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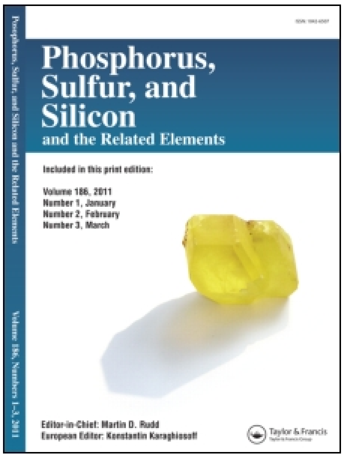

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Synthesis and Thermal Properties of Cyclotriphosphazene Containing Polyamides

Y. W. Chen-yang[a]; Y. H. Chuang[a]
[a] Department of Chemistry, Chung Yuan Christian University, Taiwan, R. O. C.

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SYNTHESIS AND THERMAL PROPERTIES OF CYCLOTRIPHOSPHAZENE CONTAINING POLYAMIDES

Y.W.CHEN-YANG and Y.H.CHUANG
Department of Chemistry, Chung Yuan Christian University
Chung-Li, Taiwan 32023, R.O.C.

Abstract A series of cyclotriphosphazene containing polyamides has been prepared by polycondensation of bis-(*p*-aminophenoxy)tetra(phenoxy)chlorocyclotriphosphazene and some diacid chlorides. The characterization, thermal stability and fire resistance of the synthesized polymers were studied. TGA showed that the polymers prepared were stable to above 320°C in nitrogen and exhibited high char contents at elevated temperature.

INTRODUCTION

Using organofunctional cyclotriphosphazenes as precursors to incorporate certain of the useful properties, such as flame retardancy, of the phosphazenes into traditional organic polymers is one of the interesting fields in the research field of phosphazene polymers.[1-4] In this study bis(*p*-aminophenoxy)tetra(phenoxy)chlorocyclotriphosphazene, (III), was prepared and reacted with some selected diacid chlorides to prepare a series of bis(aminophenoxy)tetra(phenoxy)cyclotriphosphazene containing polyamides. Synthesis and characterization of polymers will be reported. Thermal properties of the polymers will also be discussed.

EXPERIMENTAL

In a typical example, a solution containing 15ml dried THF, 0.8g (1.1mmol) (III), 0.9g (2mmol) methyltrioctylammonium chloride and 0.35g (3.3mmol) triethylamine was added in 0.22g (1.1mmol) terephthalic diacid chloride and stirred under reflux for 48hrs. After the reaction, the solution was filtered and slowly added into a large amount of methanol.

The precipitate was taken out and dissolved in small amount of THF and the precipitatation was repeated. The polymer was then dried in vacuum for overnight to obtain 0.9g (95% of theory) of homopolymer PPT.

RESULTS AND DISCUSSION

In order to increase yield and reduce reaction time bis(*p*-nitrophenoxy)tetra(phenoxy)chlorocyclotriphosphazene, (II), was prepared from hexachlorocyclotriphosphazene, (I), by phase transfer catalysis. The monomer bis(*p*-aminophenoxy)-tetra(phenoxy)chlorocyclotriphosphazene, (III), was then obtained by reduction of (II). Direct polycondensation of (III) with the selected diacid chloride was carried out for preparation of the polymers in dried THF. The polymers synthesized are designated as shown in Scheme-I.

Table I lists the NMR data and the composition of the polymers estimated from two kinds of the amide protons. Together with IR spectra, the results indicated that the cyclotriphosphazene skeleton as well as the amide skeleton were incorporated into the polymer as expected. The values of x and y shows that the reactivity of (III) is similar to that of MDA, but, is better than that of SDA.

As listed in Table II, the molecular weight of homopolymers measured by GPC are in the order of 10^4. The inherent viscosities of the polymers vary between 0.20 and 0.27 in DMSO at 25°C. It indicates that the polymers obtained have moderate molecular weights.

The glass transition temperatures (T_g) were determined by differential scanning calorimetry under nitrogen atmosphere and are listed in Table II. The lower Tg of PPS and PPSS is ascribed to a consequence of the flexible diacid portion SDC.

The thermal behavior of the polymers was investigated by thermogravic analysis under nitrogen atmosphere. The temperature with 10% weight loss ($T_{10\%}$), the temperature at which the polymer's maximum rate of weight loss occured (T_{max}), and the residue at 600°C are given in Table II. It is found that the threshold temperatures of all the polymers at which major thermal decomposition, T_{max}, occured above 320°C. The residues at 600°C in nitrogen are above 35% and increase with the content of cyclotriphosphazene. This result shows that the phosphazene portion is helpful in raising the residue at elevated temperature. A simple test also proved that the polymers were self extinguishing in a fire.

CONCLUSION

In this study, a class of cyclotriphosphazene containing polyamides were synthesized and characterized. The study showed that moderate molecular weight polymers can be prepared by polycondensation of diamino cyclotriphosphazene (III) and the selected diacid chlorides and the polymers prepared all have good heat and fire resistant properties.

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Table I. The NMR data and composition of the polymers.

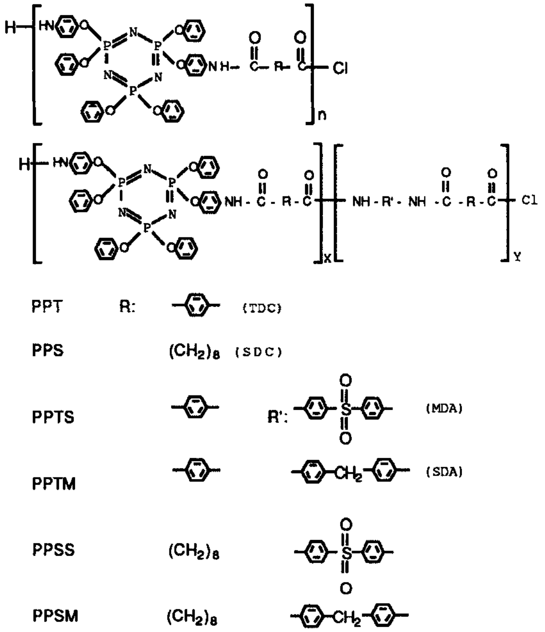
Polymer	^{31}P	^{1}H NH_x	NH_y	x* phosphazene	y* SDA	MDA
PPT	8.90	10.51	-	-	-	-
PPS	8.68	9.93	-	-	-	-
PPTS	8.86	10.50	11.24	0.70	0.30	-
PPTM	8.90	10.44	10.55	0.65	0.35	-
PPSS	9.00	9.97	10.35	0.46	-	0.54
PPSM	9.14	9.84	9.97	0.50	-	0.50

* estimated from ^{1}H NMR data.

Table II. The physical properties of the polymers.

Polymer	Mn ($x10^{-4}$)	η_{inh}*	Tg (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	char yield (%)
PPT	4.8	0.24	77.7	320	324	54.8
PPS	1.6	0.20	41.9	320	322	46.7
PPTS	-	0.22	-	320	320	52.0
PPTM	-	0.27	-	331	331	54.8
PPSS	-	0.20	39.8	348	354	43.8
PPSM	-	0.27	82.9	373	375	35.6

* 0.5 g/dl of DMSO at 25°C



Scheme-I