.
3 M.A. Abd-Alla, J. Macromol. Sci. Chem., 27 (1990) 1531.
4 M.A. Abd-Alla, High Perform. Polym., 2 (1990) 121.
5 M.A. Abd-Alla and K.I. Aly, High Perform. Polym., 2 (1990) 223.
6 M.A. Abd-Alla and K.I. Aly, High Perform. Polym., 2 (1990) 235.
7 M.A. Abd-Alla and A.S. El-Shahawy, J. Appl. Polym. Sci., 42 (1991) 461.

8 M.A. Abd-Alla, M.F. El-Zohry and M.A. Osman, Polym. Bull., 25 (1991) 287.
9 M.A. Abd-Alla and R.M. Mahfouz, J. Appl. Polym. Sci., 42 (1991) 2225.
10 M.A. Abd-Alla, K.I. Aly and A.A. Geies, J. Macromol. Sci. Chem., 28 (1991) 269.
11 M.A. Abd-Alla and A.S. El-Shahawy, Macromolecules, 24 (1991) 5528.
12 K.I. Aly and M.A. Abd-Alla, Polym. J. Jpn., 24 (1992) 165.
13 M.A. Abd-Alla and A.S. El-Shahawy, Polymer, 33 (1992) 1525.
14 M.A. Osman, A.A. Othman and M.A. Abd-Alla, Polymer, 33 (1992) 52
15 M.A. Abd-Alla and K.I. Aly, J. Macromol. Sci. Pure Appl. Chem., 29 (1992) 185.
16 K.I. Aly, M.F. El-Zohry and M.A. Abd-Alla, Polym. Int., 30 (1993) 313.
17 V.V. Korshak (Ed.), Phosphorus-Containing Polymers, Izd. Nauk, Moscow, 1982.
18 W.W. Wendlandt, Thermal Methods of Analysis, Vol. 19, Chemical Analysis, Wiley-Interscience, New York, 1974.
19 T. Nguyen, E. Zaurin and E.M. Barral, J. Macromol. Sci. Rev. Macromol. Chem., 20 (1981) 1.
20 H.R. Kricheldorf and H. Koziel. J. Macromol. Sci. Chem. A, 23 (1986) 1337.
21 M.M.M. Abd El-Wahab and M.A. Abd-Alla, High Perform. Polym., 4 (1992) 215.
22 Gy. Pokol, G. Gal, J. Satalisz, L. Domokos and E. Pungor, in J. Wood (Ed.), Reactivity of Solids, Plenum Press, New York, p. 209.
23 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.