polymer reports

Synthesis of aromatic polyphosphonate: low temperature solution polycondensation of 4,4′-sulphonyldiphenol with phenoxy dichlorophosphate

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This paper describes the synthesis of an aromatic polyphosphonate from the reaction of phenoxy dichlorophosphate (PDCP) with 4,4′-sulphonyldiphenol (SDP) in a chlorinated hydrocarbon solvent under low temperature conditions. The glass transition temperature (T_g) and melt temperature (T_m) of PDCP/SDP polymer are 69°C and 133°C, respectively. The lower T_g value of PDCP/SDP compared to that of phenyl phosphonic dichloride/SDP may be attributed to the flexible ether linkage. This polymer started to lose weight at around 300°C under air or nitrogen atmosphere. The PDCP/SDP polymer has good flame retardancy, as indicated by high limiting oxygen index of 47.0.

(Keywords: aromatic polyphosphonate; glass transition temperature; limiting oxygen indices; solution polycondensation)

INTRODUCTION

The low temperature solution polycondensation process has been widely used to prepare polymers such as polyesters and polycarbonates[1]. However, published results for polyphosphonates using this technique are relatively scarce. Polyphosphonates are of commercial interest because of their flame retardant characteristics[2] and potential as high performance plastics[3].

Several researchers have published results on syntheses of polyphosphonates by interfacial polycondensation[4–8], by melt[9,10] or by high temperature solution polymerization[11]. For example, Massai *et al.*[11] investigated the high temperature solution copolymerization of phenyl phosphonic dichloride (PPD) with 4,4′-sulphonyldiphenol (SDP) in tetrachloroethane, using $CaCl_2$ as a catalyst. Kim[12] studied the low temperature polycondensation of PPD with 4,4′-thiodiphenol (TDP) and SDP. Natansohn[13] reported that an aryl polyphosphonate with an inherent viscosity of 0.08 dl g^{-1} was synthesized from the reaction of chloromethylphosphonic dichloride with SDP.

This paper describes the low temperature solution polycondensation of phenoxy dichlorophosphate (PDCP) with SDP. The effects of a flexible ether linkage at the phosphorus atom on the thermal behaviour and flame retardant characteristics are discussed. Comparisons are made with PPD/SDP polymers.

EXPERIMENTAL

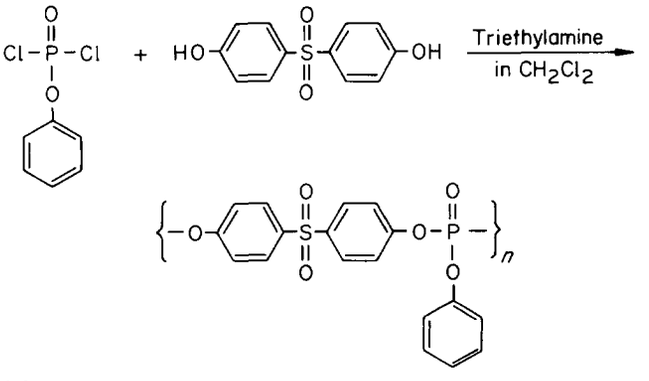
Materials

PDCP was prepared by refluxing a mixture of phenol (47.06 g, 0.5 mol) and phosphorus oxychloride (230 g, 1.5 mol), followed by distillation several times under reduced pressure; b.p. 108–109°C, 1.07 kPa. The yield was 85.5%. The PDCP thus obtained was characterized by analytical techniques using i.r., ^{1}H n.m.r. and ^{31}P n.m.r. I.r.: $\bar{\nu}$ (P=O), 1302 cm^{-1}, $\bar{\nu}$ (P–O–C), 1182, 1024 cm^{-1}. $\bar{\nu}$ (⬡), 1587, 1487 cm^{-1}. ^{1}H n.m.r. (in $CDCl_3$): δ 7.15–7.28 (⬡—O—). ^{31}P n.m.r. ($CDCl_3$): δ 2.97. Gas chromatography showed the purity of the sample to be higher than 99.9%.

Polymerization

A flask equipped with a paddle stirrer, addition funnel and reflux condenser was charged with 5.00 g (20 mmol) of SDP, 60 ml of methylene chloride, and 4.44 g (44 mmol) of triethylamine, and subjected to vigorous stirring at 0°C. Then a solution of 4.22 g (20 mmol) of PDCP and 10 ml of methylene chloride was slowly added to the flask (~1 h). During the addition an exothermic reaction occurred. After the whole quantity was added, the reaction mixture was allowed to warm to room temperature and was subsequently refluxed for 4 h. *Scheme 1* illustrates the synthesis.

The polymer solution was washed with dilute HCl (1%) and distilled water until the aqueous phase was



Scheme 1

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neutral to litmus paper. The solution was filtered and the polymer precipitated with methanol. The white polymer was dried *in vacuo* at 60°C for 24 h. The yield was determined as 93% (7.12 g).

Elemental analysis of $[C_{18}H_8SO_6P]_n$ Calcd: C, 55.67; H, 3.35; S, 8.25%. Found: C, 55.12; H, 3.63; S, 8.51%.

Characterization

The inherent viscosity of the polymer at a concentration of 0.1 g dl^{-1} in 1,2-dichloroethane was 0.33 dl g^{-1} at 25°C. The glass transition temperature (T_g) was measured with a DuPont 9000 differential scanning calorimeter at a heating rate of 5°C min^{-1}. The midpoint in the baseline shift was taken as T_g. T.g.a. data were obtained with a DuPont 9900 thermogravimetric analyser with a heating rate of 10°C min^{-1}, under a nitrogen atmosphere. The weight average molar mass ($\bar{M}_w$) was determined by light scattering using an Otsuka DLS-700 photometer. ASTM D-2863-77 procedure was used to measure the limiting oxygen index (LOI). ^{31}P n.m.r. spectra were taken on a Bruker AM-300 WB.

RESULTS AND DISCUSSION

The polymers obtained from condensation of PDCP and SDP were insoluble in aliphatic hydrocarbons and alcoholic solvents but soluble in chlorinated aliphatic hydrocarbons such as CH_2Cl_2 and $CHCl_3$, and aprotic solvents such as dimethylsulphoxide (DMSO) and dimethylformamide (DMF). *Table 1* shows the i.r. spectral data of PDCP/SDP polymer. The ^{1}H n.m.r. spectrum shows that there are two peaks at 7.99 and 7.15–7.28 ppm which are attributed to the protons in *ortho* and *meta* position to the sulphonyl group resonance, respectively[13]. The resonance of the phenoxy group also falls in the range of 7.15–7.28 ppm.

The results of low temperature polycondensation of PDCP with SDP in various solvents by using triethylamine as an acid acceptor are summarized in *Table 2*. It may be concluded that chlorinated aliphatic hydrocarbons such as methylene chloride or chloroform are the best polymerization solvents. Dichloroethane is also suitable for polymerization. However, no polymer was obtained in chlorobenzene. *Table 3* shows the effect of acid acceptor on the viscosity of PDCP/SDP polymers with the molar mass measured by light scattering. It indicates that the condensation system requires a moderate base such as triethylamine or tri-n-butylamine as an acid acceptor. The PDCP reaction did not proceed in the presence of weaker bases such as pyridine or *N*,*N*-dimethyl aniline. This phenomenon has been reported previously by Kim[12] for the polycondensation of PPD with TDP, and by Schlott *et al.*[14] for 4,4′-biphenyl disulphonyl chloride with bisphenol-A. A ^{31}P n.m.r. spectrum of the polycondensation products also confirms the formation of phosphonate (a singlet at 11.7 ppm for the PDCP/SDP polymer in DMSO-d_6, reference H_3PO_4). Results from elemental analyses (see above) are in agreement with the proposed polyphosphonate structure.

Table 1 IR spectral data of PDCP/SDP polymer

	Characteristic group (cm^{-1})
P=O	1290
P–O–C	1194, 954
SO_2	1150, 1300
Ph	3050, 1586, 1487, 760

Table 2 Effect of solvent on the preparation of PDCP/SDP polymer

Solvent	Yield (%)	η_{inh}[a] (dl g^{-1})
CH_2Cl_2	93	0.33
$CHCl_3$	92	0.34
$ClCH_2CH_2Cl$	90	0.29
C_6H_5Cl	0[b]	–

[a] Solution (0.1 g dl^{-1}) of 1,2-dichloroethane
[b] Yields insoluble amine/SDP complexes

Table 3 Effect of acid acceptor on the preparation of PDCP/SDP polymer

Acid acceptor	pK_b[a]	Yield (%)	η_{inh}[b] (dl g^{-1})	$\bar{M}_w$[c]
Triethylamine	3.1	93	0.33	20900
Tri-n-butylamine	3.1	86	0.21	7110
Pyridine	7.8	0	–	–
Dimethyl aniline	8.0	0	–	–

[a] Data from Hall[15]
[b] Solution (0.1 g dl^{-1}) of 1,2-dichloroethane
[c] Measured by light scattering

Table 4 Thermal behaviour data of PDCP/SDP polymer ($\bar{M}_w$ = 20900)

		Decomposition temperature[b] (°C)		Weight remaining at 800°C (%)	
T_g[a] (°C)	T_m[a] (°C)	Air	N_2	Air	N_2
69	133	425	425	8	40

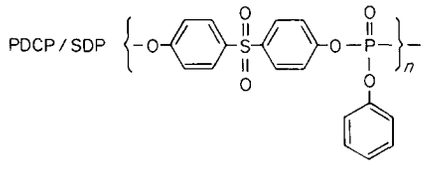
[a] Determined at a heating rate of 5°C min^{-1} in nitrogen
[b] Temperature at which at 10% weight loss was recorded by t.g.a. at a heating rate of 10°C min^{-1}

Table 5 LOI of polyphosphates

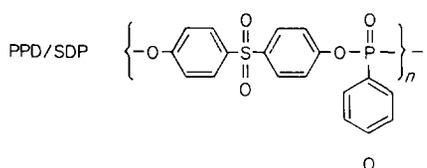
Copolymer	LOI	P (%)	T_g (°C)	T_m (°C)
PDCP/SDP	47	8.0	69	133
PPD/SDP[a]	50	8.2	146	185
PPD/TDP[a]	60	9.1	83	170

[a] Data from Kim[12]

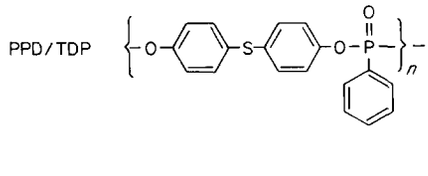
PDCP / SDP



PPD / SDP



PPD / TDP



The PDCP/SDP polymer with $M_w = 20900$ has a melting temperature (T_m) of 133°C and a T_g of 69°C. The difference in T_g between PDCP/SDP (69°C) and PPD/SDP (146°C) is dramatic[12]. This may be attributed to the flexible ether linkage of the PDCP/SDP polymer. T.g.a. data for the polyphosphonate are shown in *Table 4*. The PDCP/SDP polymer begins to lose weight at about 300°C under nitrogen and a 10% weight loss was measured at approximately 425°C. The weight percentage remaining at 800°C is 8% and 40% under air and nitrogen atmosphere, respectively.

The flame resistance of the polymer was measured by its LOI values. As shown in *Table 5*, the PDCP/SDP polymer containing 8.0% phosphorus has LOI = 47. It is not surprising that the LOI value of PDCP/SDP is slightly lower than that of PPD/SDP. This could be explained in terms of the higher content of phosphorus in the latter.

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