

Synthesis and characterization of macroinitiators and block copolymers by ATRP using functionalized monomers

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1. Abstract.

Atom transfer radical polymerization (ATRP) has been used to prepare polymers of with the functional group $-\text{AsO}(\text{OH})_2$ salt form. The synthesis of macroinitiators based on sodium *o*-methacryloylaminophenylarsonate (*o*-MAPHA-Na), *p*-methacryloylaminophenylarsonate (*p*-MAPHA-Na), sodium methacrylate (MA-Na), sodium acrylate (AA-Na) and acrylamide (AAD) by ATRP in organic and aqueous media was carried out at 48 °C. ATRP polymerizations were performed using the initiators Allyl 2-bromo-2-methyl-propionate (ABIB) and methyl 2-chloro-propionate (MCP) as well as the $\text{CuBr}/N,N,N',N',N''$ -pentamethyldiethylenetriamine (PMDETA) as catalytic complex. Macroinitiators were characterized by ^1H NMR and FTIR.

2. Introduction.

Water soluble polymers including neutral polymers, polyelectrolytes and ionomers, are widely used in the fabrication of superabsorbents, ion exchange resins, water purification materials, selective membranes, controlled delivery drugs etc [1]. These polymers are mainly produced by free radical polymerization. However, a major drawback of conventional radical polymerization is the lack of control over molecular weight distribution and the impossibility to prepare well-defined complex structures such as end-functionalized polymers or block copolymers due to rapid transfer and termination reaction. These intrinsic problems for conventional radical polymerization can be overcome using one of the controlled radical polymerization techniques developed in the past decade [2]. Atom transfer radical polymerization (ATRP) [3] is one of the most broadly applied and versatile methods of controlled radical polymerization. ATRP is usually performed in bulk or in an organic solvent. During the past few years, there has been a tendency to replace organic solvents used in synthetic reactions with reaction medium less harmful to environment like water [4], supercritical carbon dioxide [5] and ionic liquids [6]. However, heterogeneous and homogeneous aqueous ATRP systems exhibit several side reactions and for these reason the number of water-soluble monomers polymerized in controlled fashion is still limited. The effect of aqueous media to the copper-based ATRP catalyst [7] and the solvolitic loss of

halide ligand from the deactivating higher oxidation state metal complex [7] are some of these side reactions.

We are interested in the polymerization by ATRP in aqueous medium of *o*- and *p*-MAPHA-Na, AA-Na, AM-Na and AAD because the *o*- and *p*-MAPHA-Na monomers structure containing a chelating group, particularly the arsonic acid ($-\text{AsO}(\text{OH})_2$), which has been used for separations of some ionic metals such as In, Th and Zr. On the other hand, the COO^-H^+ and COHN_2 groups are able to form coordination bonds with metal ions.

In the present work, is reported the synthesis of macroinitiators of *o*-MAPHA-Na, *p*-MAPHA-Na, AM-Na, AA-Na, and AAD by ATRP. The polymerizations were carried out in aqueous medium at 48°C and CuBr/L as catalyst system. Characterization of macroinitiators was determined from FTIR and ^1H NMR.

3. Experimental section.

3.1. Monomer Synthesis: The *o*- and *p*-MAPHA monomers were obtained by condensation reaction of methacryloyl chloride with the corresponding *o*- and *p*-APHA, according to the reported procedure (yield 40% and 77% respectively) [8]. *o*- and *p*-MAPHA-Na, AA-Na and AM-Na were synthesized by neutralization reaction with NaOH (yield: 94%, 96%, 90% and 77%, respectively) [8].

3.2. Synthesis of ATRP macroinitiators: Polymerizations were carried out using a molar ratio $[\text{M}]/[\text{I}]/[\text{CuX}]/[\text{L}]$ 100:5.7:7. Monomers (3.125mmoles) and catalytic complex (CuBr or CuCl 0.21875 mmoles and ligand 0.21875 mmoles) were dissolved in 5mL of solvent or mixing of solvents. The reaction solution was bubbled by argon gas for 20 minutes and then was added to a solution of initiator (0.125 mmoles) which was previously purged by argon. The reaction solution was placed in a water bath at 48°C (± 0.02) for 45h. The polymerization was stopped by cooling the glass ampule in ice-water bath. The polymer was precipitated in acetone and they were placed in a vacuum oven at 90°C for 36h. The systems evaluated are shown in table 1.

3.3. Synthesis of *o*-MAPHA-Na macroinitiators without ligand: The procedure following for this reaction is described in 3.2.4, but in this case the catalytic complex was not added. Only the $[\text{M}]/[\text{I}]/[\text{CuCl}]$ was used (table 2).

Table 1. Systems evaluated for synthesis of ATRP macroinitiators

Label	System [M] ₀ /[I] ₀ /[CuX] ₀ /L ₀	Molar ratio	Reaction media	T (°C)	Time (h)
1	AM-Na/ABIB/CuBr/PMDETA	100:5:7:7	Ethanol:H ₂ O (70:30)	48	45
2	AA-Na/ABIB/CuBr/PMDETA	100:5:7:7	Ethanol:H ₂ O (70:30)	48	45
3	AAD/ABIB/CuBr/PMDETA	100:5:7:7	Ethanol	48	45
4	<i>o</i> -MAPHA-Na/ABIB/CuBr/PMDETA	100:5:7:7	DMF:H ₂ O (20:80)	48	45
5	<i>p</i> -MAPHA-Na/ABIB/CuBr/PMDETA	100:5:7:7	Methanol:H ₂ O (20:80)	48	45

Table 2. Systems evaluated for synthesis of *o*-MAPHA-Na macroinitiators without ligand

Label	System [M] ₀ /[I] ₀ /[CuX] ₀	Molar ratio	Solvent or Mixing of solvents	T (°C)	Time (h)
6	<i>o</i> -MAPHA-Na/MCP/CuCl/-	100:10:2	DMF:H ₂ O 60:40	48	45
7	<i>o</i> -MAPHA-Na/MCP/CuCl/-	100:10:2	DMSO	25	0.083

4. Results and Discussion.

The characterization by FTIR and ¹H NMR of products obtained in reactions **1**, **2**, **4** and **5** shows that the polymers were formed, however ¹H NMR spectrum did not present any signal from the initiator, which indicated that the initiator was not as terminal group, so the polymers were obtained via conventional radical polymerization. This behavior could be due to the equilibrium reaction insitu, because it may be that there is a high concentration of stationary radicals, i.e. the deactivation rate is very slow or even does not exist, and the activation rate must be high.

On the other hand, for the reaction **3**, ¹H NMR of polymer obtained (figure 1a) clearly shows a signal arising from the initiator (ABIB) at δ 4.0-4.2 ppm (corresponding to -CH₂ of ester), confirming that the initiator is covalently attached to the polymer as a terminal group.

The reactions **6** and **7** were carried out in order to evaluate if it was possible to obtain *o*-MAPHA-Na macroinitiators without using a ligand. In reaction **7**, it was obtained a polymer by conventional radical polymerization. This reaction was very fast, i.e. in 5 minutes a gel had been formed, it is probably the DMSO has accelerated the reaction, because this behavior was not observed in reaction with DMF:H₂O solvent, which indicates the influence of solvent on reaction. On the other hand, from ¹H NMR characterization of the reaction **6** product (figure 1b), it is clearly shown a signal arising from the initiator (MCP) at δ 4.0-4.2 ppm (corresponding to -CH₃ of ester), confirming that the initiator is covalently attached to the polymer chains as terminal group.

Additionally, it was made a reaction with *o*-MAPHA-Na and MCP initiator ([M]/[I] system without catalytic complex), it was found *o*-MAPHA-Na can be polymerized only initiator, which suggest an interaction between halide and this monomer.

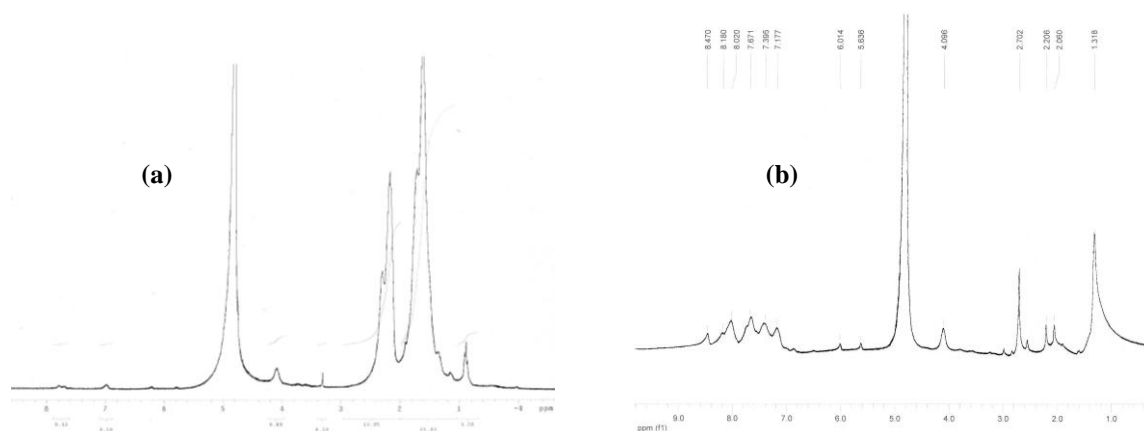


Figure 1. ^1H NMR spectrum of: (a) polymer 3 and (b) polymer 6

5. Conclusions.

The monomers *o*- and *p*-MAPHA-Na, AA-Na and AM-Na polymerized by conventional radical polymerization. For *o*- and *p*-MAPHA-Na, AA-Na, and AM-Na was observed the effect of different factors (solvent catalytic complex etc.,) that could be influence on the ATRP polymerization. On the other hand, for the AAD monomer the polymer obtained has the initiator covalently attached as a terminal group. Finally, it was demonstrated it was possible obtain a *o*-MAPHA-Na macroinitiator without ligand.

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7. References.

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