Synthesis of Random Copolymers Poly (methylmethacrylate-*co*-azo monomer) by ATRP-AGET

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Summary: The synthesis of the azo molecule 1-(2-(4-nitrophenyl) diazenyl) naphtalen-2-ol which has been functionalized with a methacryloxyl fraction is now reported. This azo monomer was copolymerized with methyl methacrylate (MMA) by ATRP where the active species is prepared "*in situ*" after the reduction reaction of the metal complex Cu (II) - HMTETA by tin 2-ethylhexanoate in 2-butanone as solvent. Experimental conditions for the controlled homopolymerization of MMA were established. By adjusting the amount of reducing agent, a good correlation between theoretical and experimental molecular weight was obtained. Such conditions were also employed for the random copolymerization of MMA with the synthesized azo monomer.

Keywords: atom transfer radical polymerization (ATRP); azo polymers; copolymerization; synthesis

Introduction

Azo dyes are aromatic molecules containing the chemical structure Ar–N=N–Ar with an absorbance range from 400–700 nm (visible region). Such chromophores exhibit yellow to red colors and have been used in many applications since they were discovered, mainly by dispersing them into different kinds of materials.

The chemical structure of the azo dyes can be modified in order to prepare methacrylic monomers which can be copolymerized through the atom transfer radical polymerization technique (ATRP) which has been extensively used to prepare functionalized polymers.[1–6] An interesting modification for the ATRP mechanism is the generation of the active species *in situ* from the copper II complex through a redox reaction; reducing agents such as tin 2-ethyl hexanoate,[7] glucose[8] or ascorbic acid[9] have been used for this purpose.

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This variation of ATRP, when the activators are generated by electron transfer (ATRP-AGET) is based on the reduction of the transition metal complex from Cu (II) to Cu (I). Most papers related with ATRP-AGET in the literature describe polymerization reactions in miniemulsion, emulsion or microemulsion, in this case we report organic solution ATRP-AGET reactions.

Experimental Part

Analytical Equipment

^{1}H NMR spectra were recorded on a Brucker spectrometer (500 MHz), Bruker Advance III; molecular weights and polydispersities were measured by gel permeation chromatography (GPC) using a HPLC HP 1100 series equipped with refractive index and UV detectors and employing THF as mobile phase. Mn and Mw were calculated from polystyrene standards. Commercially available chemicals were used without further purification. The azo monomer (E)-1-(2-(4-nitrophenyl)diazenyl) naphthalene-2-methacryloxyl was obtained in 95% yield after esterification

of the commercially available pigment named *para*-red.

General Procedure for the Homopolymerization of MMA

0.1283 g (0.5744 mmol) of $CuBr_2$, 0.1366 g (0.5929 mmol) of HMTETA and 11.3795 g (0.1136 mol) of MMA, dissolved in 6 mL of MEK, were placed in a Schlenk oxygen-free tube with argon atmosphere, adapted for magnetic stirring, and the mixture was stirred for 30 min. Then, 0.116 g (0.4428 mmol) of tin 2-ethyl hexanoate and 0.0585 g (0.2999 mmol) of ethyl 2-bromo isobutyrate were also added. The reaction mixture was frozen with liquid nitrogen and vacuum was applied. After several freeze-thaw cycles, the Schlenk tube was sealed under vacuum and placed in an oil bath preheated at 80 °C. The reaction lasted 150 min, after which the solid was removed from the Schlenk tube and dissolved in THF, precipitated in hexane and purified by passing it through a silica gel column.

Results and Discussion

The azo monomer was prepared according to the synthetic route shown on Figure 1. The first step involves the diazonium coupling between aniline and 2-naphtol. This product was esterified with methacryloyl chloride and catalyzed by triethylamine in acetone as solvent.

The azo monomer was characterized by NMR, FT-IR and mass spectroscopy (MS). Because of the poor thermal stability of the compound, MS was obtained by direct insertion probe (DIP). The mass spectrum shows an ion mass of 361 m/z with a relative intensity lower than 1%. The main fragment of 293 m/z suggests the loss of the methacryloxyl group. By ^{1}H NMR the characteristic signals corresponding to the vinyl protons of the methacryloxyl with a chemical shift of 5.8 and 6.2 ppm as well as the methyl protons at 2.15 ppm can be appreciated. Aromatic protons of the molecule were assigned by correlation spectroscopy (COSY) confirming the 1,2-substitution over the naphthalene ring.

In order to get the best conditions for the preparation of poly (methyl methacrylate-co-azo monomer) by ATRP-AGET, the homopolymerization of MMA was selected as a model to optimize the experimental conditions. The Cu (II)-multidentated amine complex was generated *in situ* by a redox reaction promoted by tin 2-ethylhexanoate, which was selected as the reducing agent. Two multidentated amines HMTETA and PMDETA were evaluated as complexes with the Cu^{2+} ion from $CuBr_2$. Both metal complexes were dissolved in 2-butanone and 2-bromo

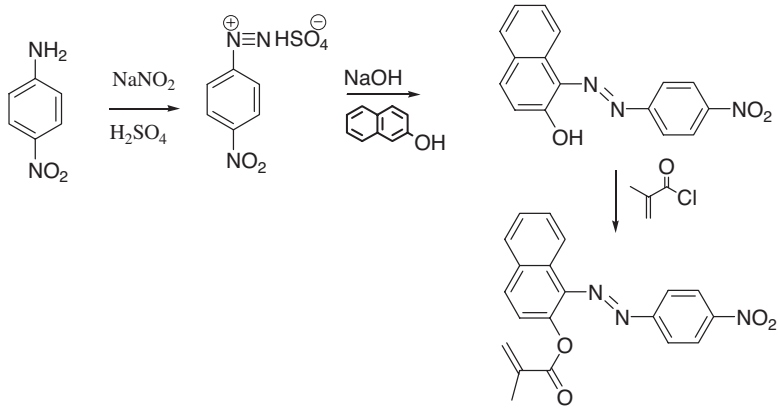

Figure 1.
Preparation of the azo monomer (E)-1-(2-(4-nitrophenyl)diazenyl) naphthalene-2-methacryloxyl.

Figure 2.
Reduction reaction of Cu (II) - complex promoted by tin 2-ethylhexanoate.

isobutyrate was used as initiator for the homopolymerization of MMA.

Analyzing the chemical reaction between the tin 2-ethylhexanoate and the Cu-complex, it can be deduced that the Sn atom provides two electrons for the reduction reaction of the Cu-complex from Cu (II) to Cu (I); in agreement with this statement the molar ratio Sn:Cu must be 1:2. This reaction can be depicted on Figure 2.

According to the literature, the molar ratio between the reducing agent and the Cu (II) ion commonly used in aqueous solution is 3:1. However, it must be kept in mind that this molar ratio depends on the solubility of the Sn salt in the monomer droplets during emulsion polymerization. The mechanism can be established as follows: once the Cu (I)-complex is formed by the oxidation of the Sn salt, it can react with the halogenated derivate used as initiator. This step generates a free radical in the initiator moiety starting the polymerization process; then, the control as well as the subsequent steps are based on the typical ATRP process. Nevertheless, an excess of the reducing agent concentration in the system provides an extra amount of electrons which affects the activation/deactivation equilibrium by reducing the concentration of Cu (II) needed for the generation of the dormant species. The increase of the free radical concentration drives to an uncontrolled polymerization reaction.

In order to confirm the previous statement, several molar ratios of the Sn:Cu were used for the homopolymerization of MMA. Experiments 1 and 2 were selected to evaluate the differences between HMTETA and PMDETA. Experiments 3 and 4 were chosen to evaluate the differences between normal ATRP (3) and the use of Sn (II) as reducing agent (4). The results obtained are included in Table 1.

As it can be clearly seen, the use of three equivalents of Sn (II) in experiments 1 and 2 results in an uncontrolled polymerization of MMA since PDIs higher than 1.5 were obtained. Instead, good control was achieved when 0.5 equivalents of tin 2-ethylhexanoate was used, even better when compared with typical ATRP polymerization.

Experiment 4 shows that using the molar ratio Cu(II):Sn(II) 1:0.5 where the catalyst complex is Cu (II)-HMTETA at 80 °C controlled homopolymerization of MMA occurs. In this experiment, a linear behavior between the molecular weight and conversion, good correlation between theoretical and experimental molecular weight and low polydispersity values were observed as can be appreciated in Figure 3.

Once experimental conditions were established, copolymerization reactions were performed in order to prepare the random copolymers poly (methyl methacrylate-*co*-azo monomer) by using a monomer mixture which contains a 90% (w/w) of MMA and 10% (w/w) of the photochromic monomer. After 12 hours of reaction the random copolymer MMA-*co*-(E)-1-(2-(4-nitrophenyl)diazenyl)-2-methacryloxyl naphthalene was obtained in 36% yield.

Table 1.
Homopolymerization of MMA by ATRP-AGET promoted by Sn (II).

Experiment	Yield (%)	$[MMA]_o$	$[CuBr_2]_o$	$[Sn\ (II)]_o$	Ligand	Mn_{GPC}	PDI
1	68	200	1	3	HMTETA	20296	2.6
2	42	200	1	3	PMDETA	10400	6.8
3	40	200	0	0	HMTETA	20495	1.25
4	88	200	1	0.5	HMTETA	16035	1.3

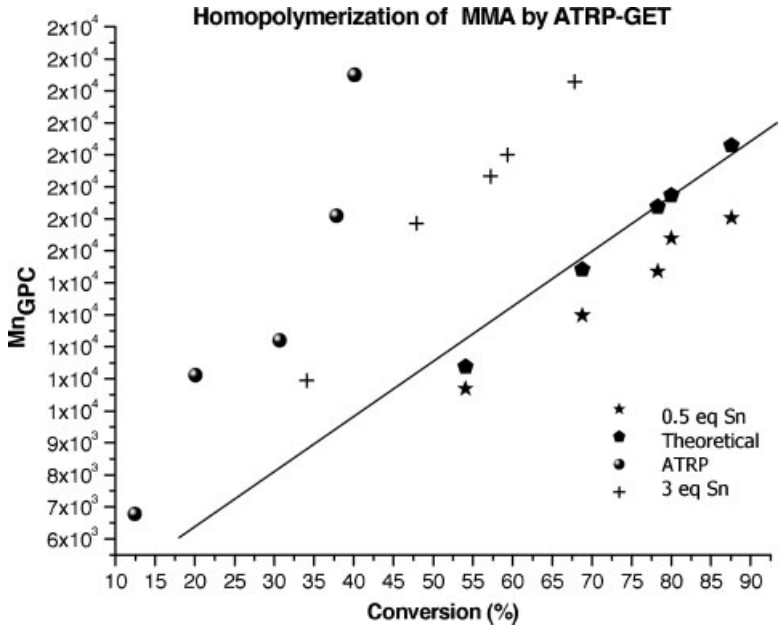

Figure 3.
Relation between conversion and molecular weight (Mn) for the homopolymerization of MMA by ATRP-AGET.

Copolymer composition was analyzed by NMR, showing that the azo content is about 13.56% (w/w). In Figure 4, the characteristic signals from the main protons in the copolymer are identified. Ha and Hb correspond to the methyl protons from MMA and the azo fraction. Then Hc is associated to the methylene protons in the copolymer, Hd to the methoxy protons and He is attributed to the aromatic protons from the azo monomer present in the polymer chain.

Figure 5 shows linear behavior of the molecular weight with conversion for the copolymerization reaction, confirming the controlled character of the reaction.

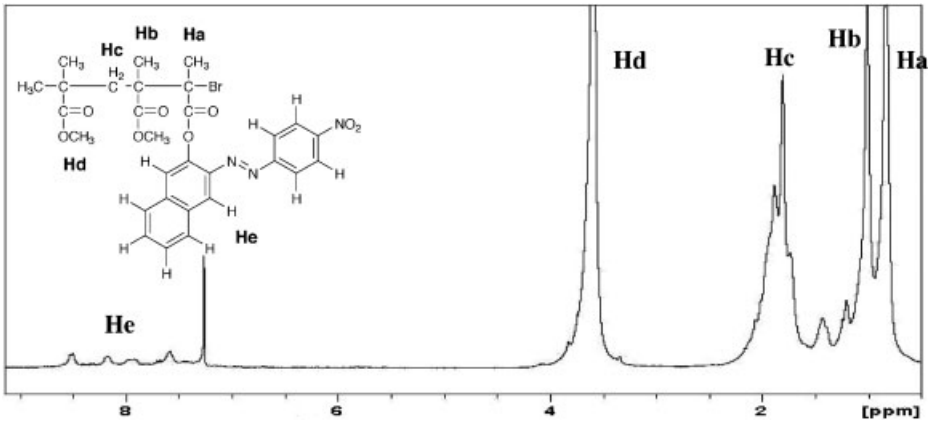

Figure 4.
NMR spectrum for the copolymer MMA-*co*-(E)-1-(2-(4-nitrophenyl)diazenyl)-2-methacryloxyl naphthalene.

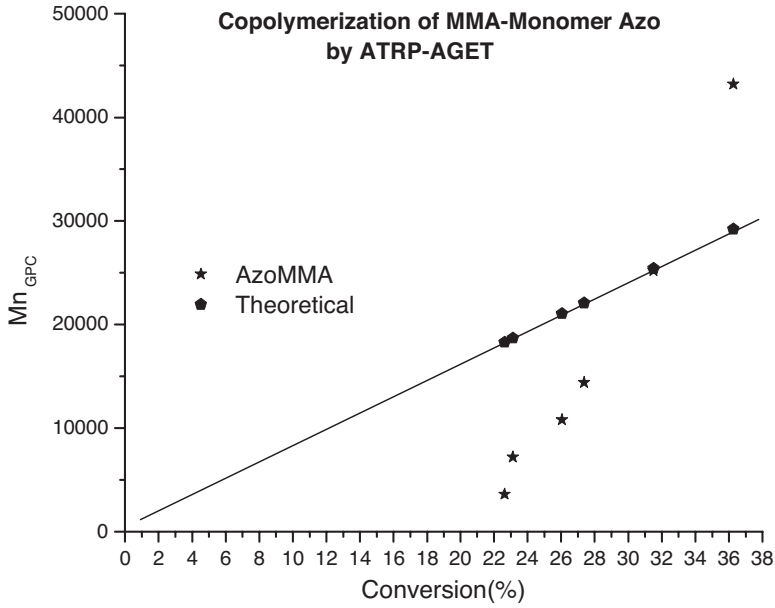

Figure 5.
Copolymerization reaction between MMA and the synthesized azo monomer by ATRP-AGET.

Conclusions

An azo monomer was synthesized from esterification of the commercially available *para*-red pigment. Then, controlled homopolymerization of MMA under ATRP-AGET conditions was performed, where the molar ratio between Cu (II) and Sn was 1:0.5. This experimental conditions were used to prepare random copolymers MMA-*co*-(E)-1-(2-(4-nitrophenyl)diazenyl)-2-methacryloxyl naphthalene in 36% yield The azo monomer resulted in low reactivity. Such behavior is attributed to the electronic effect generated by the presence of the electron withdrawing nitro group in the azo molecule.

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