

Organic solvent-free synthesis of phosphorus-containing polymers*

Smaranda Iliescu, Gheorghe Ilia[‡], Aurelia Pascariu, Adriana Popa, and Nicoleta Plesu

Institute of Chemistry Timișoara, Romanian Academy, 24 Mihai Viteazul Bvd., 300223 Timișoara, Romania

Abstract: Direct, efficient, organic solvent- and catalyst-free synthesis of a series of polyphosphates was accomplished. The reaction involved a gas–liquid interfacial polycondensation between arylphosphoric dichlorides and bisphenol A. The polyphosphates were characterized by IR, ¹H NMR, ³¹P NMR, inherent viscosity, thermal analysis, and molar mass. Yields in the range 70–90 % and inherent viscosities in the range 0.30–0.40 dl/g were obtained. The thermal stability of the polyphosphates was investigated by using thermogravimetry.

Keywords: polyphosphates; solvent-free; arylphosphoric dichlorides; gas–liquid interfacial polycondensation; polyphosphates; bisphenol A.

INTRODUCTION

In recent years, polymeric phosphate and phosphonate are of commercial interest, because of their flame-retardant characteristics [1,2] and their potential use as high-performance plastics [3]. Much attention has been drawn to a new class of biodegradable polymers belonging to polyphosphate [4,5]. These polyphosphates have been investigated as biomaterials in drug delivery, gene delivery, tissue engineering, and agriculture [5–7]. The most important method which generates polyphosphonates and polyphosphates is polycondensation by melt [8], solution [9], ultrasound solid-phase [10], and interfacial polycondensation [11].

In a previous paper, we presented the synthesis of polyphosphonates by liquid–liquid interfacial polycondensation [12]. More attention has been recently paid to both environmental protection and ecological balance. It is known that the best solvent is no solvent, but if a solvent is needed, then water has a lot to recommend it. Organic solvent-free synthesis is an important part of green chemistry. Avoiding a solvent reduces the number of components in a reaction, stops any solvent emission problems, and gets around any solvent recycling requirements.

This paper presents our recent progress in the efficient synthesis of new polyphosphates through gas–liquid interfacial polycondensation [13]. The avoidance of organic solvents as media and the absence of catalysts represent significantly eco-friendly characteristics in this methodology.

Pure Appl. Chem.* **79, 1831–2100. An issue of reviews and research papers based on lectures presented at the 1st International IUPAC Conference on Green–Sustainable Chemistry, held in Dresden, Germany, 10–15 September 2006.

[‡]Corresponding author: E-mail: ilia@acad-icht.tm.edu.ro

Experimental

Chemicals

Arylphosphoric dichlorides and diols were received from Aldrich Chemical Company. Because the dichlorides are readily hydrolyzed, they were always vacuum-distilled just prior to reaction. Bisphenol A was recrystallized from toluene before use.

Instruments

The IR spectra were recorded on a SPECORD M80 spectrophotometer and ^1H NMR and ^{31}P NMR spectra on a Bruker DRX 400 MHz spectrometer. All NMR spectra were recorded in CDCl_3 using TMS as internal standard. The polymer was characterized by viscosity, on a Ubbelohde suspended-level viscometer at 30 °C. The molecular weights were determined by gel permeation chromatography, on an evaporative light scattering detector, PL-EMD 950 (2 \times PL gel MIXEDC 300 \times 7.5 mm columns; $T = 25$ °C; DMF as solvent; calibration with polystyrene as standard). Thermogravimetric analyses were carried out on a TGA/SDTA 851-LF1100 Mettler apparatus, by heating in air (5 mg) from initial temperature of 20 to 1100 °C with a rate of 10 °C/min.

General procedure

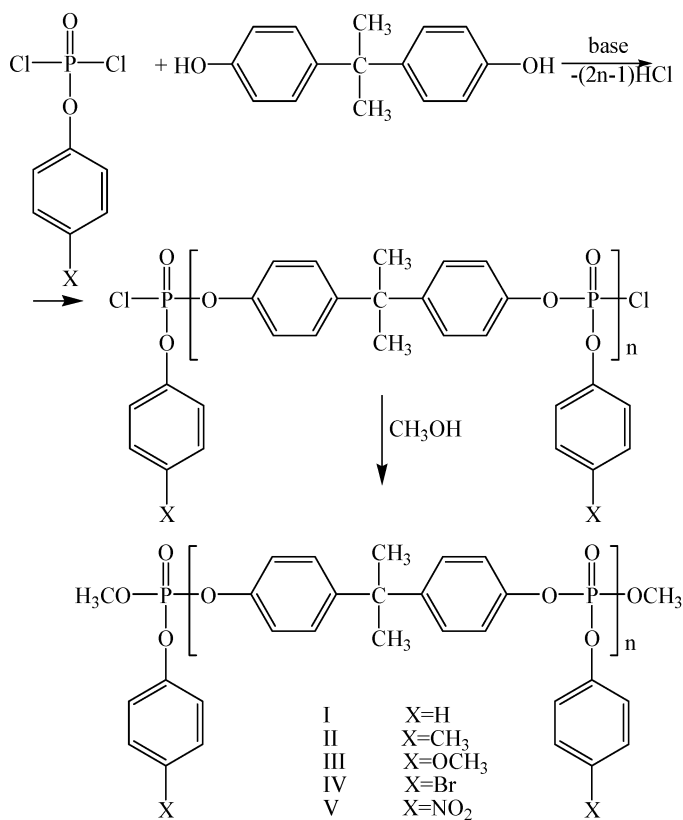
The appropriate arylphosphoric dichloride at 80–90 °C was evaporated with the aid of a stream of nitrogen, into a solution of the diol in aqueous 1 M sodium hydroxide. The solvent for diols is water since it readily dissolves the phenolate formed. The nitrogen stream acts as carrier gas for the arylphosphoric dichloride, as reaction mixture protector from the atmospheric oxygen, and for agitation of the reaction mixture. The reaction rate can be controlled by the nitrogen flow rate. In order to prevent the possibility of condensation of the vapors on apparatus walls, the vapor mixture is overheated or is diluted so that the partial pressure of the vapor reagent in the gas mixture is lower than its saturation vapor pressure. The carrier gas flow, which produced bubbles in the formed product that expanded and burst at the top of the reaction flask, was continued 15 min after the entire quantity of arylphosphoric dichloride is trained. Polymer separates after 30 min from solution as tacky, coherent mass, adhering to the container surface. The solid polymer was washed with distilled water until free of chloride ion, was then dissolved in chloroform and refluxed with methanol for 2 h; the higher-molecular-weight fraction was precipitated by adding excess of methanol. The polymer was then dried at 50 °C, in vacuum. The obtained polymer shows wide ranges of consistency and softening.

RESULTS AND DISCUSSIONS

Gas–liquid polycondensation utilizes pairs of highly reactive monomers with one of the monomers in the gaseous state and the other in solution. A typical gas–liquid polycondensation procedure is presented in previous papers [13,14]. Since arylphosphoric dichlorides are more volatile than diols, they are preferentially employed in the gas phase.

The gas–liquid interfacial polycondensation technique was successfully used to synthesize the five polyphosphates by reacting arylphosphoric dichlorides (vapor) with sodium salts of the bisphenol A (Scheme 1).

Synthesis of polymers by interfacial polycondensation requires an alkaline catalysis. Hydroxyl ions concentration changed during polycondensation can promote competing reactions (hydrolysis of the phosphoryl chloride groups of the reagent or of the chain end groups of the polyphosphonate). This secondary reaction may cause immediately a decrease of the molecular weight of polymer. In order to get data for preparing polyphosphonates with high molecular weights, the effect of alkaline medium on yield and inherent viscosity was studied [15]. Those reaction conditions must be chosen to obtain higher yields and inherent viscosities in order to prevent the degradation of polymer and competing reactions.



Scheme 1 Gas-liquid interfacial synthesis of polyphosphates I-V.

The method does not require an organic solvent and catalyst reaction taking place in water, and for that reason the auxiliary procedures in gas-liquid interfacial polycondensation are simplified considerably.

The yields, inherent viscosities, molecular weights, and phosphorus content for the obtained polyphosphates are presented in Table 1. The high inherent viscosity and molecular weights about 10^4 obtained, prove that the propagation rate is higher than the competing reactions rate.

The structure of the polyphosphates synthesized was elucidated by IR, ^1H NMR, and ^{31}P NMR spectroscopy. A complex set of $\text{P}=\text{O}$ at $1250\text{--}1300\text{ cm}^{-1}$ and characteristic aromatic C-H stretches at 2900 cm^{-1} were seen for all five polymers. Polymeric structure was supported by P-O-C stretch at 925 cm^{-1} and the disappearance of the broad O-H stretch of bisphenol A. All the polymers showed strong absorptions around 1180 and 960 cm^{-1} , which correspond to P-O-C (aromatic) stretching. Also, it was observed that the P-O-C (aliphatic) stretching absorptions is weak for all polymers, since this group is present only at the chain ends. The spectra of polymers I and II showed small percentages of bisphenol end groups. In the others it is completely absent. The other absorptions were characteristic of the aliphatic, aromatic groups present in the polymers and support the polyphosphate structure.

Table 1 Results of gas–liquid interfacial polycondensation of arylphosphoric dichlorides with bisphenol A.^a

Polym.	Yield %	η_{inh}^b dl/g	M_n^c $\times 10^3$	M_w^c $\times 10^3$	M_w/M_n^c	%P ^d	
						calc.	exp.
I	90	0.40	42.5	76.6	1.8	8.45	8.34
II	80	0.35	40.5	70.8	1.75	8.68	8.36
III	75	0.32	38.4	72.9	1.9	8.31	8.28
IV	70	0.30	34.5	79.3	2.3	7.35	7.30
V	82	0.33	36.8	77.3	2.1	7.98	7.84

^aReaction conditions: 0.10 mol arylphosphoric dichlorides, 0.040 mol bisphenol A, 0.090 mol NaOH 1 M, 50 min, reaction temperature 60 °C; temperature of arylphosphoric dichlorides maintained by an oil bath at 80–90 °C.

^bThe inherent viscosities η_{inh} were determined for solutions of 0.5 g/100 ml in tetrachlorethane, at 30 °C.

^cMolecular weights measured by GPC, in chloroform, polystyrene was used as standard (M_n = number-average molecular weight, M_w = weight-average molecular weight, M_w/M_n = polydispersity).

^dDetermined by Schöniger method.

The ¹H NMR and ³¹P NMR are summarized in Tables 2 and 3.

Table 2 ¹H NMR spectral data of the polyphosphates.

No	Chemical shift values in ppm				Others
	C(CH ₃) ₃	P–O–CH ₃	Main chain phenyl	Side chain phenyl	
I	1.6 (s)	3.8 (d)	7.0 (s)	7.4 (s)	6.5–7.0 (m) (bisphenol end group)
II	1.6 (s)	3.8 (d)	7.0 (s)	7.1 (s)	6.5–7.0 (m) (bisphenol end group;
III	1.6 (s)	3.8 (d)	7.2 (s)	6.7–7.4 (m)	2.1 (s) (CH ₃) 3.6 (s) (OCH ₃)
IV	1.6 (s)	3.8 (d)	7.2 (s)	7.8–7.3 (m)	–
V	–	3.8 (d)	7.1 (s)	7.2 (s)	–

Table 3 ³¹P NMR spectral data of the polyphosphates.

Polymer	Chemical shift values (ppm)	
	P at the chain end	P in the repeat unit
I	–11.4	–18.1
II	–11.2	–18.1
III	–11.3	–18.0
IV	–12.5	–18.6
V	–11.6	–18.5

The temperatures corresponding to 10 % weight loss, 50 % weight loss, inception of fast degradation, and the char remaining at 700 °C are presented in Table 4. All the polyphosphates except polymer II are stable between 250 and 300 °C. The NO₂ group is found to have much effect on the thermal degradation, whereas the other substituents do not influence the thermal stability.

Table 4. Thermal properties of polyphosphates.

Polym.	$T_d^{10\%}$ (°C)	Inception of fast degradation (°C)	$T_d^{50\%}$ (°C)	Residue at 700 °C (%)
I	250	300	450	19
II	200	220	320	12
III	280	370	460	22
IV	260	270	520	26
V	240	260	510	30

Where $T_d^{10\%}$ is the temperature at which 10 % mass loss was observed, and $T_d^{50\%}$ is the temperature at which 50 % mass loss was observed.

CONCLUSIONS

This article presents the recent activity and eco-friendly features of the solvent-free reactions. There are distinct advantages of these solvent-free protocols since they provide reduction or elimination of solvents thereby preventing pollution in organic synthesis “at source”.

This modern synthetic methodology was applied to produce polyphosphates by gas–liquid interfacial polycondensation of arylphosphoric dichlorides with bisphenol A. Water is a very attractive solvent for reaction chemistry. It is inexpensive, safe to use, and environmentally benign.

The solvent-free conditions make the method more attractive. The simplification of reaction protocols is an important concept in designing new clean methodologies.

A series of polyphosphates were synthesized by gas–liquid interfacial polycondensation. Optimum conditions for this process are 60 °C reaction temperature, 1 M NaOH solution, and an excess of arylphosphoric dichloride. The reactions did not require long reaction time (approx. 50 min). The structures of these polymers were confirmed by IR, ^1H NMR, and ^{31}P NMR spectra.

Owing to the advantages from the use of aqueous medium in organic synthesis and the absence of the solvent and catalyst, a strong development in the future is expected.

ACKNOWLEDGMENTS

This study was financially supported by MENER (633/03.10.2005). The authors are grateful to Prof. Stefan Berger, Institute for Analytical Chemistry, Leipzig for providing access to the NMR spectrometer and to Dr. Tincuta Avram, Romanian Academy “Petru Poni” Institute of Macromolecular Chemistry for the molecular mass determinations.

REFERENCES

1. D. J. Liaw, W. C. Liaw, W. C. Shen. *Polymer* **34**, 1336 (1993).
2. D. J. Liaw, P. S. Chen. *Polymer* **36**, 4491 (1996).
3. S. Minegishi, S. Komatsu, A. Kameyama, T. Nishikubo. *J. Polym. Sci., Part A: Polym. Chem.* **37**, 959 (1999).
4. M. Richards, B. I. Dahiyat, D. M. Arm, P. R. Brown, K. W. Leong. *J. Biomed. Mater. Res.* **25**, 1151 (1991).
5. Z. Zhao, J. Wang, H. Q. Mao, K. W. Leong. *Adv. Drug Delivery Rev.* **55**, 483 (2003).
6. A. Gupta, S. Lopina. *Polymer* **45**, 4653 (2004).
7. A. Akelah. *Mater. Sci. Eng.* **C4**, 83 (1996).

8. H. Shoba, H. Johnson, M. Saukarapandian, Y. S. Kim, P. Raugarajan, D. C. Baird, J. E. McGrath. *J. Polym. Sci., Part A: Polym. Chem.* **39**, 2904 (2001).
9. P. Sakthiel, P. Kannan. *Polymer* **46**, 9821 (2005).
10. L. E. Elizalde, N. P. Torres, J. G. Rodriguez. *Macromol. Rep.* **A30**, 295 (1993).
11. S. Roy, S. Maiti. *J. Polym. Mater.* **21**, 39 (2004).
12. S. Iliescu, G. Ilia, A. Popa, G. Dehelean, G. Macarie, L. Pacureanu. *Rev. Roum. Chim.* **46**, 115 (2001).
13. S. Iliescu, G. Ilia, N. Plesu, A. Popa, A. Pascariu. *Green Chem.* **8**, 727 (2006).
14. G. Ilia, S. Iliescu, A. Popa. *Green Chem.* **7**, 217 (2005).
15. S. Iliescu, G. Ilia, A. Popa, G. Dehelean, L. Maacrie, L. Pacureanu. *Polym. Bull.* **46**, 165 (2001).