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Photochromic Block Copolymer Poly(styrene-*b*-azo monomer) by ATRP

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Summary: Photoactive monomers [(E)-1(4-methacryloxyphenyl)-2-(nitrophenyl) diazene] (azo 1) and (E)-1-(4-methacryloxyethyl-phenyl)-2-phenyl-diazene (azo2) were synthesized. The azo 1 monomer showed poor reactivity under the evaluated polymerization method. The Azo 2 monomer was used in the block copolymerization with polystyrene by the normal ATRP methodology. Several polystyrene macroinitiators were prepared with molecular weights of 10, 20 and 30 k g/mol. The end functionality was increased by the addition of 0.1 equivalents of copper II chloride. Block copolymers in 30% yield and low polydispersity were synthesized by ATRP from the polystyrene macroinitiators and the azo monomer. The block copolymer exhibits good photochromic activity.

Keywords: atom transfer radical polymerization (ATRP); block copolymers; polystyrene

Introduction

Scientific and technological applications of photochromic organic molecules are well known; they have been extensively studied by incorporating them in polymer matrices creating new materials. In this photoresponsive system, properties can be easily manipulated by light.[1] However, their applications in optical devices, depend on the way these materials are incorporated into a substrate.[2,3] Recently, it was suggested that after nanophase segregation,[4] block copolymers can exhibit at the nanometric scale a specific property which is defined by one of the blocks. For instance, it can be possible to identify a changing color property at nanomeric scale when one of the blocks is a photochromic monomer. On the other hand, interest concerning the synthesis of azo compounds has grown due to the increasing application of such kind of molecules in the development of information-storage devices, ultra high density optical devices, photochromic switches, etc. There are just a few examples related to the preparation of colored block copolymers including azo compounds in their chemical structure in the literature.[5] As an example, the preparation by anionic polymerization of polyisoprene functionalized with a block of an azo monomer should be mentioned as it exhibits liquid crystal properties.[6] In addition, the synthesis of diblock and triblock copolymers by anionic polymerization has also been reported.

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 an 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. Photoactive monomers were named as azo 1 [(E)-1(4-methacryloxyphenyl)-2-(nitrophenyl)diazene] and

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azo 2 [(E)-1-(4-methacryloxyethyl-phenyl)-2-phenyl-diazene].

General Procedure for the Preparation of the Polystyrene Macroinitiator

In an oxygen free Schlenk tube with argon atmosphere, adapted for magnetic stirring, 0.084 g (1 eq, 0.585 mmol) of CuBr, 0.146 g (1.2 eq, 0.634 mmol) of HMTETA and 8.84 g (100 eq, 85 mmol) of styrene, were charged. Then, 6 mL of methyl-ethyl-ketone (MEK) and 0.169 g (1eq, 0.938 mmol) of ethyl-2-bromopropionate were also added. The mixture was frozen with liquid nitrogen and vacuum was applied. After several freeze-thaw cycles, the flask was sealed under vacuum and placed in an oil bath preheated at 110 °C. The reaction lasted 180 min, the solid was removed from the Schlenk tube and dissolved in THF to be then precipitated in hexane and purified by passing it through a silica gel column.

General Procedure to Prepare Block Copolymers

0.0115 g (0.117 mmol) of CuCl were charged in a Schlenk tube oxygen-free with argon atmosphere adapted for magnetic stirring. Then, 3 mL of THF, 0.0288 g (0.125 mmol) of HMTETA and 2.101 g of (E)-1-(4-methacryloxyethyl-phenyl)-2-phenyl-diazene (azo 2) were added and stirred for 10 minutes. At this point, 1.695 g (Mn = 13,567 g/mol, PDI = 1.37) of the polystyrene macroinitiator were added. The reaction mixture was frozen with liquid nitrogen and vacuum was applied. After several freeze-thaw cycles, the flask was sealed under vacuum and placed in an oil bath preheated at 85 °C. The reaction lasted 900 minutes; the final solid resulting was dissolved in THF and precipitated in methanol.

Results and Discussion

The monomer azo 1 (E)-1-(4-methacryloxyphenyl)-2-(nitrophenyl)diazene was prepared from the phenol diazonium coupling with *p*-nitroaniline in 85% yield. After purification by column chromatography, this phenol group in the azo compound was esterified by methacryloyl chloride using an excess of triethylamine in acetone. Azo 1 was obtained in 90% yield according to the procedure in Figure 1.

The azobenzene monomer was characterized by ^{1}H NMR where a pair of doublets (J = 1.5 Hz) corresponding to the pair of vinylic hydrogen atoms from the methacryloyl group at 5.8 and 6.45 ppm can be observed.

The synthesis of the monomer azo 2 E-2-(4-methacryloxyethylphenyl)-1-phenyldiazene is schematically shown in Figure 2. This synthesis is based on the reaction between the phenyl-N-oxide and 4-hydroxyethyl aniline. The alcohol obtained was then esterified with methacryloyl chloride.

The mass spectra recorded by the direct insertion probe shows the mass fragment ion of 294 m/z with a relative intensity of 9%, and the more abundant ion (208 m/z) shows the loss of methacrylic acid. The ^{1}H NMR spectra shows two triplets (J = 8.5 Hz) at 4.2 and 3.8 ppm and the signals from the methacryloyl group (doublet J = 1.5 Hz at 6.4 ppm and doublet J = 1.5 Hz at 5.80 ppm).

ATRP has proved to be a very powerful polymerization technique for the preparation of block copolymers from a wide variety of monomers. In this work, a polystyrene macroinitiator was used to copolymerize with the azobenzene methacrylate monomer. The PS-Br macroinitiator was first prepared by ATRP and was analyzed by ^{1}H NMR by calculating the percentage of Br-functionalization at the end of each chain. The best system is constituted by CuBr (I), 1,1,4,7,10,10-hexamethylethylenetetramine (HMTETA) and 2- bromoethylpropionate and styrene used as monomer.

The Br-functionalization is one of the most important parameters to be considered when a PS-Br macroinitiator is synthesized. Lutz et al.[7] state that even when the polymerization is under control, the bromine atom can be lost due to a disproportionation reaction between the catalyst on its

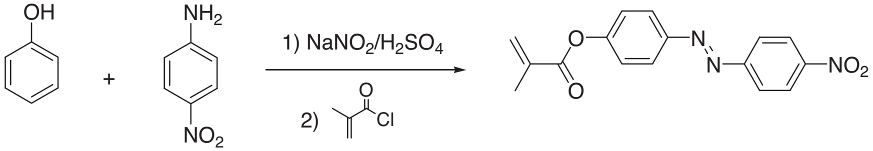

Figure 1.
Preparation of the photoactive monomer Azo 1.

highest oxidation number and the growing radical. To solve this problem, Lutz diminishes the initial amount of initiator in his experiments; however, the ratio between the concentration of the initiator and monomer has to be adjusted according to the desired molecular weight. An alternative, proposed by Klumperman,[8] is the addition of Cu (II) salts in order to increase the dormant species during the propagation of the polymerization.

Here we followed the strategy proposed by Klumperman and the experimental conditions and results concerning the preparation of the PS-Br macroinitiators can be appreciated in Table 1.

As can be appreciated in Table 1, the experiments 1 to 3 are oriented to evaluate the addition of 0.5 equivalents of the copper II and its influence on the molecular weight. In a similar way, the addition of 1 equivalent of copper II is evaluated on experiments 4–6.

High end-functionality yield was obtained when the ratio of Cu(I):Cu(II) is equal to 1 as can be observed in experiments 4 to 6 from Table 1. The end bromine functionalization to estimate the degree of activity was calculated by NMR measuring the ratio between the methine hydrogen atoms from the carbon atom next to the bromine atom (Ha in spectra) and methylene hydrogen atoms from the initiator molecule (Hb). Those signals are shown in Figure 3.

The copolymerization reaction with the photoactive monomers and the Ps-Br was achieved with the macroinitiator derived from experiment 6. At the beginning, for the preparation of the photoactive copolymers an additional amount of Cu (II) was added in order to increase the dormant species concentration, considering two important parameters: 1) that cross-propagation between benzylic and methacrylic radicals is slow and 2) a rapid initiation and low cross-propagation rate may result in the loss of end functionality.

Even when experimental conditions were adjusted, the copolymerization reaction between the monomer azo 1 and the three PS-Br macroinitiators prepared was unsuccessful. NMR analysis of the solid obtained showed that the Br-functionaliza-

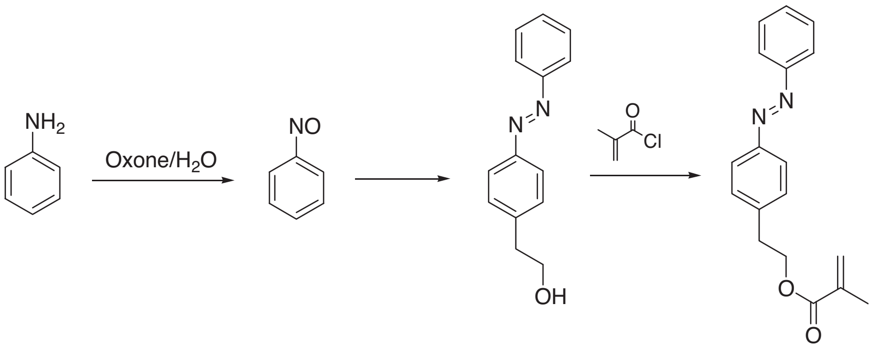

Figure 2.
Preparation of the photoactive monomer Azo 2.

Table 1.
Preparation of PS-Br macroinitiators by ATRP (concentrations in gmol/L).

Exp.	$[M]_o$	$[I]_o$	$[Cu(I)]_o$	$[Cu(II)]_o$	$Mn_{(GPC)}$ (g/mol)	Conversion (%)	PDI	F* (%)
1	100	1	1	0.5	8,137	73	1.485	32.5
2	200	1	1	0.5	10,869	70	1.37	73.1
3	300	1	1	0.5	18,321	71	1.469	42.5
4	100	1	1	1	11,308	66	1.292	86.5
5	200	1	1	1	17,044	49	1.322	77.4
6	300	1	1	1	13,567	51	1.341	92.4

*F end- functionalization.

tion at the end of the polymer chain was lost during polymerization. The low reactivity of the azo monomer was confirmed during its homopolymerization at 110 °C where only a 3% yield was reached, this low reactivity was attributed to the free radicals formed during cross- propagation, very stable methacryloxy radicals are formed lowering the propagation rate.[9] On the other hand, by introduction of the ethyl moiety in the structure of the monomer (azo 2) the homopolymer monomer was recovered in 40% yield.

Block copolymerization between PS-Br macroinitiator (Mn: 13,567 g/mol funcionality 92.40% and 1.341 IPD) and the monomer azo 2 was carried out at 100 °C with addition of 0.5 eq of Cu (I) and 0.5 eq of Cu (II). At the end of the reaction a block copolymer was obtained in 30% yield. The behavior of the molecular weight with conversion is depicted in Figure 4.

As can be seen in this graph, the copolymer obtained has a lower molecular weight than the theoretical one. This result can be attributed to a transfer reaction

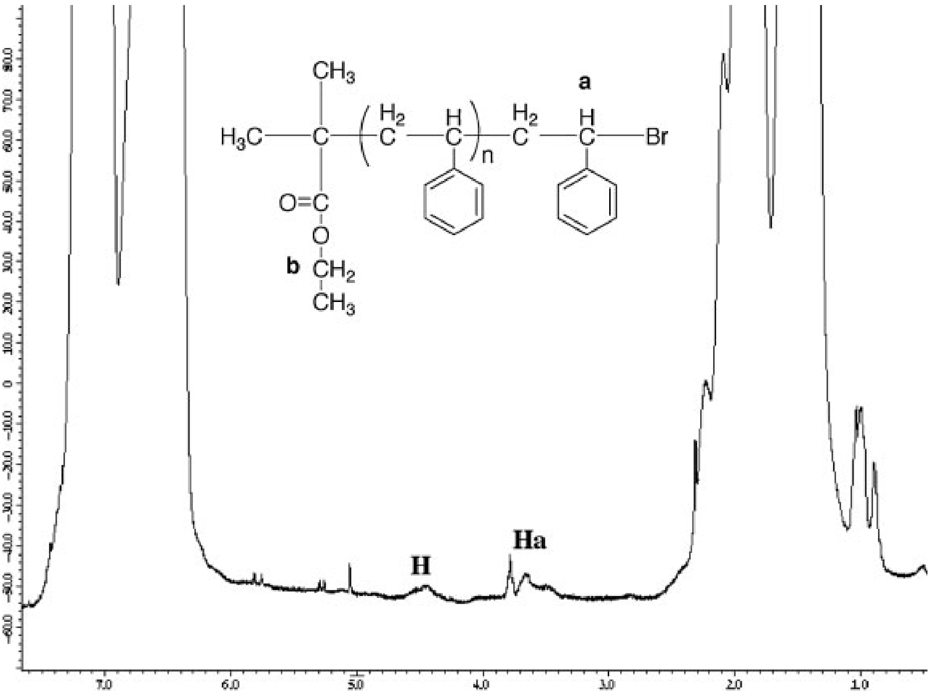

Figure 3.
^{1}H NMR from PS-Br macroinitiator, Mn: 13,567 g/mol funcionality 92.4%.

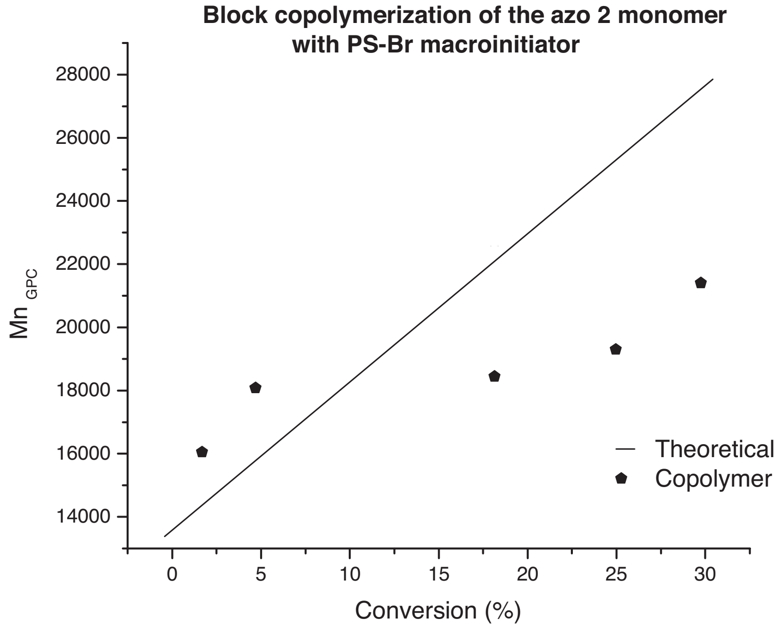

Figure 4.
Copolymerization of the azo 2 monomer with Ps-Br macroninitiator under ATRP conditions.

between the growing free radical and the azo compound.[10,11] In spite of this result, a block copolymer was recovered with 30% yield which contains 11.6% molar of the photochromic azo-monomer. Figure 5 shows the ^{1}H-NMR spectra of this polymer.

The photoactive properties were tested when a solution (10^{-5} M) of the block copolymer was irradiated with an ultraviolet lamp (313 nm) and it showed good photochromic properties since the absorption band was located at 450 nm on the

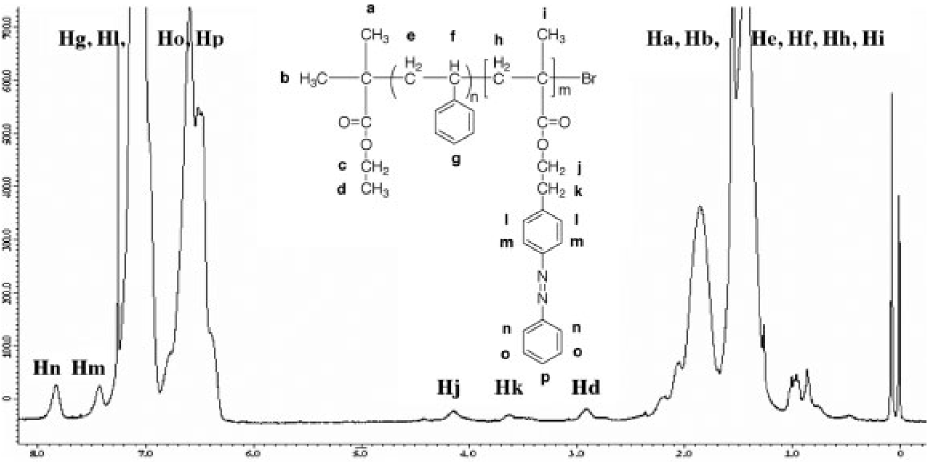

Figure 5.
^{1}H-NMR spectra of the photochromic block copolymer (Mn 21,400, IPD 1.47 and 11.6% molar of the azo monomer and 88.4% molar of styrene).

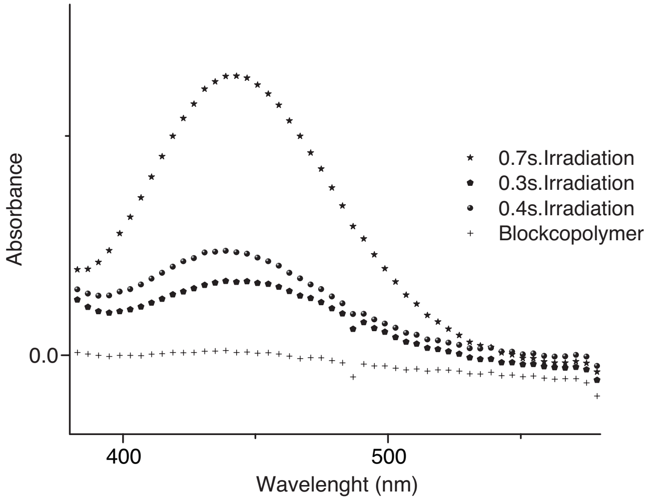

Figure 6.
UV-vis spectra of a solution of poly(styrene-*b*-azo2) before and after u.v. irradiation.

visible region, as can be seen on its absorption spectra in Figure 6.

Conclusions

Azo monomers (1 and 2) were obtained in high yields, but these molecules showed low reactivity during their homopolymerization by ATRP and copolymerization with styrene. Meanwhile, by adjusting some experimental conditions, such as the Cu (I) and Cu (II) ratio, the block copolymer poly (styrene-*b*-azo 2) was obtained in 30% yield.

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