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Unconventional method used in synthesis of polyphosphoesters

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Abstract Polyphosphonates, polyphosphates, polyarylazophosphonates and polyarylazophosphates were synthesized by a new alternative to the classical phase transfer catalysis, respectively, the modified inverse phase transfer catalysis (IPTC) polycondensation of various phenylphosphonic (phosphoric) dichlorides (phenylphosphonic dichloride, phenylphosphoric dichloride, *p*-chlorophenylphosphoric dichloride) with bisphenols: bisphenol A, tetrabromobisphenol A, bis-(4-hydroxyphenyl)methane (bisphenol F), 4,4′-dihydroxyazobenzene. The polymers were characterized by infrared spectroscopy and magnetic resonance (^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR) spectroscopy. Yields in the range of 63.5–85% and molecular weights (M_w) of ~2,000–8,200 g mol^{-1} were obtained. Polyphosphonates were stable up 210–270 °C and polyphosphates up 190–220 °C in air atmosphere. For a correct estimation of the thermal behavior of similar compounds, a kinetic analysis using a modified version of Non Parametric Kinetic method for representative polyphosphonate and polyphosphate was realized. The studies made on the hydrolytic degradation of the synthesized polyphosphates show that the most stable polymer under alkali-catalyzed degradation is the polyphosphate obtained by IPTC of phenylphosphoric dichloride and bisphenol A.

Keywords Polyphosphoesters · Polyphosphates · Polyphosphonates ·
Inverse phase transfer catalysis

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Introduction

There is great interest on polyphosphoesters due to their attractive properties that make them useful for a wide range of applications. One of the present interests lies in the intensification of the efforts concerning fire proofing of this macromolecular compounds [1].

Recently, a relatively new class of polyphosphoesters were evaluated as biodegradable polymers [2–4]. As shown in Fig. 1, polyphosphonates (I) and polyphosphates (II) are characterized by the P(O)–O–C linkage in the polymer backbone and the pentavalent phosphorus atom which allows attachment of a pendant component

These polymers are biodegradable because of the hydrolysable ester groups, or P(O)–O–C bond, in the backbone.

The interest displayed to these types of polymers obtained by phase transfer catalysis (PTC) [5–10], gave us the reason to continue the development of the research in the domain of the synthesis of phosphorus containing polymers in order to obtain new polymers able to be used in interdisciplinary domains. The greatest advantage of polymer synthesis by PTC is that a large reaction rate is achieved even at a moderate reaction temperature. The feature of this technique is to allow the reagents present in different phases to react with the aid of a catalyst, which transfers anions, in the form of an ion pair, from the aqueous phase into the organic phase. The reaction with water-insoluble hydrophobic species takes place in organic phase. Quaternary ammonium and phosphonium salts, crown ethers, poly(ethyleneglycol)s, and cryptates have been used as phase transfer catalysts.

In contrast to the PTC technique, a new PTC methodology, namely inverse phase transfer catalysis, IPTC, was presented by Mathias and Vaidya [11]. In a previous paper [12] we have reported the possibility of obtaining polyphosphates by this new method in polymer chemistry, the inverse phase transfer catalysis. The polyphosphate obtained by IPTC polycondensation of methylphosphoric dichloride with bisphenol A was reported. 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. This new approach consists of substituting the quaternary lipophilic onium salts, used as phase transfer catalysts, by typical inverse phase transfer catalysts: pyridine, pyridine-1-oxide, 4-dimethyl-aminopyridine and different cyclodextrin derivatives. The polyphosphate was obtained by

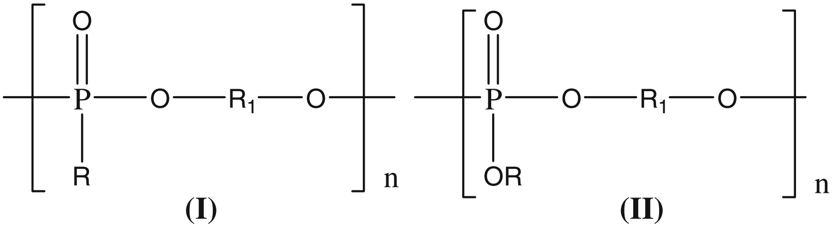


Fig. 1 Polyphosphonates (I) and polyphosphates (II)

IPTC technique under slow-speed stirring (100–500 rpm) whereas PTC process occurs only under vigorous stirring (>10,000 rpm).

Our main objective was to conduct experiments in order to optimize the IPTC polycondensation in an effort to obtain a new series of polyphosphonates and polyphosphates with high yields and to examine their thermal and degradability behaviors. It was used a new alternative to the IPTC method, which consists in the inversion 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, 4-dimethyl-amino-pyridine (DMAP), was added to the organic phase prior to the addition of the aqueous phase.

The polymers were synthesized by IPTC (see Table 1 for designation of P1-P8) polycondensation of phenylphosphonic (phosphoric) dichlorides (PD): phenylphosphonic dichloride (PPD), phenylphosphoric dichloride (O-PPD), *p*-chlorophenylphosphoric dichloride (O-*p* PPD Cl) with bisphenols (B) : bisphenol A (BPA), tetrabromobisphenol A (BrBPA), bis-(4-hydroxyphenyl)methane (HPM or bisphenol F), 4,4′-dihydroxyazobenzene (DHB). The polymers were characterized by IR, ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR, inherent viscosity, molecular weights, phosphorus content and thermal analysis. The incorporation of rigid azoxy linkages in the main chain of aromatic polyphosphonates and polyphosphates is expected to enhance thermal properties because of the extended conjugation and resonance stabilization [13].

This procedure eliminates 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). This method requires no reagents purification and affords the desired compounds in reasonable yield without the formation of unwanted side products.

Table 1 Reaction conditions and results of IPTC polycondensation of various phenylphosphonic(phosphoric) dichlorides with bisphenols

Polym	PD	B	Yield, %	η_{inh}^{a}, dl g^{-1}	% P^{b}	
					Calc.	Exp.
P1	PPD	BPA	86.5	0.40	8.85	8.50
P2	PPD	BrBPA	65.5	0.32	4.97	4.20
P3	O-PPD	BPA	78.5	0.35	8.47	8.20
P4	O-PPD	BrBPA	63.5	0.30	4.54	4.10
P5	O-*p*PPDCl	HPM	68.5	0.28	9.65	9.20
P6	PPD	DHB	80.8	0.45	9.39	8.95
P7	O-PPD	DHB	80.2	0.42	8.9	8.20
P8	PPD	HPM	60.0	0.25	9.62	9.10

[a] The inherent viscosities η_{inh} were determined for solutions of 0.5 g 100 mL^{-1} in tetrachloroethane, at 30 °C

[b] Determined by Schöniger method

Accelerated hydrolytic degradation studies of the synthesized polyphosphates were conducted under alkaline conditions [14].

For a correct estimation of the thermal behavior of similar compounds, a kinetic analysis using a modified version of Non Parametric Kinetic (NPK) method for representative polyphosphonates and polyphosphates was realized.

Experimental

Materials

Reagents phenylphosphonic dichloride (PPD), phenylphosphoric dichloride (O-PPD), *p*-chlorophenylphosphoric dichloride (O-*p* PPD Cl), bisphenol A (BPA), tetrabromobisphenol A (BrBPA), bis-(4-hydroxyphenyl)methane (HPM or bisphenol F), 4,4′-dihydroxyazobenzene (DHB) from Aldrich, catalyst 4-dimethylaminopyridine (DMAP)from Fluka and solvent (methylene chloride- from Aldrich) were used without purification.

The IR spectra were recorded on a JASCO 430-FT-IR spectrophotometer and ^{1}H-NMR a ^{31}P-NMR and ^{13}C-NMR spectra on a Bruker DRX 400 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ using TMS as internal standard, at 25 °C. The polymers were characterized by viscosity, on an Ubbelohde suspended level viscometer, at 30 °C, and by gel permeation chromatography, on an Evaporative Light Scattering Detector, PL-EMD 950 (2× PL gel MIXEDC 300 × 7.5 mm columns; T = 25 °C; DMF as solvent; calibration with polystyrene as standard). The thermoanalytical curves TG, DTG and DTA (as heat flow) were drawn by a Perkin Elmer Diamond device, in dynamic air atmosphere and heating rates of 5, 7, 10 and 12 °C min^{-1}.

Procedure

IPTC polycondensation

The polymers were synthesized according to the following procedure: 0.005 mol diol dissolved in 20 ml aqueous solution NaOH (0.8 g) was added to a stirred solution of 0.005 mol phenylphosphonic (phosphoric) dichlorides, 0.0025 mol catalyst in 10 ml CH_2Cl_2, keeping the temperature below 15 °C; then the mixture was stirred (1,000 rpm) for 90 min at 15 °C. The polycondensation can be carried out at pH 9–10, to minimize the hydrolysis side reactions. The supernatant aqueous layer was decanted and the organic layer was washed successively with water to neutral pH and to remove any residual impurities. The organic mixture was precipitated by pouring the solution into excess hexane. The polymer was collected, and dried under vacuum, at 50 °C, until constant weight, and then characterized.

Thermal behavior

The thermogravimetric (TG), derivative thermogravimetric (DTG) and the differential thermoanalitical (DTA) curves were used in order to describe the thermal behavior of the polymers.

The kinetics of the thermo oxidative degradation was established by means of a modified version of the Non Parametric Kinetic (NPK) method [15]. This method was validated for kinetics of complex processes [16]. Essentially, the temperature dependence of the reaction rate is considered the classical Arrhenius equation and the conversion function is the Sestak–Berggren equation [17].

$$g(\alpha) = \alpha^m (1 - \alpha)^n$$

By simultaneous multistep processes the contribution of each step "i" is estimated by the explained variance λ_i, so that $\sum \lambda_i = 1$.

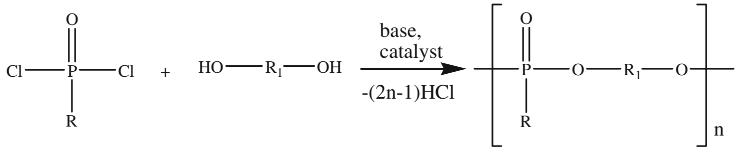
Hydrolytic degradation of the polymers

100 mg polymer was pressed at 10 atm as pellet. The pellet dimensions are diameter of 10 mm and thickness of 2.6 mm. 5 pellets were introduced in 5 tubes with hole at the bottom and placed on an appropriate stand. The stand was maintained in thermostat containing NaOH solution, at 30 °C. After given time intervals, the tubes were removed from thermostat, washed with distilled water and placed in HCl 1% solution for 10 min. Then, the pellets were dried in a vacuum dessicator for 36 h and weighted. The percentage of weight loss was calculated as difference between initial and final weights of the pellets.

Results and discussion

In our previous paper [12] it was demonstrated that IPTC polycondensation was useful for the preparation of polyphosphates. Therefore, the modified method in which the aqueous phase was added to organic phase was applied to the IPTC polycondensation of phenylphosphonic (phosphoric) dichlorides (PPD,O-PPD, O-*p* PPD Cl) with bisphenols: BPA, BrBPA, HPM, DHB (Fig. 2).

Phenylphosphonic (phosphoric) dichloride is dissolved in one solvent medium (methylene chloride) while the diol is dissolved in a second solvent medium immiscible with the first (aqueous alkaline solution). The inverse phase transfer



R= C_6H_5 (PPD), OC_6H_5 (O-PPD), *p* OC_6H_4Cl (O-p PPD Cl)

R_1= C_6H_4-$C(CH_3)_2$-C_6H_4 (BPA), $C_6H_2Br_2$-$C(CH_3)_2$-$C_6H_2Br_2$ (BrBPA), C_6H_4-CH_2-C_6H_4 (HPM), C_6H_4-N=N-C_6H_4 (DHB)

Fig. 2 Polyphosphonates, polyphosphates obtained by IPTC polycondensation catalyst is useful in promoting higher inherent viscosities and molecular weights and is added to the organic phase before mixing the two phases. The ratio of phenylphosphonic (phosphoric) dichloride and diols were 1:1. The alkaline aqueous solution of alkali salt of the diol is added drop-wise (approx. 3 mol % min^{-1}) to the organic phase and the rate was controlled. When all of the aqueous phase has been added to the organic phase, the reaction mixture was stirred for one hour and a half.

The results of polymer syntheses and characterizations were summarized in Table 1. The most appropriate conditions for the synthesis of high inherent viscosity and molecular weight polymers by this method are as follows: reaction temperature 15 °C, molar ratio PD: B: DMAP = 1:1:0.005, 1 M $NaOH_{aq}$, 90 min, CH_2Cl_2 as solvent, 1,000 rpm.

Yields in the range 63.5 and 85% were obtained. The inherent viscosity of the polymers was in the range of 0.25–0.48 dl g^{-1}, determined with an Ubbehlode viscosimeter. The polyphosphonates and polyphosphates are soluble in $CHCl_3$, acetone, dimethylsulfoxide and *N*,*N*-dimethylformamide.

IR spectra, ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR spectra and molecular weights

The IR, ^{1}H-NMR and ^{31}P-NMR spectra confirmed the structure of these polymers (Table 2).

Polymeric structure was supported by P–O–C_{phenyl} stretch. The disappearance of the O–H groups can be therefore considered as an evidence of the fact that the polycondensation reaction took place. All polymers contain phosphorus in the main

Table 2 IR, ^{1}H-NMR and ^{31}P-NMR spectral data of the polyphosphonates and polyphosphates obtained by IPTC polycondensation

Polym	IR, cm^{-1}	^{1}H-NMR, ppm	^{31}P-NMR, ppm	
			P at the chain end	P in the repeat unit
P1	1,480 (P–$C_{aromatic}$); 1,250,(P = O,P–O–$C_{aromatic}$), 930 (P–O–$C_{aromatic}$)	6.8–8.15 (m, C_6H_5); 1.53 (m, 6H, $C(CH_3)_2$)	14.9	11.8
P2	1,460 (P–$C_{aromatic}$); 1,240 (P = O, P–O–$C_{aromatic}$); 920 (P–O–$C_{aromatic}$); 530 (C–Br)	1.6 (s, 6H,$C(CH_3)_2$); 6.9–8.3 (m, C_6H_5)	15.8	12.2
P3	1,300 (P = O); 960, 1,140 (P–O–$C_{aromatic}$)	1.6 (s, $C(CH_3)_2$); 6.8–7.7 (m, C_6H_5)	−12.0	−17.3
P4	1,300 (P = O); 970, 1,180 (P–O–$C_{aromatic}$); 550 (C–Br)	1.6 (s, $C(CH_3)_2$); 6.6–7.9 (m, C_6H_5)	−11.0	−17.5
P5	1,320 (P = O); 950, 1,150 (P–O–$C_{aromatic}$)	1.58 (s, $C(CH_3)_2$); 7.0–8.2 (m, C_6H_5)	−11.4	−17.0
P6	1,260 (P = O); 1,440 (P–$C_{aromatic}$); 1,140 (P–O–$C_{aromatic}$), 1,470 (N = N)	6.2–8.1 (m, C_6H_5)	12.3	12.7
P7	1,300 (P = O); 1180, 980 (P–O–$C_{aromatic}$), 1,570 (N = N)	6.8–7.7 (m, C_6H_5)	−11.6	−18.3
P8	1,400 (P–$C_{aromatic}$); 1,280 (P = O,P–O–$C_{aromatic}$), 920 (P–O–$C_{aromatic}$)	7.5–8.2 (m, C_6H_5); 3.6–3.9 (m, CH_2)	15.6	12.6

chain and show characteristic absorptions peaks at 3,060 cm^{-1} (C–H), 1,600 and 1,500 cm^{-1} (aromatic C = C).

The polyphosphonate structure of the polymers P1, P2, P6 and P8 was confirmed by the absorptions peaks at 1,480–1,470 and 1,020–1,030 cm^{-1} (P–C$_{phenyl}$), 1,250–1,240 cm^{-1} (P = O) and 1,150 and 930 cm^{-1} (P–O–C$_{phenyl}$).

In the IR spectra of P3, P4, P5 and P7 polyphosphates, it was observed that in the regions 1,200–1,300 and 900–1,000 cm^{-1} significant modifications characteristic to P = O and P(O)–O–C$_{phenyl}$ groups appeared. The IR band attributed to the P–O–C$_{phenyl}$ appears shifted in polyphosphates at 960 cm^{-1} comparing with 920–940 cm^{-1} corresponding to polyphosphonates. The polymers with arylazo groups showed characteristic IR absorption bands near 1,480 and 1,580 cm^{-1} do to –N = N– stretching for polymers P6, respectively, P7.

From ^{1}H-NMR it was observed that the peak corresponding to OH proton was missing, attesting the formation of polyphosphates and polyphosphonates as reaction products. In all polymers, the aromatic protons give chemical shifts in the range of 6.2–8.2 as multiplets.

The ^{31}P-NMR spectra of the synthesized polyphosphoanates and polyphosphates show two signals: one corresponding to the P in the repeat unit and the other one to the P at the chain end. The polyphosphonates P1, P2, P6, P8 give the chemicals shifts in the range 11.5–12 ppm for the P atom situated in the repetitive unit and 14–17 ppm for the P in the end chain. The signals for polyphosphates P3, P4, P5, P7 appear between −11 and −12 ppm for the P in the repetitive unit and between −18 and −22 ppm for the P in the end chain.

At the P2 and P4 polymer, the Br atom situated in *ortho* position of the phenyl ring due to its electronegative character gives an –I effect and the chemical shift appears at a lower field. The effect is not so strong to affect the adjacent carbons.

^{13}C-NMR spectra for representative polyphosphonates P1, P2 and polyphosphates P3, P4 were performed. The numbering of the C atoms is given in Fig. 3.

In Table 3 the chemical shifts for polyphosphonates are presented.

The numbering of the representative polyphosphates P3, P4 is given in Fig. 4 and the ^{13}C-NMR data in Table 4.

The molecular distribution for the polymers (measured by GPC, in chloroform, polystyrene was used as standard) synthesized is presented in Table 5.

Thermoanalytical analysis

The characteristics of the thermal behavior are systematized in Table 6, i.e., the temperatures corresponding to 1% (T$_{d}^{1\%}$), the maximum of the DTG curves

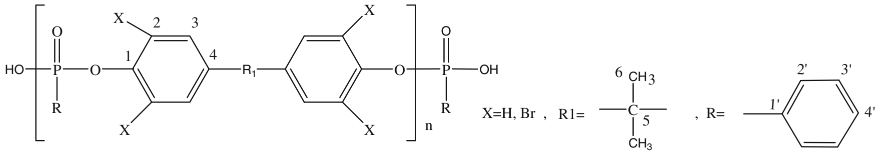


Fig. 3 The numbering of the carbon atoms of polyphosphonates

Table 3 The ^{13}C-NMR data for polyphosphonates

No.	R1	R	X
P1	$C(CH_3)_2$	C_6H_5	H
P2	$C(CH_3)_2$	C_6H_5	Br

No.	Carbon atom, ppm									
	1	2	3	4	5	6	1′	2′	3′	4′
P1	148.6	120.5	129.7	147.0	48.3	39.2	139.0	132.6	127.3	131.8
P2	147.9	116.1	132.1	145.1	52.6	42.1	142.5	133.3	128.4	130.7

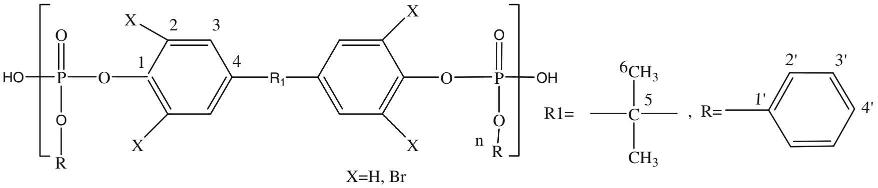


Fig. 4 The numbering of the carbon atoms of polyphosphates

Table 4 The ^{13}C-NMR data for polyphosphates

No.	R1	R	X
P4	$C(CH_3)_2$	C_6H_5	Br
P3	$C(CH_3)_2$	C_6H_5	H

No.	Carbon atom									
	1	2	3	4	5	6	1′	2′	3′	4′
P4	149.6	117.2	131.1	144.1	52.6	42.4	152.0	120.9	130.0	125.4
P3	151.7	120.1	128.7	148.3	48.5	39.2	149.6	120.6	130.2	125.4

Table 5 Molecular distribution of the polymers synthesized by IPTC polycondensation

Polym	Mn, g mol^{-1}	Mw, g mol^{-1}	Polydispersity
P1	1,800	2,400	1.3
P2	1,900	2,000	2.3
P3	2,260	6,600	2.9
P4	2,050	2,200	1.3
P5	1,700	5,500	3.2
P6	7,200	8,200	1.2
P7	2,250	5,500	2.4
P8	1,600	2,900	1.5

Table 6 Thermal properties of polyphosphates

Polym.	$T_d^{1\%}$ (°C)	Max. DTG (°C)	Residue at 700 °C (%)
P1	220	250	12
P2	230	280	25
P3	200	230	28
P4	220	250	26
P5	190	260	22
P6	270	480	35
P7	250	420	47
P8	210	200	30

(corresponding to the maximum of the reaction rate) and the char remaining at 700 °C.

By inspecting the data in Table 6, a reasonably good thermal stability was evidenced. The degradation up to 200 °C is due to complex thermooxidative process. Taking into account the max DTG values, these are with 20–50 °C higher for polyphosphonates in comparison with polyphosphates, and this is due to the stronger P–C_{phenyl} bond (in comparison with the P–O–C_{phenyl} bond). Regarding the influence of the bisphenol, we can mention that DHB induces by rigid azoxy linkages an increase of max. DTG with 200 °C. Also an increase of max DTG with 20–30 °C was observed by the bromine containing bisphenol.

Unfortunately, the above considerations are rather qualitative. A quantitative discussion on the thermooxidative degradation of the studied compounds is possible on the basis of the determined kinetic parameters.

The Non-Parametric Kinetic (NPK) method [16] allows an objective analysis of the relevance of the two or more elementary steps of a complex process. At the same time, a separation between the temperatures was possible. The data are systematized for two representative polymers (polyphosphonate P1 and polyphosphate P3) in Table 7.

A complete different distribution between the preponderant and the secondary process, as well as the low value of the activation energy of the preponderant process is a clear indication of a lower thermal stability of polyphosphates. Indeed, the P–O–C_{phenyl} bond is less stable in comparison with the P–C bond.

Noticeable is that by all polymers, the conversion dependence of the reaction rate by the preponderant process describes a chemical phenomenon ($n \neq 0$), without

Table 7 Kinetic parameters by the NPK method

Sample	Process	λ, %	E, kJ mol^{-1}	A, min^{-1}	m	n
P1	Prep.	83.4	55.6	4.19×10^4	–	1
	Sec.	15.6	71.1	3.15×10^6	1	–
P3	Prep.	62.0	28.6	2.04×10^2	–	2
	Sec.	34.2	87.9	3.04×10^8	3/2	–

any contribution of a physical one ($m = 0$). This is in connection with the very low vitrifying point of such phosphorus chain polymers. The thermal decomposition of polyphosphonates and polyphosphates is essentially a chemical phenomenon, without an important influence of the physical ones, and this happens due to the reactions in the plastic state of the polymers.

Hydrolytic degradation

It is known that the polymers with hydrolysable P(O)–O–C bond in the backbone are biodegradable [14]. The study of the accelerated hydrolytic degradation of polyphosphates synthesized by IPTC polycondensation was realized under alkaline conditions, with NaOH 4 M. The time of experiments was 8 h. At the end of 8 h the percentage weight loss for all polymers was: 15.0% (P3); 26.0% (P4); 10.5% (P5) and 35.5% (P7). The polyphosphate P5 is the most stable, and the less stable is P7.

Conclusions

This paper presents the synthesis of phosphorus-containing polymers by variation in chemical constitution of the phosphorylating and bisphenol agents, using the inverse phase transfer catalysis. A new alternative of IPTC for the phosphorus containing polymers, which consists in the inversion the order of addition of one phase to another, by adding the aqueous phase to the organic phase, is presented. The IPTC method requires no reagent purification and affords the desired polymers in high yields and acceptable molecular weights, without the formation of unwanted side products. This procedure leaves out the major inconvenience of the classical methods (high temperatures, corrosion) but also of the phase transfer catalysis methods (high stirring speed ≥10,000 rpm). Polyphosphates, polyphosphonates, polyarylazophosphonates and polyarylazophosphates with high yields and inherent viscosities were obtained by IPTC technique. The obtained polymers were characterized by IR, ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR, molecular weight and inherent viscosities determinations, thermal analysis. Phosphorus containing polymers exhibit a relative high thermal stability, especially the polyphosphonates. For a correct, less speculative estimation of the thermal behavior of similar compounds, a kinetic analysis using different data processing strategies is realized.

The study of accelerated hydrolytic degradation of the polyphosphates synthesized by IPTC polycondensation under alkaline conditions shows that the P5 is the most stable.

The results show that IPTC polycondensation is an interesting alternative to the classical PTC and a versatile method for preparing polyesters with phosphonyl(phosphoryl) groups in the main chain.

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