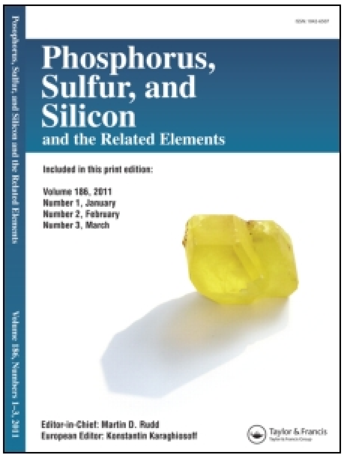

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PHOSPHORUS AND METAL CONTAINING OLIGOMERS

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PHOSPHORUS AND METAL CONTAINING OLIGOMERS

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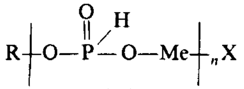


Phosphorus and metal containing oligomers of the type $R\left[O-\overset{\overset{O}{\|}}{P}(H)-O-Me\right]_n X$ were synthesized through the interaction between dialkylphosphites and metal salts of the type MeX_2. The oligomers exhibit a high thermal stability.

INTRODUCTION

The recently studied interaction between dialkylphosphites and metal salts[1] is a convenient method for the synthesis of phosphorus and metal containing monomers, which can find application as modifiers of polyethylenterephthalates and as catalysts in the production of acetophenone and formaldehyde.[2]

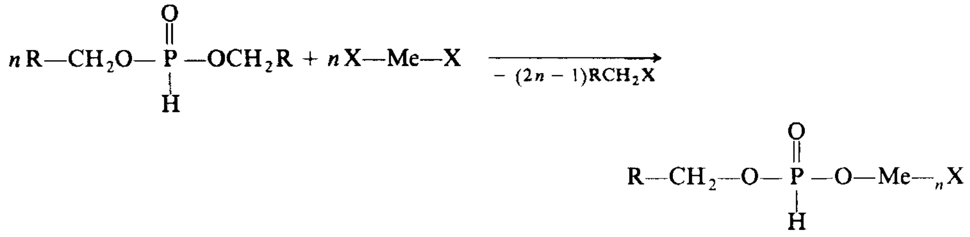
The aim of the present paper is to apply this reaction for the synthesis of phosphorus and metal containing oligomers.

RESULTS AND DISCUSSION

The interaction of dialkylphosphites and metal salts of the type MeX_2 at a molar ratio of 2 : 1 produced various phosphorus- and metal-containing monomers.[1] The investigation of the mechanism of this interaction revealed that when the starting monomers are correctly selected it is possible to obtain oligomers and polymers. Depending on the functionality of the salt employed one can produce either linear or cross-linked final products. In the present paper we have studied the synthesis of the linear oligomers in view of their scientific and practical significance.

The metal salts used were chlorides or acetates, since it was found earlier,[1] that the substitution of the two chlorine anions and the two acetate groups proceeds at the same rate.

In the interaction between dialkylphosphites and metal salts of the MeX_2 type at a molar ratio 1 : 1 the following phosphorus- and metal-containing oligomers were synthesized:



$$nR{-}CH_2O{-}\underset{H}{\overset{\overset{O}{\|}}{P}}{-}OCH_2R + nX{-}Me{-}X \xrightarrow[-(2n-1)RCH_2X]{} R{-}CH_2{-}O{-}\underset{H}{\overset{\overset{O}{\|}}{P}}{-}O{-}Me{-}_nX$$

where R = H; CH_3; C_3H_7; X = Cl; $OCOCH_3$; Me = Zn; Ca; Co; Cd; Mn.

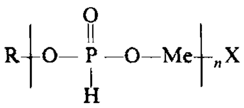
The proposed reaction scheme indicates that, depending on the duration of the reaction, it is possible to synthesize oligomers with different molecular weights. This possibility is confirmed experimentally by the data in Table I.

As established in the preceding paper[1] the interaction between dialkylphosphites and metal salts is a bimolecular nucleophilic substitution, the rate of which depends on the strength of the nucleophile, and on the value of the positive charge of the α-carbon atom.

The experiments carried out showed that the interaction between dimethylphosphite and cadmium acetate occurs at 85°C, at which temperature there is no interaction between diethylphosphite and manganese acetate. The nucleophile in both cases is one and the same (the electronegativities of Cd (1.7) and Mn (1.5) are very close and they will exert one and the same influence on the nucleophilic strength), whereas the positively charged centres are different. The difference between the interaction temperatures of dimethylphosphite with cadmium acetate on one hand and diethylphosphite with manganese acetate on the other is most likely due to the higher positive charge of the α-carbon atom in dimethylphosphite as compared with that of diethylphosphite. It is to be expected that the positive charge of dimethylphosphite is larger having in mind the positive constant of polarization of hydrogen, which will reduce more strongly the electronic density of the carbon atom than the methyl group.

TABLE I

Phosphorus- and metal-containing oligomers with general formula:



$$R\left[O{-}\underset{H}{\overset{\overset{O}{\|}}{P}}{-}O{-}Me\right]_nX$$

R	Me	X	Yield %	Me, %	P, %	Cl, %	n	Molecular weight
C_4H_9	Zn	Cl	85	43.0	20.63	3.30	8	1100
C_2H_5	Ca	Cl	90	26.2	22.25	1.95	15	1800
CH_3	Cd	$OCOCH_3$	95	44.5	12.75	—	—	—
CH_3	Co	Cl	95	30.0	16.04	11.75	2	300
C_2H_5	Mn	$OCOCH_3$	90	20.2	26.96	—	—	—

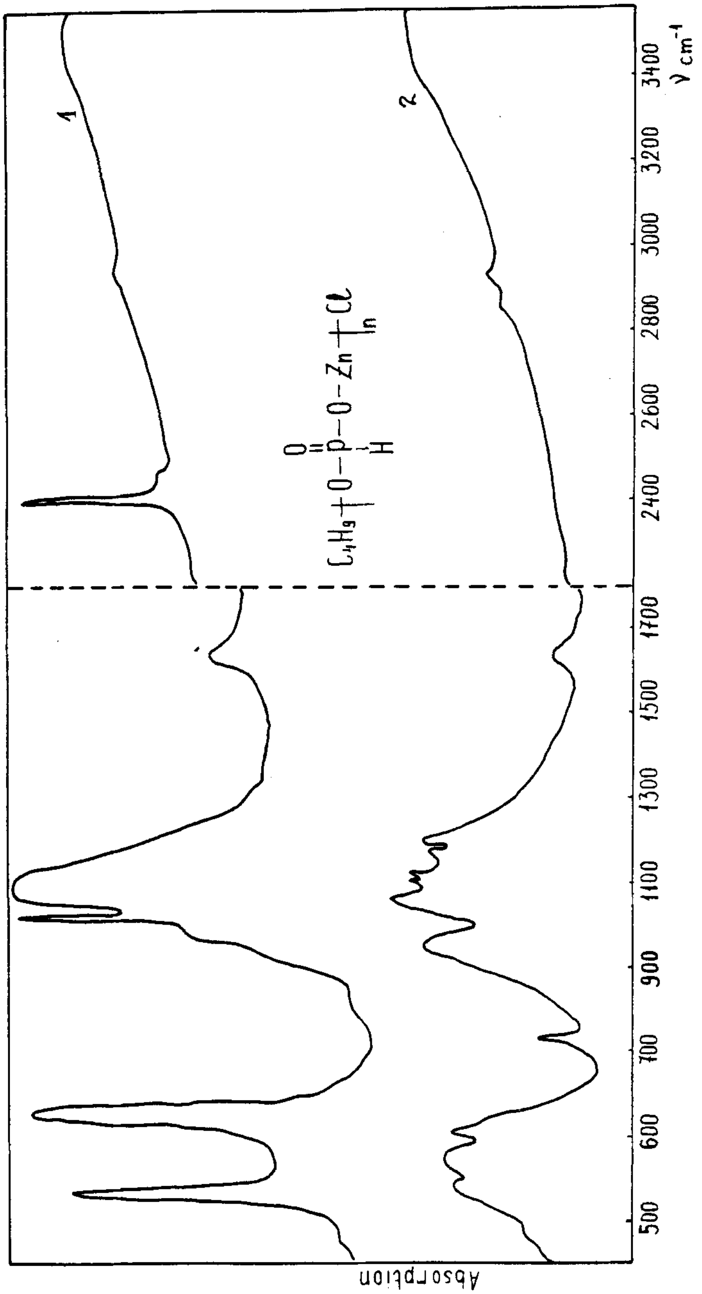


FIGURE 1 IR spectra of oligomers, synthesized from dibutylphosphite and $ZnCl_2$ (curve 1); curve 2—after thermal treatment.

The conditions under which the rest of the interaction occur correlate well with the nucleophilic strength and the magnitude of the positive charge of the cationic centre.

The structures of the oligomers were determined by IR spectroscopy and elemental analysis of the metal (by atomic absorption spectroscopy) and phosphorus.

The IR spectrum of the oligomer obtained from dibutylphosphite and zinc chloride (Figure 1, curve 1) reveals the following absorption bands: 2420 cm^{-1}, characteristic for the P—H group, 1185 cm^{-1}, for the P=O group, 1080 cm^{1} for the P—O—C group. The 575 cm^{-1} band can be attributed to the Me—O group.[3]

The elemental analysis for metal and phosphorus confirmed the compositions of the oligomers (Table I). The molecular weights of the oligomers containing Cl were determined by the method of terminal groups.

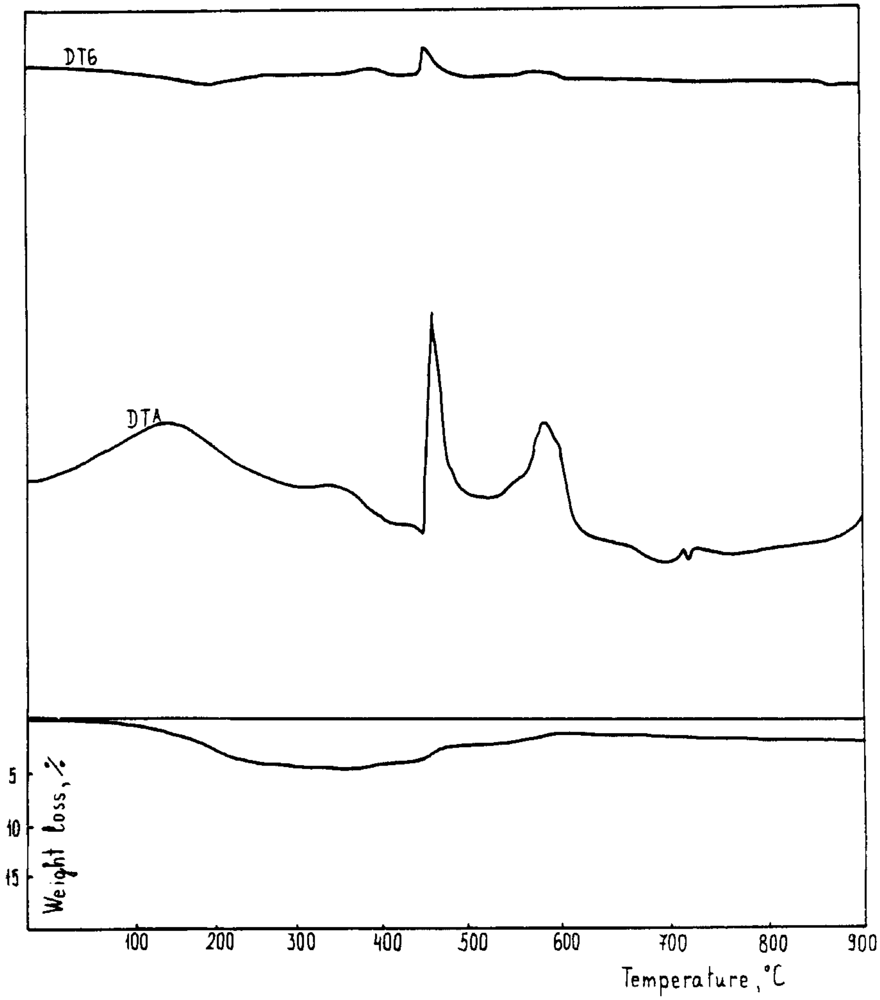


FIGURE 2 DTA curves of oligomers synthesized from dibutylphosphite and $ZnCl_2$.

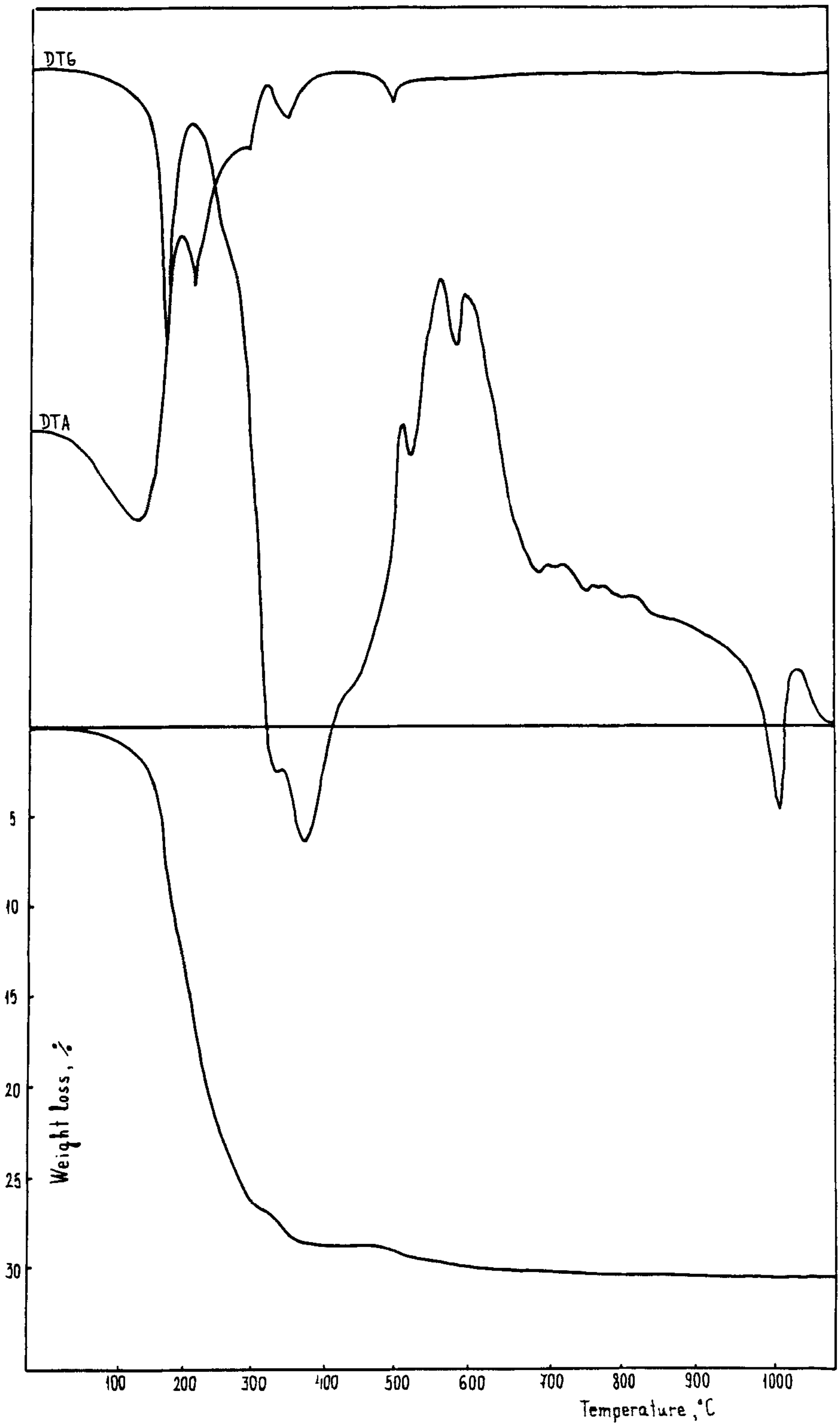


FIGURE 3 DTA curves of oligomers synthesized from diethylphosphite and Mn acetate.

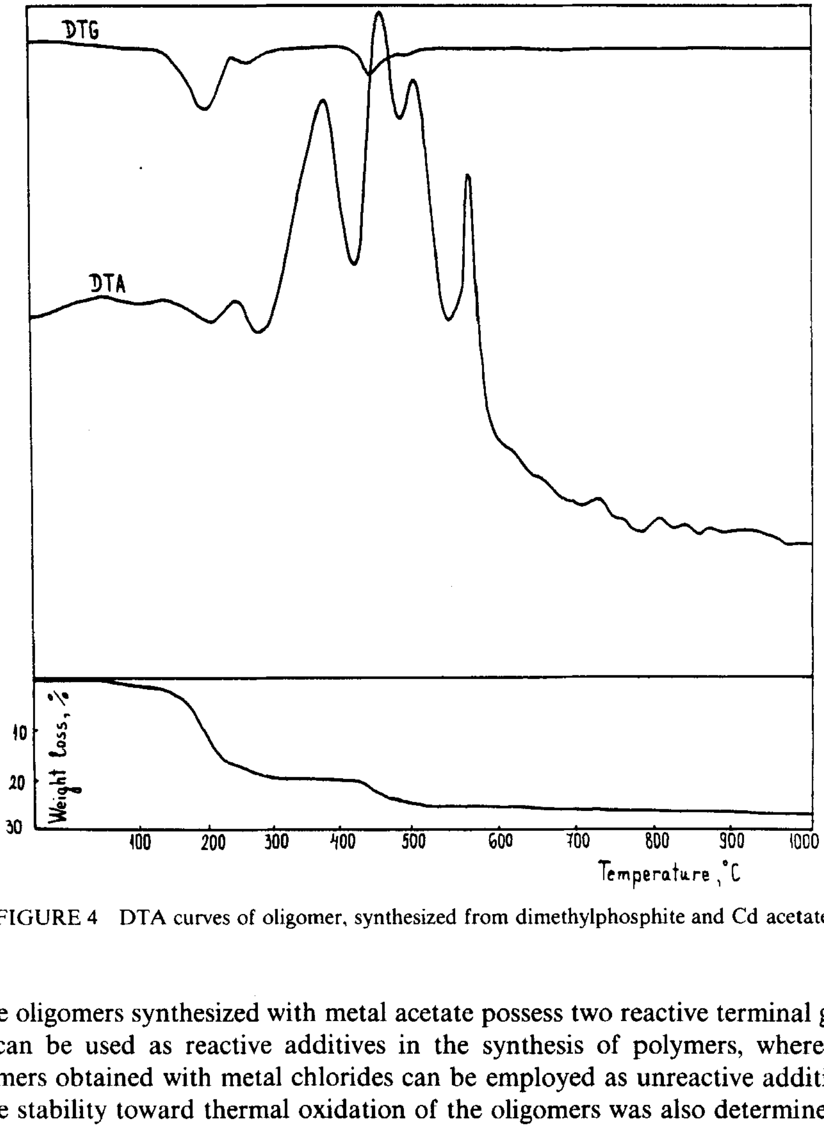


FIGURE 4 DTA curves of oligomer, synthesized from dimethylphosphite and Cd acetate.

The oligomers synthesized with metal acetate possess two reactive terminal groups and can be used as reactive additives in the synthesis of polymers, whereas the oligomers obtained with metal chlorides can be employed as unreactive additives.

The stability toward thermal oxidation of the oligomers was also determined.

The oligomer obtained from dibutylphosphite and zinc chloride exhibited a high thermal stability (Figure 2). Up to 200°C the oligomer loses only 3% of its weight, while between 200°C and 400°C no weight losses were detected. The DTA curve exhibits an exotherm at 450°C, which is associated with a weight gain of about 1.5%, most likely due to oxidation reactions. The comparison of the IR spectra of the oligomer before and after the thermal destruction (Figure 1, curve 2) reveals that as a result of the destruction the band at 2410 cm^{-1} characteristic for the P—H group disappears, while the bands of the P=O and P—O—C groups are strongly reduced. Up to 1000°C this oligomer loses 2.5% in weight.

The oligomer obtained from diethylphosphite and manganese acetate begins to decompose at 120°C (Figure 3). Up to 1000°C it loses 30% of its weight. This significantly lower thermal stability in comparison with that of the oligomer ob-

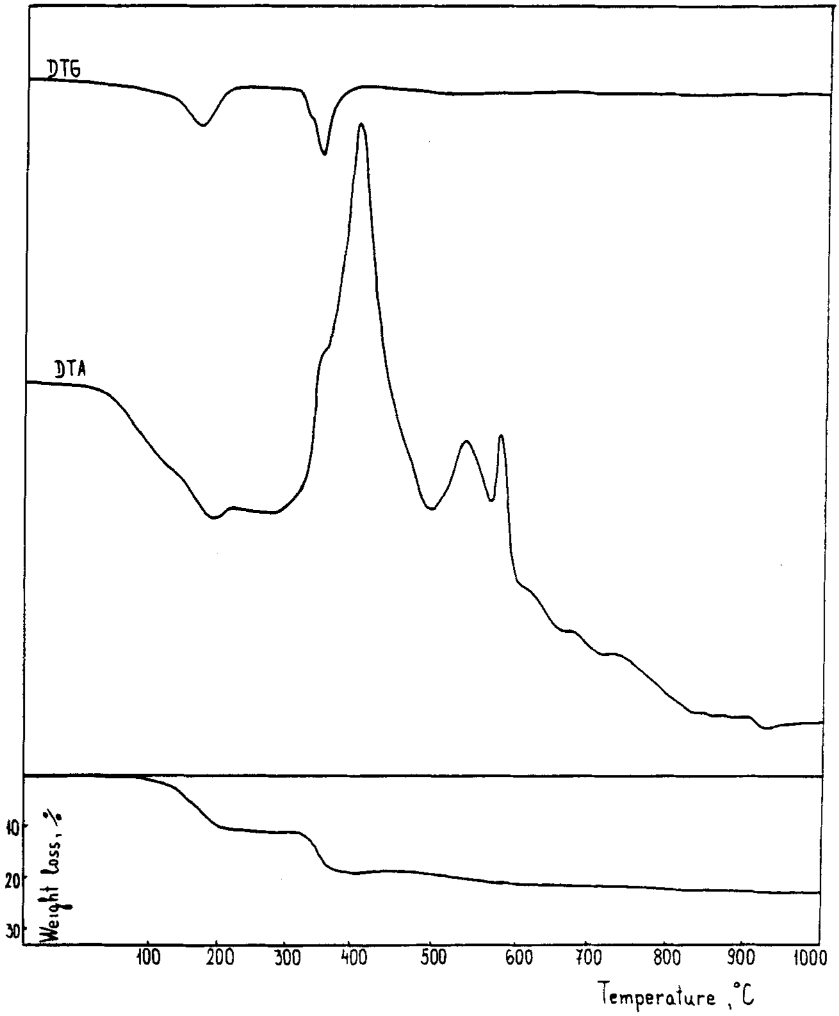


FIGURE 5 DTA curves of oligomer synthesized from dimethylphosphite and $CoCl_2$.

tained from dibutylphosphite and zinc chloride is probably associated with its structure. Its chain is built up of bonds that are less stable than the metal-chlorine ionic bond. The results of the thermal studies of the oligomers synthesized from dimethylphosphite and cadmium acetate (Figure 4), dimethylphosphite and cobaltous chloride (Figure 5), and diethylphosphite and calcium chloride (Figure 6) confirmed this assumption. The last two chlorine containing oligomers lose 10–15% less in weight upon heating than those synthesized with cadmium acetate.

A relationship was established between the weight losses and the molecular weight of the oligomer. For example, the oligomers obtained from diethylphosphite and calcium chloride with a molecular weight of 1800 loses ca. 12% of its weight (Figure 6), whereas the oligomer synthesized from dimethylphosphite and cobaltous chloride with a molecular weight of 300 loses ca. 22% (Figure 5). This relationship is

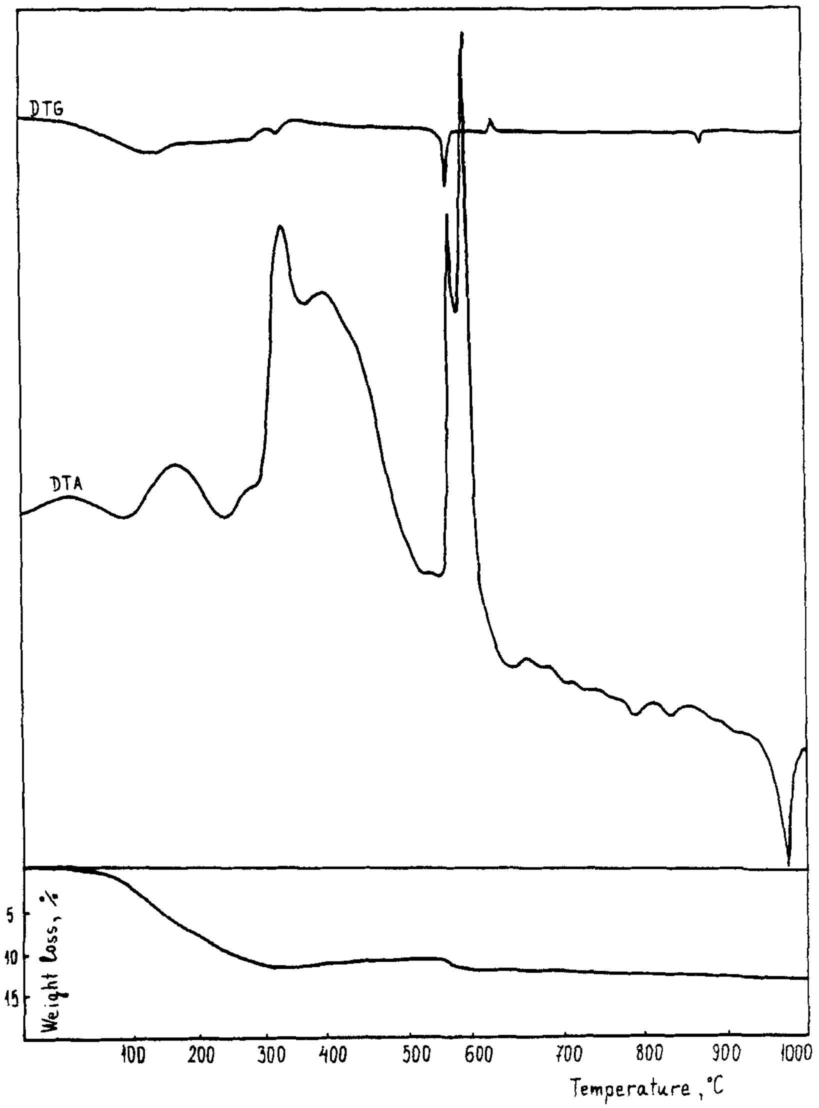


FIGURE 6 DTA curves of oligomer synthesized from diethylphosphite and $CaCl_2$.

explained by the fact that at a lower molecular weight, the percentage of aliphatic groups in the oligomer is higher and vice versa.

These oligomers are of practical significance, since when used as co-monomers or additives, they introduce phosphorus and metal in the polymers, and in cases where the molecular weight is lower, chlorine will be introduced in the polymers as well.

EXPERIMENTAL

Starting compounds: dibutyl-, diethyl- and dimethylphosphites from Fluka; $ZnCl_2$, $CaCl_2$, $CoCl_2$, Mn acetate and Cd acetate.

Interaction between dibutylphosphite and $ZnCl_2$. A mixture of 40 g (0.29 moles) of $ZnCl_2$ and 57.05 g (0.29 moles) of dibutylphosphite is poured into a three-neck flask provided with a stirrer, thermometer and a reflux condenser. The reaction is carried out under continuous stirring. At 105°C the reaction mixture becomes homogeneous and at 125°C butyl chloride is generated. The reaction proceeds at 135°C. After the evolution of butyl chloride ceases, the viscous reaction product is purified by reprecipitation from solutions of ethanol, methanol or hexane with a yield of 85%.

Interaction between dimethylphosphite and $CaCl_2$. 26.5 g (0.24 moles) of $CaCl_2$ and 33.5 g (0.24 moles) of dimethylphosphite are mixed to react in the same flask at 120°C. The final product, a solid, is purified by reprecipitation from solutions of ethanol or hexane with a yield of 90%.

Interaction between dimethylphosphite and Cd acetate. 87.8 g (0.38 moles) of Cd acetate and 42.0 g (0.38 moles) of dimethylphosphite are mixed and heated to 95°C. The solid product is purified by reprecipitation from solutions of hexane or ethanol with a yield of 95%.

Interaction between dimethylphosphite and $CoCl_2$. 23.85 g (0.18 moles) of $CoCl_2$ and 20.6 g (0.18 moles) of dimethylphosphite are mixed and heated. The solid product is purified by reprecipitation from solutions of ethanol or hexane with a yield of 95%.

Interaction between diethylphosphite and Mn acetate. 24.4 g (0.14 moles) of Mn acetate and 20.65 g (0.14 moles) of diethylphosphite are mixed and heated to 120°C. The reaction product is purified by reprecipitation from a solution of hexane with a yield of 90%.

All oligomers are solid substances. They do not melt.

The resistance against thermal oxidation of the products was determined by a MOM derivatograph in air at a rate of heating of 10°C/min. The IR spectra were recorded by a UR-20 spectrometer in KBr tablets.

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