Synthesis of poly(alkyl/arylphosphazene)s with ester substituents*

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A series of polyphosphazenes with ester side groups was prepared from a derivative of poly(methylphenylphosphazene) that contained alcohol functional groups. The synthesis involved treatment of $\{[Ph(Me)P=N]_2(Ph[Me_2C(OH)CH_2]P=N)\}_n$ with acid chlorides, $RC(=O)Cl$, where $R=(CH_2)_nCH_3$ ($n=2$, 4, 6, 8, 10, 12 and 14) in the presence of triethylamine. These new polymers were characterized by ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy, i.r. spectroscopy, size exclusion chromatography and thermal analysis (d.s.c. and t.g.a.). The systematic dependence of the glass transition temperatures of these new polymers on the number of methylene groups is discussed.

(Keywords: polyphosphazene; ester substituents; poly(methylphenylphosphazene))

INTRODUCTION

The field of inorganic and organometallic polymers has been a rapidly expanding area of materials science and polymer chemistry for about two decades. Among these polymers, polyphosphazenes, $[R_2PN]_n$, with an inorganic backbone of alternating single and double bonds between phosphorus and nitrogen, have been particularly exciting because they have such a wide range of chemical and physical properties. The versatility of polyphosphazenes is due largely to the variety of substituents that can be attached to the backbone phosphorus atom. For example, with appropriate substituents, polyphosphazenes can be flame retardant, radiation resistant, flexible at low temperatures[1–3], water soluble[4,5], ionically conducting[6,7], biologically active or compatible[8], liquid crystalline[9,10] and second order non-linear optical materials[11].

The methods for preparing polyphosphazenes can be placed into four general categories[12]. By far the most work has been done on the first and second methods which involve the ring-opening polymerization of halogenated or partially halogenated cyclic phosphazenes (e.g. $[Cl_2PN]_3$) and subsequent nucleophilic substitution reactions at the halogens[1–3,8]. A third method is the condensation polymerization of either N-silylphosphoranimines, $Me_3SiN=P(OR')R_2$ (refs 13–15) or the dichlorophosphoryl phosphoranimine, $Cl_2P(=O)N=PCl_3$ (refs 16 and 17). While the latter gives halogenated polymers suitable for nucleophilic displacement reactions as above, the former is a direct approach to polyphosphazenes that contain simple alkyl/aryl[13,14] or alkoxy or aryloxy[15] groups. The fourth method for preparing new phosphazene polymers involves the derivatization of preformed poly(alkyl/arylphosphazene)s[18] that are obtained by the condensation polymerization of N-silylphosphoranimines[5,12]. While each of the methods has particular advantages, they also differ in terms of the type of polymers that they produce. Thus, for example, polymers with large groups such as steroids[19] or procaine derivatives[20] attached to phosphorus by C-O-P or C-N-P linkages are only accessible through nucleophilic substitution of poly(dichlorophosphazene). On the other hand, polyphosphazenes with simple alkyl and aryl groups directly attached to every phosphorus via P-C linkages must be prepared by the condensation polymerization approach.

The focus of the work in our laboratory has been the development of the derivatization of poly(alkyl/arylphosphazene)s for the purpose of extending the range of properties of this class of polyphosphazenes. Poly(methylphenylphosphazene), $[Me(Ph)PN]_n$, **1**, is especially interesting because there are three reactive sites in this polymer, each of which has been studied to some extent. One site is the phenyl groups which can be partially substituted with nitro groups when treated with a mixture of nitric and sulfuric acid[21]. The lone pairs of electrons on the backbone nitrogen are very basic and constitute the second reactive site in this polymer. Thus, simple adducts are formed with Lewis acids such as MeI (ref. 22), $AlCl_3$ (ref. 23), acetic acid and transition metal cations[22]. The third and best studied reactive site is the methyl substituent in **1**. The hydrogens are sufficiently acidic to undergo deprotonation or metal–hydrogen exchange upon treatment with n-BuLi giving a reactive polymer anion, **2** [equation (1)]. Subsequent reaction of the anion with various electrophiles has resulted in the preparation of polyphosphazenes with alcohol[24], ferrocenyl[25], thiophenyl[24], carboxylic acid, ester, and carboxylate salt[5], substituted silyl[26], ether[27], fluoroalkyl[28], bromo and phosphino[29] groups [equation (1)]. The anion

* Presented at the American Chemical Society, Division of Polymer Chemistry '17th Biennial Symposium on Advances in Polymerization and High Performance Polymeric Materials', 22–25 November 1992, Palm Springs, CA, USA

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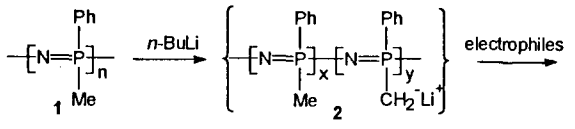
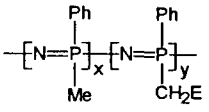
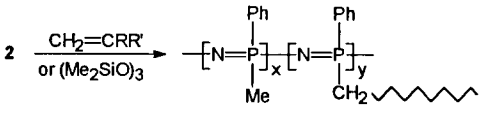
0032-3861/94/23/4985–05

has also been used to initiate the grafting of both organic [polystyrene[30] and poly(methyl methacrylate)[22]] and inorganic (polydimethylsiloxane)[31] polymers to the polyphosphazene backbone [equation (2)].





(1)



(2)

As part of our studies on the scope of the derivatization reactions of poly(alkyl/arylphosphazene)s, we have begun to study the feasibility of extending this process an additional step. Several of the new polyphosphazenes discussed above have potentially reactive sites that are suitable for further derivatization. Such reactions can provide methods for incorporation of groups that cannot be readily attached by simple deprotonation–substitution reactions. In this study the utility of alcohol groups for the attachment of ester functionalities was examined. When significant changes in glass transition temperature (T_g) were observed, the study was extended to assess the effect of varying the chain length of the ester substituents on the T_gs and on solubility.

EXPERIMENTAL

Materials

Poly(methylphenylphosphazene), $[Ph(Me)PN]_n$, **1**[13,14] and its alcohol derivative, $\{[Ph(Me)P=N]_2(Ph[Me_2C(OH)CH_2\}P=N)\}_n$, **3** [equation (3)][24] were prepared by published procedures and were dried under vacuum at 50°C for at least 24 h before use. All acid chlorides (98–99%), Et_3N and methanol were purchased from commercial sources and were used as obtained. Hexane was distilled from CaH_2 and tetrahydrofuran (THF) was distilled from Na/benzophenone immediately prior to use.

Instrumentation and general procedures

Elemental analyses were performed on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. S.e.c. measurements were performed on a Waters Associate GPC instrument with Maxima software for data handling using μstyragel columns (500, 10^3, 10^4, 10^5 Å). The s.e.c. operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-}Bu)_4N^+Br^-$, a flow rate of 1.5 ml min^{-1}, a temperature of 30°C, and a sample size of 50 μl of 0.1% solution. Calibration was accomplished with a series of narrow molecular weight polystyrene standards. The ^1H, ^{31}P and ^{13}C n.m.r. spectra were recorded on an IBM WP-200SY Fourier transform n.m.r. spectrometer in $CDCl_3$. Positive ^1H n.m.r. and ^{13}C n.m.r. resonances are downfield from the external reference Me_4Si and positive ^{31}P n.m.r. resonances are downfield from the external reference phosphoric acid. I.r. spectra were recorded as thin films or as $CDCl_3$ solutions on Perkin–Elmer 283 or Perkin–Elmer Series 1600 Fourier transform i.r. spectrometers. T.g.a. measurements were performed on a Du Pont TGA model 951 instrument equipped with a Du Pont 1090 thermal analyser data station. Samples (~50 mg) were heated at a rate of 10°C min^{-1} from room temperature to 800°C under a constant flow of air. D.s.c. measurements were made under nitrogen on a Du Pont 910 instrument using an aluminium reference and a temperature range of 0–150°C. Each sample was heated and cooled at least two times. The inflection point for the final heating cycle is listed in *Table 2*.

Synthesis of ester derivatives

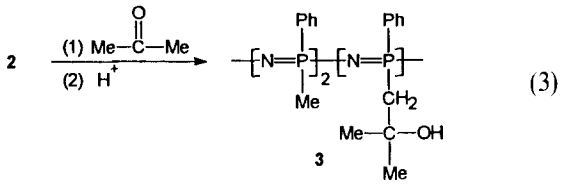
In a typical procedure 1.0 g (6.0 mmol) of the alcohol derivative, **3**, was placed in a 100 ml three-necked flask and dried overnight in a vacuum oven at 65–70°C. The flask was fitted with a magnetic stirrer, a nitrogen inlet adapter and a rubber septum. After purging the flask with nitrogen, 10 ml of freshly distilled THF was added by syringe. Upon dissolution of the polymer, 8.0 mmol of Et_3N was added by syringe. The flask was then cooled to 0°C and 5.0 mmol of the acid chloride was added slowly over ~10 min to the stirred solution [equation (4)]. Stirring was continued for 2 h at 0°C and then overnight at room temperature. The reaction mixture was then poured slowly into a beaker filled with 600 ml of distilled water. The precipitated polymer was collected and dissolved in 20 ml of THF and precipitated into water twice more. A final precipitation from THF into hexane and subsequent drying under vacuum at 50°C overnight afforded polymers **4a–c** as cream coloured powders. Because polymer derivatives **4d–g** did not precipitate well into hexane, the final purification was precipitation from THF into MeOH. Upon drying under vacuum at 50°C for a minimum of 24 h, **4d–g** were isolated as light brown coloured, gum-like materials. Typical yields were between 65% and 80%.

RESULTS AND DISCUSSION

Prior to this work, two other methods for preparing ester derivatives of poly(methylphenylphosphazene) were investigated[5]. Both involved esterification of the carboxylic acid derivative, $\{[Me(Ph)PN][Ph(HOOCCH_2)PN]\}_n$. Coupling reactions with alcohols using dehydrating reagents such as 1,3-dicyclohexylcarbodiimide were unsuccessful, even upon heating for several days. Attempts were also made to convert the carboxylic acid substituents to acid chlorides with thionyl chloride, but these reactions were accompanied by chain cleavage caused by the evolution of HCl at elevated temperatures*. Thus we investigated the reactions of simple commercially available acid chlorides with a derivative of poly(methylphenylphosphazene) that contained alcohol substituents. This polymer, $\{[Ph(Me)P=N]_2(Ph[Me_2C(OH)CH_2]P=N)\}_n$, **3**, was prepared by reaction of acetone with the polymer anion, **2** [equation (3)] as reported previously[24]. A tetrahydrofuran (THF) solution of **3** was then treated with acid chlorides in the presence of a slight excess of triethylamine [equation (4)]. The new ester derivatives

* Numerous experiments in our laboratory have demonstrated that the poly(alkyl/arylphosphazene)s and their derivatives undergo chain degradation when heated in the presence of HCl or HBr or their ammonium salts

were purified by precipitation into water to remove the triethylammonium hydrochloride salts and any carboxylic acids formed by the hydrolysis of unreacted acid chlorides.



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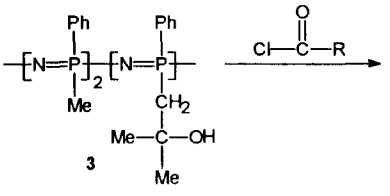

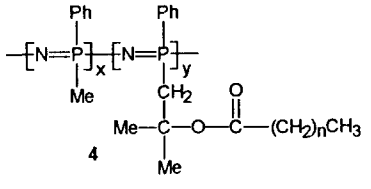

(4)

$R = (CH_2)_nCH_3$

Polymer no.	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**
n	2	4	6	8	10	12	14

Like the alcohol derivatives, the new ester derivatives were soluble in THF, CH_2Cl_2 and $CHCl_3$. Though most were insoluble in hexane, those with longer alkyl side groups, where $n = 10$–14, appeared to be somewhat hexane soluble. Thus, it was not possible to further purify these polymers by precipitation from THF into hexane. Instead, water from prior work-up was removed by precipitation into methanol followed by drying under vacuum.

In general, the ester derivatives were off-white powders with shorter alkyl groups or sticky, gum-like materials when the alkyl groups were longer ($n = 10$–14). I.r. spectra of these polymers contained the expected carbonyl signal at $\sim 1720\,cm^{-1}$ (*Table 1*) rather than that of either acid chlorides (1790–1810) or carboxylic acids (1750–1765)[32]. Moreover, the signal at 3280–3340 cm^{-1} for the OH stretch in the alcohol-substituted precursor[32] completely disappeared indicating complete conversion of the alcohol group to the ester functionality. This was corroborated by the fact that the signal for the alcohol OH group (δ 6.1) in the ^1H n.m.r. spectra of the starting polymer, **3**, was not observed in the ^1H n.m.r. spectra of the esters.

The ^1H n.m.r. spectra of the esters contained the expected signals for the phenyl group at δ 7.1–7.8 and the P-CH_2 protons at δ 2.1–2.5. Generally, the terminal CH_3 groups for the alkyl chain were also clearly distinguishable at δ 0.7–0.9. The remaining alkyl methylene groups overlapped with the unsubstituted methyl groups on phosphorus resulting in broad signals at δ 1.2–1.6. Integration of the total alkyl region *versus* the phenyl region and simple algebraic manipulations were used to estimate the per cent substitution, i.e. the proportion of backbone phosphorus atoms containing ester side groups. These values were typically between 25% and 30%, analogous to the alcohol precursor that had similar degrees of substitution. The elemental analysis data, however, indicated slightly lower degrees of substitution. As shown in *Table 2*, best agreement for the analysis is generally at 20% (i.e. $x = 4$, $y = 1$ in **4**). This seeming discrepancy is most likely due to the inaccuracies of the spectral integrations. It could also indicate that the alcohol functionality was not completely converted to ester. However, elemental analysis calculations that allow for incomplete reaction of the OH group do not change the results significantly. For example, the calculated values for ester **4e** where n is 10 for simple 20% substitution and for 20% ester substitution with 10% unreacted OH groups are C, 64.85, H, 7.40, N, 7.56 and C, 64.62, H, 7.30, N, 7.70, respectively. The experimental values of C, 64.22, H, 7.65, N, 7.26 fit reasonably well with either. Nonetheless, since there is no evidence of OH groups in either the ^1H n.m.r. or i.r. spectra, it appears that essentially all of the alcohol groups have successfully been converted to ester. It should be noted that for all seven of the new esters the degree of substitution is remarkably consistent at 20%.

The ^{13}C n.m.r. and ^{31}P n.m.r. spectroscopic data for the ester polymer derivatives were also obtained. The ^{31}P n.m.r. spectra were similar to those of the alcohols with broad signals and/or multiple peaks between δ 1 and 4. The ^{13}C n.m.r. spectra contained numerous signals between δ 12 and 37 for the various alkyl carbons and typical aryl signals at δ 127 to 144. The number of alkyl signals increased as the alkyl chain grew longer. More definitive features of the ^{13}C n.m.r. spectra were the PCH_2 resonance at δ 45 and the carbonyl group at δ 172.

The molecular weights determined by s.e.c. were somewhat larger than those of the alcohol substituted polymer used to prepare the esters (*Table 2*) but the polydispersities changed very little. It is particularly noteworthy that no decreases in molecular weight were observed. This indicates that all traces of the byproduct, $Et_3NH^+Cl^-$, had been removed since heating the poly(alkyl/arylphosphazene)s with these salts is known to cause backbone degradation.

T.g.a. indicated that the thermal stability of the esters is similar to that of the alcohols. Onsets of decomposition ranged from 250 to 315°C. The most interesting thermal data, however, came from the d.s.c. measurements. The T_g decreased upon conversion of the alcohol to an ester, presumably because hydrogen bonding was eliminated. Hence, the T_g of **4a** was only 37°C, while the T_g of the parent alcohol substituted polymer, **3**, was 55°C.

Table 1 Spectroscopic data for the ester derivatives

Polymer (*n*)	^1H n.m.r. (δ)	^{31}P n.m.r. (δ)	I.r. ν (C=O stretch)
4a (2)	0.8, 1.3–1.6, 2.5, 7.1–7.6	1.1, 6.1[a]	1723
4b (4)	0.8, 1.3–1.5, 2.1, 7.1–7.8	2.7, 6.0	1716
4c (6)	0.7, 1.2–1.5, 2.2, 7.2–7.8	1.6, 2.2[a]	1720
4d (8)	0.7, 1.2–1.5, 2.5, 7.2–7.8	1.5, 2.2	1720
4e (10)	0.9, 1.3–1.4, 2.1, 7.1–7.7	2.3, 5.6	1719
4f (12)	0.9, 1.2–1.5, 2.3, 7.1–7.6	1.6, 2.3	1719
4g (14)	0.9, 1.2–1.4, 7.1–7.7	0.5, 4.2	1720

[a] Broad shoulder

Table 2 Analytical, s.e.c. and d.s.c. data

Polymer (*n*)	C[a] (%)	H[a] (%)	N[a] (%)	% substitution	M_w[b]	M_w/M_n[b]	T_g (°C)
	61.65	6.67	8.85				
4a (2)	(61.99)	(6.44)	(8.61)	20	147 000	1.8	37
	62.87	6.85	8.26				
4b (4)	(62.78)	(6.71)	(8.32)	20	129 000	1.9	27
	63.88	7.58	8.55				
4c (6)	(63.52)	(6.95)	(8.05)	20	149 000	1.7	23
	64.15	7.31	8.08				
4d (8)	(64.21)	(7.18)	(7.80)	20	156 000	1.7	10
	64.22	7.65	7.26				
4e (10)	(64.85)	(7.40)	(7.56)	20	147 000	1.9	14
	65.45	7.64	7.98				
4f (12)	(65.47)	(7.61)	(7.34)	20	149 000	1.7	21
	65.48	7.38	7.28				
4g (14)	(66.04)	(7.80)	(7.13)	20	163 000	2.0	29

[a] Calculated values in parentheses
[b] Obtained by g.p.c. The alcohol substituted polymers from which these esters were made had $M_w = 130\,000$ and $M_w/M_n = 2.1$

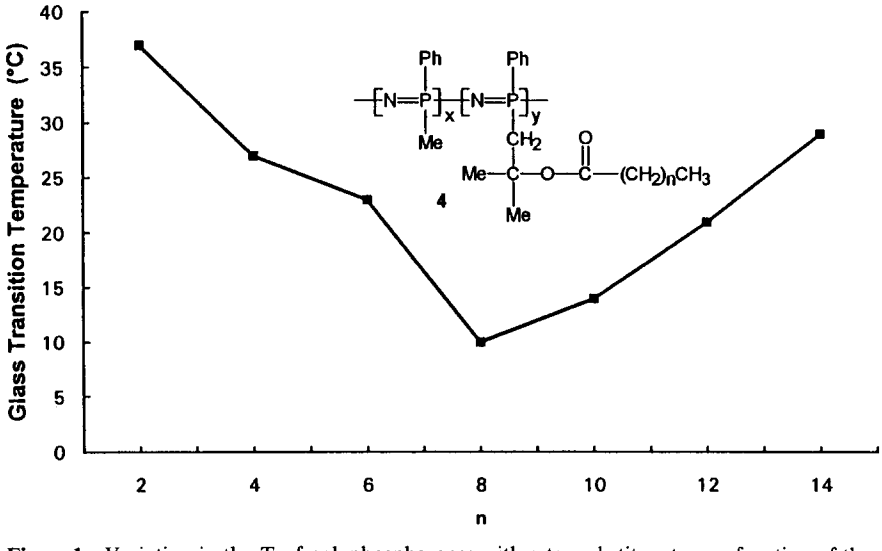

Figure 1 Variation in the T_g of polyphosphazenes with ester substituents as a function of the length of the ester alkyl groups

Moreover, the T_g was only 27°C for **4b** where the alkyl ester group was two carbon atoms longer (*Table 2*). This trend, as illustrated in *Figure 1*, continued for increasing chain length until a minimum T_g was reached at $R = (CH_2)_8CH_3$ in **4d**. For **4e**, **f** and **g**, where the alkyl groups were still longer, the T_g values increased with chain length. A similar effect was observed[33] for the poly(dialkoxyphosphazene)s, $[(RO)_2PN]_n$. For the esters reported here, the initial lowering of T_g by removal of hydrogen bonding is further enhanced when additional CH_2 groups remove other restrictions to backbone mobility. The shorter side groups essentially act as chain ends and increase free volume of the polymers. These groups can also interfere with interactions of the phenyl groups. On the other hand, chain to chain interactions become more important for the polymers with longer alkyl side groups. These may act as crosslinks which lower backbone mobility and decrease free volume, thus raising the T_g[34,35].

In summary, the variety of groups that can be attached to the backbone of polyphosphazenes by direct P-C linkages has been expanded to include ester moieties. In addition to adding another dimension to controlling such properties as the T_g and the solubility of this class of polymers, the ability to form ester linkages provides methods for attaching a number of other groups associated with biological or optical properties.

ACKNOWLEDGEMENTS

We thank the Robert A. Welch Foundation and the US Army Research Office for generous financial support of this work. Thanks are also extended to Dr John Banewicz for the elemental analyses of the polymers.

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