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Novel synthesis of phosphorus containing polymers under inverse phase transfer catalysis

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Abstract

A novel synthesis of polyphosphates by inverse phase transfer catalysis (IPTC) was investigated. The reaction of methylphosphoric dichloride (MPD) and sodium salt of bisphenol A (BA) in two-phase H_2O/CH_2Cl_2 medium under IPTC is presented and the results are evaluated by the yield and inherent viscosity values. The biphasic medium does not require rigorous stirring. The polyphosphate was characterized by IR, ^1H NMR, ^{31}P NMR, inherent viscosity, thermal analysis, and molar mass. Pyridine (Py), pyridine-oxide (PNO) and 4-dimethylamino-pyridine (DMAP) were used as the inverse phase transfer catalysts. DMAP was found to be the best catalyst.

Keywords: Polyphosphate; Inverse phase transfer catalysis; Biphasic medium

1. Introduction

Phase transfer catalysis (PTC) is a well-established technique in preparative chemistry and has been widely used for organic synthesis, particularly for nucleophilic substitution [1]. 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.

The greatest advantage of organic synthesis by PTC is that a large reaction rate is achieved even at a moderate reaction temperature. The PTC techniques have been successfully applied to polymer synthesis. Various phosphorus containing polymers, in particular polyphosphonates and polyphosphates have been obtained by this technique [2–7].

In the last years we have described the synthesis of polyphosphonates by liquid–liquid interfacial polycondensation [8,9] and vapor–liquid interfacial polycondensation [10–12]. We have focused our attention on the influence of the base concentration in the aqueous phase, reaction temperature, solvents, stirring speed and nature of the catalysts.

In contrast to the PTC technique, a new PTC methodology, namely inverse phase transfer catalysis, IPTC, was presented by Mathias and Vaidya [13]. 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 used inverse phase transfer catalysts include pyridine, pyridine-oxide, 4-dimethylamino-pyridine and different cyclodextrin derivatives. Recently, the application of IPTC in organic synthesis has been reviewed by Li et al. [14].

Continuing our work in the synthesis of phosphorus containing polymers, we present in this paper 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 IPTC technique. Our main objective was to investigate the factors that affect the yield and

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inherent viscosity for the IPTC reaction between methylphosphoric dichloride (MPD) and sodium salt of bisphenol A (BA), in H_2O/CH_2Cl_2 medium. This new approach consists of substituting the quaternary lipophilic onium salts, used as phase transfer catalysts, by typical inverse phase transfer catalysts: pyridine (Py), pyridine-oxide (PNO) and 4-dimethylamino-pyridine (DMAP). The results are presented in comparison to those obtained by the synthesis of other polyphosphonates in PTC system [9].

2. Experimental

2.1. Materials

Reagents (MPD, BA — from Aldrich), catalysts (Py, PNO, DMAP — from Fluka) and solvent (CH_2Cl_2 — from Aldrich) were used without purification.

2.2. Procedure

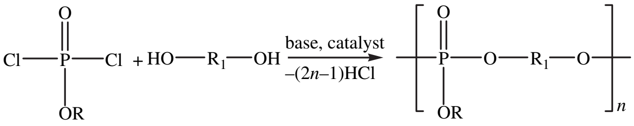
The polyphosphate was synthesized according to the following procedure: 0.005 mol BA were dissolved in 20 ml aqueous solution of NaOH (0.8 g) and 0.0025 mol catalyst were added. To this solution, 0.005 mol MPD in 10 ml CH_2Cl_2 were added drop wise, keeping the temperature below 15 °C; then the mixture was stirred (500 rpm) for 1 h at 15 °C. The polycondensation can be carried out at pH 9—10, to minimize the side reactions of hydrolysis. The supernatant aqueous layer was decanted and the organic layer was washed successively with water to neutral pH. 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 characterized.

2.3. 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 an internal standard. The polymer was 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). Thermogravimetrical analyses were carried out on a TGA/SDTA 851-LF1100 — Mettler apparatus, by heating in air (5 mg) from initial temperature of 20 °C to 1100 °C with a rate of 10 °C/min.

3. Results and discussion

The polyphosphate derived from BA and MPD was synthesized under IPTC conditions, in CH_2Cl_2 as solvent, using several inverse phase transfer catalysts. Reaction conditions were 0.005 mol MPD, 0.005 mol BA, 20 ml aqueous solution of NaOH (0.8 g), 0.0025 mol DMAP, reaction time = 1 h, 500 rpm, 10 °C (reaction 1).



$$Cl-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR}{\underset{|}{P}}}}-Cl + HO-R_1-OH \xrightarrow[-(2n-1)HCl]{\text{base, catalyst}} \left[-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR}{\underset{|}{P}}}}-O-R_1-O- \right]_n \quad (1)$$

$R = CH_3$ $R_1 = C_6H_4{-}C(CH_3)_2{-}C_6H_4$

The polymer was characterized by IR, ^1H NMR and ^{31}P NMR, and the spectral data were in accordance with the proposed structure. The IR spectrum shows strong absorptions of $\nu_{P=O}$ at 1280 cm^{-1}, $\nu_{P-O-C\ (aromatic)}$ at 1170 and 950 cm^{-1} and $\nu_{P-O-C\ (aliphatic)}$ at 1000 cm^{-1}. The disappearance of the OH band was observed. The ^1H NMR spectrum shows a singlet at 1.6 ppm for the isopropylidene protons, a doublet for the $P-O-CH_3$ at 3.7 ppm and a multiplet at 6.6—7.1 ppm for the bisphenol end group and aromatic protons. The ^{31}P NMR spectrum shows two signals at −4.0 ppm which corresponds to P in the end chain and at −10.0 ppm for P in the repeat units, which are attached to two aryloxy and one alkoxy groups.

The molecular weights of the polymer were determined by gel permeation chromatography (Fig. 1).

The polymer starts to degrade between 180 °C and 220 °C. Temperature corresponding to 1% weight loss was 180 °C, to inception of fast degradation was 220 °C and to 50% weight loss was 300 °C. The char percentage at 700 °C was 13.

The influence of the stirring speed on yield and inherent viscosity of the polyphosphate obtained by IPTC polycondensation was studied.

It was observed that yields and inherent viscosities for the obtained polymer do not depend on stirring speed, and with a magnetic stirring ranging from 100 to 500 rpm a polymer with high yield (90—94%) and inherent viscosity

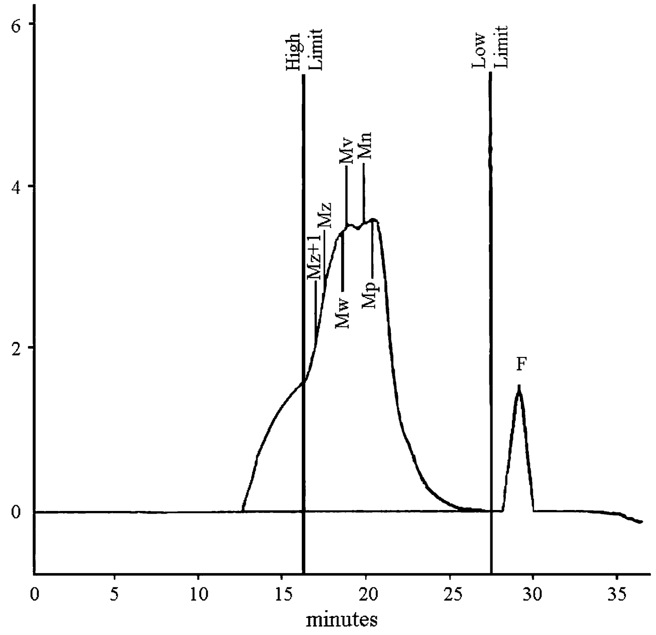


Fig. 1. GPC trace of the polyphosphate obtained by IPTC. Mn = 57.6 × 10^3; Mw = 118 × 10^3; Mw/Mn = 2.05 (based on polystyrene calibration within the calibration limits shown). The actual Mw and PDI are higher.

(0.625–0.655 dl/g) was obtained. So, it appeared that under slow-speed stirring, polycondensation occurs through an IPTC process, whereas PTC process occurs only under vigorous stirring (>10 000 rpm) [9].

This paper presents the influence of the inverse phase transfer catalysts on the yield, the kinetics of the reaction of phosphoric dichlorides with diols with IPT catalysts are in progress and will be the subjects of further articles.

In order to compare the relative catalytic activity of various IPT catalysts, the polycondensation should be carried out at the same reaction conditions (MPD:BA:NaOH = 1:1:2, 15 °C, 1 h, 500 rpm). The efficiency of the phase transfer process with or without IPT catalysts was studied by measuring values of the obtained polyphosphate. Results are presented in Table 1.

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.

Table 1
Influence of the type and concentration of IPT catalysts on yield and inherent viscosity[a]

IPT catalyst	Catalyst ($mol\,l^{-1}$)	Yield (%)	Inherent viscosity[b], η_{inh} (dl/g)
Py	0.05	35	0.250
	0.075	53	0.285
	0.125	65	0.350
PNO	0.05	40	0.320
	0.075	68	0.333
	0.125	80	0.450
DMAP	0.05	45	0.335
	0.075	72	0.542
	0.125	92	0.650
None	–	–	–

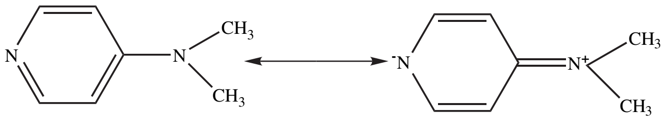
[a] Reaction conditions: 0.005 mol MPD, 0.005 mol BA, 20 ml aqueous solution of NaOH (0.8 g), reaction time = 1 h, reaction temperature = 15 °C, 500 rpm.

[b] The inherent viscosities η_{inh} were determined for solutions of 0.5 g/100 ml in tetrachloroethane, at 30 °C.

In contrast to PTC process [9], where a small amount of catalyst is enough to produce a large interfacial area, IPTC process can occur only if the catalyst concentration in the water phase is enough to solubilize a significant fraction of hydrophobic substrate.

The proposed scheme of the PNO-catalyzed reaction between methylphosphoric dichloride ($P(O)(OR)Cl_2$, $R = CH_3$) and sodium salt of bisphenol A ($HO{-}R_1{-}OH$, $R_1 = C_6H_4{-}C(CH_3)_2{-}C_6H_4$) in an aqueous solution/dichloromethane by inverse phase transfer catalysis is shown in Scheme 1.

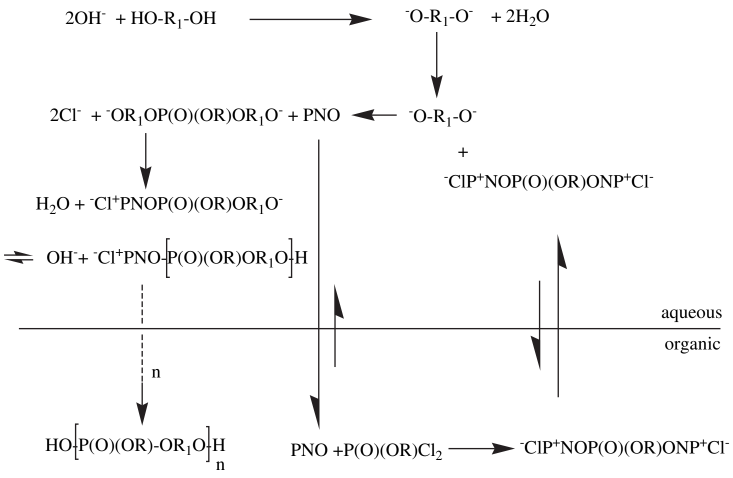
From Table 1, the observed relative catalytic reactivity is 4-dimethylamino-pyridine (DMAP) > pyridine-oxide (PNO) > pyridine (Py). An advantage of DMAP over the other pyridine catalysts is that DMAP shows catalytic activities because of its electron-donating methyl substituents. The polycondensation can be carried out at pH 9–10 to minimize the side reactions of hydrolysis. Although DMAP has lower basicity than other pyridine derivatives, DMAP is a good nucleophile due to its resonance and it is an excellent leaving group.



4. Conclusions

We have shown that IPTC can be an interesting alternative to the classical PTC.

1. The polycondensation of methylphosphoric dichloride with bisphenol A under inverse phase transfer catalysis was investigated.
2. Polyphosphate with high yield was obtained by IPTC technique under slow-speed stirring (100–500 rpm) whereas PTC process occurs only under vigorous stirring (>10 000 rpm).



Scheme 1. The PNO-catalyzed reaction of alkylphosphoric dichlorides with aromatic diols

3. We substitute phase transfer catalysts, by typical inverse phase transfer catalysts. The yields for polycondensation of methylphosphoric dichloride with bisphenol A catalyzed by inverse phase transfer catalysts, respectively, by pyridine derivatives increase with the electron-donating ability of the substituents in pyridine. The order of efficiency of the phase transfer catalysts was DMAP > PNO > Py. Using DMAP as catalyst, a high inherent viscosity ($\eta_{\mathrm{inh}} = 0.650$ dl/g) was successfully obtained. In contrast to PTC process, where a small amount of catalyst is enough to produce a large interfacial area, IPTC process can occur only if the catalyst concentration in the water phase is enough to solubilize a significant fraction of hydrophobic substrate.

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