

Conference paper

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Interfacial polycondensation method used in the synthesis of polymers containing phosphorus in the main chain

Abstract: Polyphosphoesters gained importance especially due to their use as flame retardants and as biocompatible and biodegradable materials for medicine and in the pharmaceutical industry. This paper presents the results obtained by our research group in the synthesis of polyphosphoesters by interfacial polycondensation. This reaction is rapid and irreversible polymerization at the interface between a phase containing one difunctional intermediate and another phase containing a complementary difunctional reactant. Different methods like liquid–liquid, vapor–liquid or solid–liquid were used in the synthesis of polyphosphates of polyphosphonates using aliphatic/aromatic phosphoric/phosphonic dichlorides and different diols. Aqueous NaOH, or tripotassium phosphate were used as bases. In almost all cases a catalyst is not needed.

Keywords: interfacial; liquid–liquid; polyphosphoesters; POC-2014; solid–liquid; vapor–liquid.

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Introduction

Polyphosphoesters are an important class of phosphorus-containing polymers that have received wide attention over the past decade. Versatile polyphosphoesters contain repeated P–O bonds in the backbone and function of side groups connected to the phosphorus atom can be divided as is seen in Scheme 1 [1]. Polyphosphates and polyphosphonates are known as very interesting fire retardant candidates [2–4]. Polymers with phosphoester (P–O–C) repeating linkages in the backbone are particularly interesting in drug delivery and tissue engineering research because of their biocompatibility and structural similarity to natural biomacromolecules like nucleic acids [5–8].

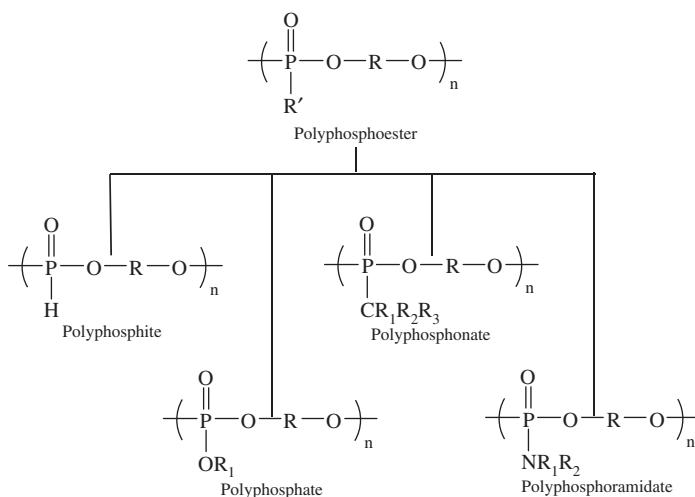
In responding to the need to develop polyphosphoesters as biodegradable and flame retardant materials, systematic studies on these polymers synthesis must be performed. The main synthetic ways to obtain polyphosphoesters are polyaddition [9, 10], polymerization [11], ring-opening polymerization [12],

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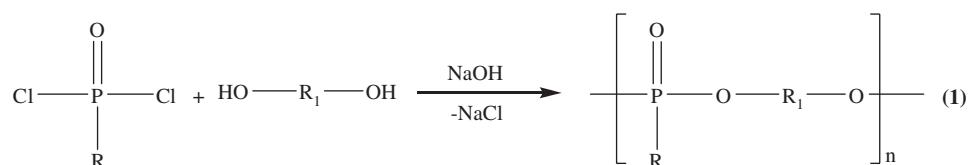
Scheme 1 Classification of polyphosphoesters.

polytransesterification [13], polycondensation in solution and melt [14–17], phase transfer catalysis or interfacial polycondensation which were frequently used in the synthesis of these polymers.

From all synthetic methods, the interfacial polycondensation gained much interest as new perspectives of the modern organic synthesis. Simplicity of operations, reduced reaction time, avoidance of secondary reactions, possibility of obtaining the polymer directly as pellicles or films, mild reaction conditions, safety, operational simplicity and selectivity, easy scale-up are widely accepted typical features of interfacial polycondensation processes. Polymers with reactive groups and high melting points can be easily obtained by this method.

One of the most important classes of polymers obtained by the application of the interfacial polycondensation technique is that of phosphorus containing polymers, especially polyphosphonates and polyphosphates [18–28]. The method follows the trend of green chemistry resulting in the reduction of environmental pollution and steady development of chemistry [29].

The first reported use of the interfacial polymerization in the synthesis of polyphosphate esters was made by Rabek and Prot [30]. The synthesis utilized bisphenols in a Schotten-Bauman-like esterification involving sodium hydroxide as scavenger of hydrogen chloride (Reaction 1).

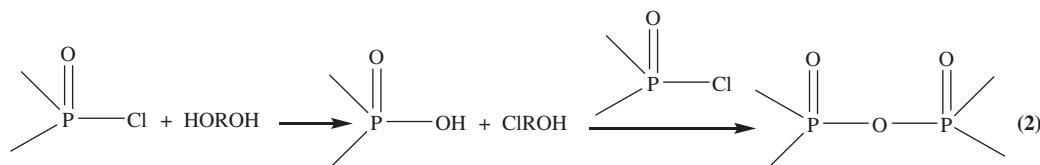


The synthesis of polymers by applying the phase transfer catalysis is a rapid and irreversible polymerization at the interface between a phase containing one difunctional intermediate and another phase containing a complementary difunctional reactant. The principal feature of interfacial polycondensation is to allow the reagents present in different phases to react with the aid of a catalyst. The catalyst has the basic function of transferring anions, in the form of ion pairs, from the aqueous phase to the organic phase, in which the reaction with water-insoluble hydrophobic species takes place [31]. The phase transfer catalysis may be applied in different systems: liquid–liquid, liquid–solid and solid–gas systems, respectively.

The aim of this paper is to systematize both theoretical and experimental results of our research group concerning the polyphosphoesters synthesis by the interfacial polycondensation. For this reason the theoretical and experimental data are discussed taking in account the general aspects of polymer synthesis by interfacial polycondensation of alkyl(aryl)phosphonic (phosphoric) dichloride with aromatic diols in the liquid–liquid (classical method and inverse method), vapor–liquid and solid–liquid system.

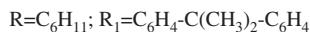
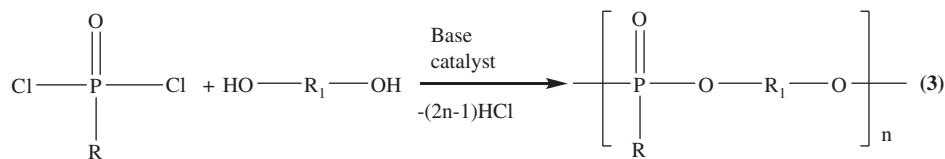
Polyphosphoesters obtained by interfacial polycondensation in the liquid–liquid system by classical method

Polyesters of pentavalent phosphorus are the best suited for the study of phosphorus ester polycondensation reactions and are free from the complications introduced by the Arbuzov rearrangement. The phosphorodichloride reactant used in the synthesis of polyphosphates is a chlorinating agent for alcohols. The resulting hydroxyl group on phosphorus generates a site for anhydride formation with additional phosphorylating agent (Reaction 2).



In the presence of water and hydroxides the possibility of hydrolyzing the phosphoryl chloride group of the starting reagent or of chain end-groups exists. The undesirable side reaction can be minimized, and high molecular weights were obtained, by using diols whose nucleophilic attractions for the phosphoryl group exceed those of water or hydroxide ion by many orders of magnitude [18–20].

Liquid–liquid base-catalyzed interfacial polycondensation of alkyl(aryl)phosphonic (phosphoric) dichlorides with diols was reported by Iliescu et al. [32] (Reaction 3).



The synthesis procedure was as follows: a mixture of phosphorus derivative (cyclohexylphosphoric dichloride, CPD) in an organic solvent was added dropwise to an aqueous solution of a diol (bisphenol A, BA) and sodium hydroxide. The catalyst used was a classical one: ammonium or phosphonium salts.

To minimize the hydrolysis of the phosphoryl chloride groups of the reagent or of the chain end-groups of the polyphosphonate, the influence of alkaline medium on yield and inherent viscosity was studied [32]. To maintain constant pH and a sufficient alkaline medium to ionize BA a series of interfacial polycondensation of CPD with BA, using different buffering agents and bases with different solubility in water was accomplished. Acid buffering agents such as $NaHCO_3$, Na_2CO_3 , Na_2HPO_4 were used. It was observed that synthesis of polymers is less dependent on chemical nature of the buffering system than the pH of the aqueous phase and polymers were not formed at $pH < 8.8$. The high inherent viscosity (~ 0.5 dL/g) and obtained molecular weights of about 10^4 indicate that in this polycondensation propagation rate is higher than the undesired competing reactions rate. Polyphosphonates obtained with bases with limited solubility, e.g., $Ba(OH)_2$, present higher inherent viscosities and molecular weights comparatively with very soluble bases, e.g., $NaOH$. The influence of hydroxyl concentration in aqueous phase also has an important role. For base concentrations between 1 M and 6 M the highest inherent viscosity was obtained when base concentration was 3 M. Low inherent viscosities were obtained both at high and low base concentrations. At hydroxide concentration lower than 3 M bisphenolate and phenolate end-groups turn into inactive sites. At hydroxide concentration higher than 3 M, hydrolysis of phosphonic dichloride and chloride end-groups of intermediate oligomers hydrolysis occurred.

Other factors, which influence the yield and the inherent viscosity, with respect to the type of solvent, reagents molar-ratio, reaction temperature, phase transfer catalyst and stirring speed were studied [33, 34]. The solvent type plays a key role in synthesis of polyphosphonates with high inherent viscosities (high molar weights) especially if it the idea that the polycondensation takes place inside the organic phase or at interface

is accepted. Better results for liquid–liquid interfacial polycondensation of CPD with BA were obtained with halogenated hydrocarbon solvents, which partially solve the obtained polyphosphonate, in contrast to hexane and benzene, which cannot solve the polymer. The highest yields were obtained at volumetric ratio $H_2O:CCl_4 = 1:0.02$ when $Ba(OH)_2$ was used and a volumetric ratio $H_2O:CCl_4 = 1:2$ when $NaOH$ was used. The highest inherent viscosities were obtained at volumetric ratio $H_2O:CCl_4 = 1:0.25$ when $Ba(OH)_2$ was used and volumetric ratio $H_2O:CCl_4 = 1:1$ when $NaOH$ was used [33].

Iliescu et al. [34] present the effect of reagents molar-ratio on yield and inherent viscosity of the polyphosphonate. Yield and inherent viscosity are influenced by reagent excess, increasing with excess of one of the reagents. The excess of phosphonic dichloride (molar ratio CPD to BA 2:1) presents the most significant influence.

The experimental data show that the yield and inherent viscosity decrease with the increasing of temperature. The best results were obtained at 20 °C [34]. At low temperature the solubility of bisphenol sodium salts decreases but in this case the increase of the yield and inherent viscosity with the decrease of temperature has been attributed to the fact that at lower temperatures the side reaction are limited, especially the hydrolysis of phosphonic dichloride. The complete hydrolysis of phosphonic dichloride leads to 0 % yield of polymers. These results contradict the experimental data obtained by Prot [30].

The influence the phase transfer catalyst was determined [34] and better yields and inherent viscosities were obtained with tetrabutylammonium bromide and tetrabutylphosphonium bromide.

In liquid–liquid interfacial polycondensation the stirring speed of 1400 rpm is sufficient to ensure an increased number of dispersed droplets, to increase the number of collisions among reactants [34].

Polyphosphoesters obtained by the inverse liquid–liquid method

Iliescu et al. [35] present for the first time an alternative to PTC reactions which enables reactions in biphasic water-solvent organic systems, in particular the synthesis of polyphosphates by inverse phase transfer catalysis (IPTC). In the classical case the reaction takes place in the organic phase near the interface and in the case of IPTC the reaction takes place in the aqueous phase and the product is transferred by catalyst in the organic phase.

In IPTC system, the organic reagent reacts with the catalyst to form a water soluble intermediate, which is active and reacts rapidly with the aqueous reactant to produce the desired product. The catalyst is regenerated in the aqueous-phase reaction. The catalysts used in inverse phase transfer catalysis include pyridine (Py), pyridine-1-oxide (PNO), 4-dimethyl-aminopyridine (DMAP) and different cyclodextrin derivatives. The factors that affect the yield and inherent viscosity for the IPTC reaction between methylphosphoric dichloride (MPD) and sodium salt of bisphenol A (BA), in H_2O/CH_2Cl_2 medium were investigated [reaction 3, $R = OCH_3$; $R_1 = C(CH_3)_2$]. The presence of the DMAP, PNO and Py, which act as IPT catalysts, enhances the yield of the reaction and in the absence of the catalyst and under slow stirring (500 rpm) no polymer was obtained. Relative catalytic reactivity decreases in the order DMAP > PNO > Py. An advantage of DMAP over the other pyridine catalysts is that DMAP shows catalytic activities because of its electron-donating methyl substituents. In contrast with the PTC process, where a small amount of catalyst is enough to produce a large interfacial area, polyphosphate with high yield was obtained by IPTC technique under slow-speed stirring (100–500 rpm), whereas the liquid–liquid process occurs only under vigorous stirring (>10 000 rpm). The IPTC process can occur only if the catalyst concentration in the water phase is enough to solubilize a significant fraction of hydrophobic substrate. This procedure leaves out the major inconvenience of the classical methods (high temperatures, corrosion, and pollution with toxic substances) but also of the phase transfer catalysis methods (high stirring speed ≥ 10 000 rpm).

Iliescu et al. [36] studied the factors that affect the yield and inherent viscosity for the inverse polycondensation between phenylphosphonic dichloride and sodium salt of bisphenol A, in H_2O/CH_2Cl_2 medium. For correlation, the simultaneous influence of the parameters (reaction temperature, alkaline medium, reagents molar ratio and stirring) on yield and inherent viscosity and for determination of the best reaction conditions the design

of experiments method was used. The method can vary many of the control factors simultaneously and so the experimentation time is shorter. The experimental results using 20 and 14 process runs, respectively, lead to an optimal synthesis procedure for polyphosphonate by the inverse technique, with the following setting values for process control factors: reagents molar ratio = 1, base concentration = 1.1 M and reaction temperature = -12 °C.

Iliescu et al. [37] used a new alternative to the IPTC method (modified IPTC), which consists of the inversion of the order of addition of one phase to another, by adding the aqueous phase to the organic phase. The rate of addition of the aqueous phase to the organic phase was rigorously controlled. The inverse phase transfer catalyst, DMAP, was added to the organic phase prior to the addition of the aqueous phase. Polyphosphates, polyphosphonates, polyarylazophosphonates and polyarylazophosphates were synthesized by modified IPTC polycondensation of phenylphosphonic (phosphoric) dichlorides: phenylphosphonic dichloride, phenylphosphoric dichloride, *p*-chlorophenylphosphoric dichloride with bisphenols: bisphenol A, tetrabromobisphenol A, bis-(4-hydroxyphenyl)methane, 4,4'-dihydroxy-azomethane. (reaction 3, R = C₆H₅; O-C₆H₅; O-C₆H₄Cl; R₁ = C₆H₄-C(CH₃)₂-C₆H₄; C₆H₄Br₂-C(CH₃)₂-C₆H₄Br₂; C₆H₄-CH₂-C₆H₄; C₆H₄-N=N-C₆H₄).

Polyphosphoesters obtained by interfacial polycondensation in the vapor–liquid system

This system utilizes pairs of highly reactive reagents with one of the reagents [alkyl(aryl)phosphonic dichloride] in the vapor state and the other one (diphenol) in solution [22]. The contact of the reagents in the vapor–liquid reaction is readily performed by bubbling the vapor (gaseous) reagents through the aqueous solution of the partner reagent. The use of the organic solvent is not required. The polymer separates from the aqueous phase and does not need complicated purification.

Iliescu et al. [38–45] developed a new and efficient synthesis method without the use of solvent and catalyst, respectively, the vapor–liquid reaction of phosphorus compounds. In the new polyphosphate and polyphosphonate with molecular weights > 10 000 by base-promoted, the vapor–liquid interfacial polycondensation were synthesized. The reaction takes place in water and for that reason the auxiliary procedures are simplified considerably. The possible environmental benefits are obvious with no concerns over solvent emissions or any byproducts derived from the solvent. Therefore, only ionic impurities (i.e., NaCl) need to be washed from the polymer. The products obtained by the vapor–liquid technique contain strongly adsorbed water which should be removed prior to further polymer characterization and applications [42].

Polymers with different viscosities were successfully prepared by this simple and green method, by the vapor–liquid interfacial polycondensation of alkyl(aryl)phosphonic (phosphoric) dichlorides with halogenated or non-halogenated diols, respectively (Reaction 3, Table 1).

Experimental results obtained by the vapor–liquid polycondensation of cyclohexylphosphonic dichloride and bisphenol A were verified with the data obtained with a second order, central, composite, rotatable experimental design [46]. The individual and simultaneous influences of various parameters (reaction time, temperature, base concentration and molar ratio) on yield and inherent viscosity of the obtained

Table 1 Polyphosphonates and polyphosphates obtained by vapor–liquid technique.

Polymer	R	R ₁	Ref.
Polyphosphonates	CH ₃ ; C ₆ H ₅ ; C ₆ H ₁₁	C ₆ H ₄ ; C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄ ; C ₆ H ₄ -C ₆ H ₄ ; C ₁₀ H ₈ ; C ₆ H ₄ -SO ₂ -C ₆ H ₄	[39]
Polyphosphonates	C ₆ H ₅	C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄	[45]
Polyphosphates	OCH ₃ ; OC ₆ H ₅ ; OC ₆ H ₁₁	C ₆ H ₄ ; C ₆ H ₆ -C(CH ₃) ₂ -C ₆ H ₄ ; C ₆ H ₄ -C ₆ H ₄ ; C ₁₀ H ₈ ; C ₆ H ₄ -SO ₂ -C ₆ H ₄	[40]
Polyphosphates	OC ₆ H ₅	C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄ ; C ₆ H ₄ -C ₆ H ₄ ; C ₆ H ₄ -SO ₂ -C ₆ H ₄	[41]
Polyphosphates	OC ₆ H ₅	C ₂₀ H ₁₂ O ₄	[42]
Polyphosphates	OCH ₃ ; OC ₂ H ₅ ; OC ₃ H ₇ ; OC ₆ H ₁₁ ; OC ₆ H ₅	C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄ ; C ₆ H ₂ B ₁₂ -C(CH ₃) ₂ -C ₆ H ₂ Br ₂	[43]
Polyphosphates	O-C ₆ H ₄ -X; X=H, CH ₃ , OCH ₃ , Br, NO ₂	C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄	[44]

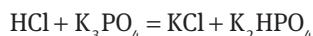
polyphosphonate was studied and correlations were realized to establish optimal reaction conditions. From the experimental and calculated data, it shows that the most important factors are the NaOH concentration and the reaction temperature. The calculated results were in concordance with the experimental data, reaction time 50–60 min; temperature 50 °C; 1 M NaOH concentration and molar ratio = 2.6:1, respectively.

Another study for the optimization of synthesis parameters in interfacial polycondensation using design of experiments was performed [47]. Design of experiments is an alternative way to the classical method in the optimization of the industrial processes. The reaction of 4,4'-cyclohexylidenebisphenol with phenylphosphonic dichloride by vapor–liquid interfacial polycondensation was studied. The most important conclusion is that these parameters have an insignificant effect on the yield and viscosity at the same time. Increased values of reaction temperature and time, respectively decreased values for NaOH concentration and gives maximum values of the quality characteristics of the synthesis.

A comparative study of polyphosphonates synthesized by liquid–liquid and vapor–liquid interfacial polycondensation of chloromethylphosphonic dichloride with 4,4'-sulfonyldiphenol (reaction 3, R = CH₂Cl; R₁ = C₆H₄-SO₂-C₆H₄) was performed [48]. The results showed that the liquid–liquid and vapor–liquid interfacial polycondensations are promising methods for preparing polyesters with phosphonyl groups. The structure of polyphosphonates was confirmed by IR and ¹H-NMR spectroscopy. The most important feature of liquid–liquid and vapor–liquid interfacial polycondensation is the dependence of the polyphosphonate inherent viscosity and yield on the temperature. Polyphosphonates obtained in the vapor–liquid system shows an increase of inherent viscosity with the increase of the temperature.

Polyphosphoesters obtained by solid–liquid interfacial polycondensation

In order to prevent the degradation of the polymer in interfacial polycondensation and terminating competing reactions and to get data for preparing thermally stable polymers with high molecular weights Iliescu et al. [49] synthesized heteroatom polymer structures by a new method, respectively, interfacial polycondensation in the solid–liquid system, when potassium phosphate is used as a unique base. The potassium phosphate acts as an acid scavenger without water formation.



Polyphosphonates and fluorine–polyphosphates by solid–liquid polycondensation of phenylphosphonic dichloride or 4-chlorophenyldichlorophosphate with bisphenols were obtained. Bisphenols with rigid structures, respectively, 4,4'-(9-fluorenylidene)diphenol and fluorine-containing bisphenol, respectively, 4,4'-(hexafluoroisopropylidene) were used (Scheme 2).

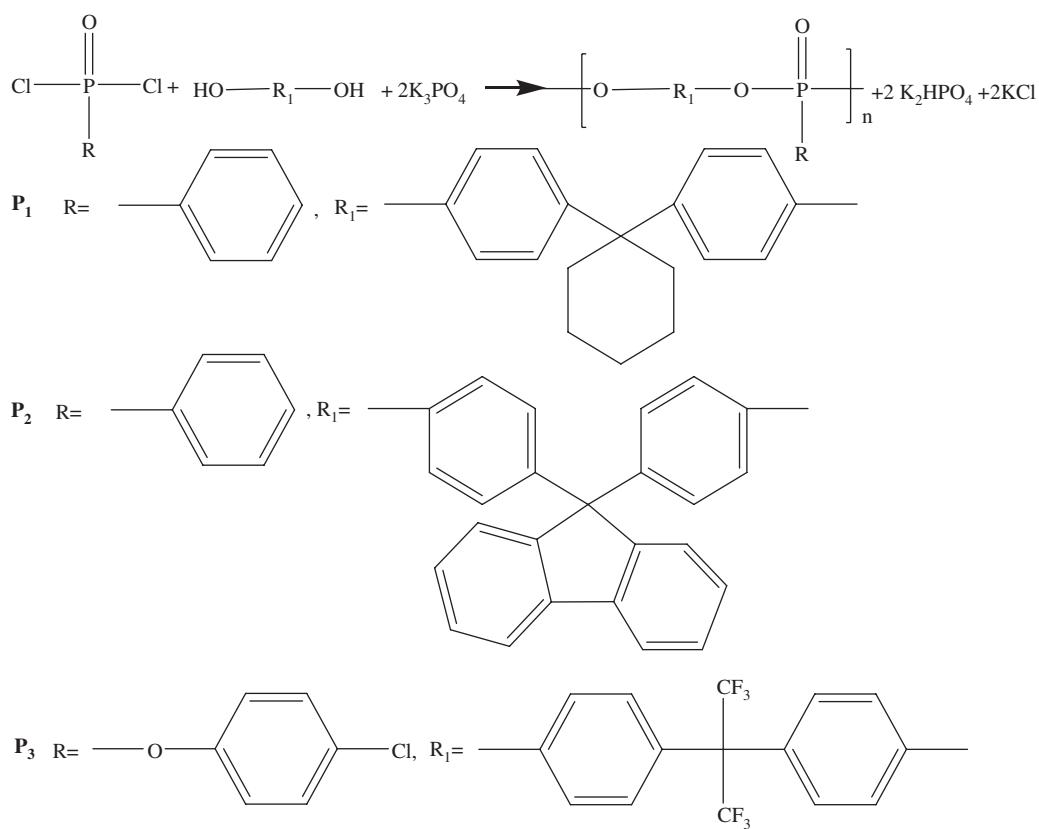
The conversion of liquid–liquid interfacial polycondensation into solid–liquid interfacial polycondensation proves to be advantageous from the point of view of suppression of side reactions, respectively, hydrolysis of the phosphoryl chloride groups of the reagent or of the chain end-groups of the polymer.

New linear phosphorus containing (co)polyesters were synthesized by solid–liquid interfacial polycondensation of phenylphosphonic dichloride with poly(ethylene glycol) (PEG 12000) with and without bisphenol A (Scheme 3) [50].

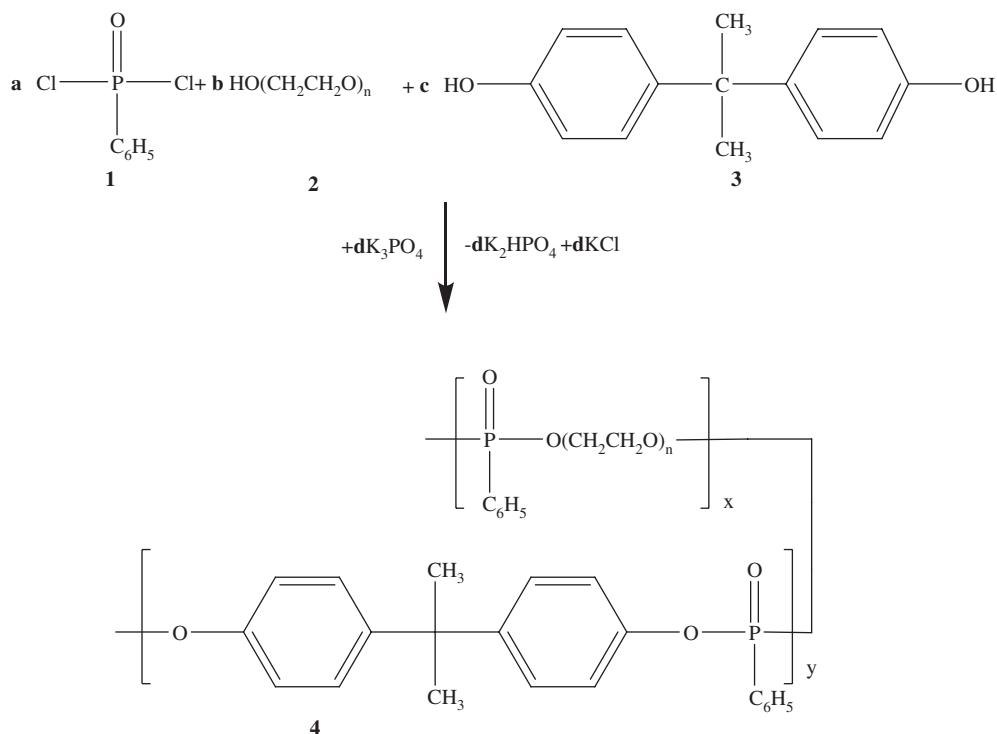
Also, a polyphosphonate was synthesized from phenylphosphonic dichloride and bisphenol M, when potassium phosphate was used as base and 2-methyltetrahydrofuran as a green solvent [47].

This methodology offers improvements for the synthesis of polymers with regard to elimination of catalysts and organic solvents or the use of green solvents. Elimination of dangerous, inconvenient, or expensive bases (the use of, K₃PO₄, etc. instead of NaOH, KOH NaH, NaNH₂, t-BuOK, R₂NLi, etc.), increased reactivity and selectivity of the active species, higher yields, higher molecular weights and simplicity of the procedure are also important improvements.

Due to the specific features of this method and its advantages presented above it should be considered as a most efficient and general green technology for polyphosphoesters synthesis.



Scheme 2 Polyphosphonates and polyphosphates obtained by solid–liquid interfacial polycondensation.



4a: a = 1; b = 1; c = 0; d = 2
4b: a = 1; b = 0.5; c = 0.5; d = 2
4c: a = 1; b = 0; c = 1; d = 2

Scheme 3 Preparation of random phosphorus containing (co)polyesters 4a-c.

Conclusions

Three methods: liquid–liquid (classical or inverse), vapor–liquid and solid–liquid were used for preparing new structures of polyphosphonates and polyphosphates with high molecular weights. All three methods are modern, do not require the purification of reagents and are easy to perform. The study of interfacial polycondensation by the inverse liquid–liquid system was performed as an alternative to the classical interfacial polycondensation for the first time by Iliescu et al.

In the vapor–liquid interfacial polycondensation a solvent and catalyst are not required. A maximum molecular weight M_n of 35 000 was obtained by this technique, which is better than compared to those reported by other techniques. The solid–liquid method is the most promising technique for the synthesis of these compounds. The usefulness of this new eco-friendly and economical method, not yet mentioned in the studied literature, in synthesis of structures of polyphosphonates and fluorine-polyphosphates having high molecular weights was demonstrated. The novelty of this method consists in the use of the potassium phosphate as a unique base in solid–liquid interfacial polycondensation. Through vapor–liquid and solid–liquid procedures the major disadvantages of the classical synthesis methods have been eliminated: high temperatures for corrosion in environmental damage caused by noxious substances, the method being part of the green chemistry trend.

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