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ARTICLE *in* MACROMOLECULES · MARCH 2011

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Transformation of the Bromine End Group into Thiol in (Meth)acrylic Polymers Synthesized by Atom Transfer Radical Polymerization

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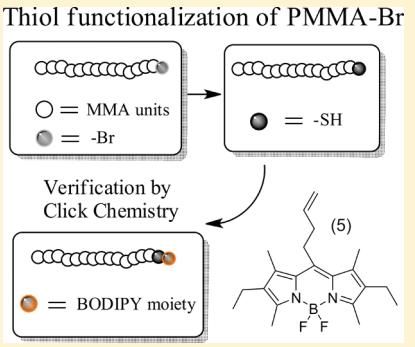
ABSTRACT: The halogen end group of polymers prepared via atom transfer radical polymerization (ATRP) can be converted into other functional groups by different chemical modifications. Herein, a new method to modify the bromine end group into a thiol functionality in (meth)acrylic polymers synthesized by ATRP is reported for the first time. Thus, the bromine end group of several poly(methyl methacrylate)s was successfully converted into a thioacetate and then in a mercapto group by a controlled hydrolysis. This end-functionalization was confirmed introducing *in situ* a fluorescent group by thiol−ene "click" reaction with a synthetic alquene tethered to a 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY) fragment. In addition, two model reactions in which bromide ATRP initiators were transformed into new thiol-functionalized molecules proved that this methodology can be applied to either methacrylic or acrylic polymers synthesized by ATRP.



INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most powerful techniques to obtain polymers with high control over composition, topology, and functionality.[1−8] A further feature of polymers obtained by ATRP is that they preserve a ω-halogen end group that can be converted into other functional groups. Thus, formation of azides, amines, hydroxyl, double bonds, and so on have been shown to be feasible.[1] However, studies aimed to provide efficient routes to transform the halogen into thiol are scarce, and until now, they have been restricted to the case to polystyrene [P(St)].[9−12]

In a pioneer work, Garamszegi et al.[9] converted the bromine end group of P(St) into an isothiouronium salt by reaction with thiourea. Subsequently, they treated this salt with a NaOH solution at 110 °C for 24 h, obtaining the corresponding thiol end-functionalized polymers. Unfortunately, a main drawback of this methodology is that this second reaction needs a high basic conditions, and therefore, it cannot be used for (meth)acrylic polymers since the ester groups would be hydrolyzed. Then, the use of ATRP for the preparation of mercapto end-functional polymers is limited to this polymer or when thiol-precursor ATRP initiators are used.[13,14] In this sense, reversible addition−fragmentation radical controlled polymerization (RAFT) could be advantageous over ATRP, since it allows obtaining thiol end-functionalized polymers by modification of the usual initiator fragment incorporated in the macromolecular chain.[15−17] Thus, several groups have investigated this thiol functionalization of RAFT polymers by aminolysis,[18−23] hydrolysis,[24−26] or metal hydrides reduction[27,28] in order to obtain new both functional polymers and macromolecular architectures.[29−33]

The demand of well-defined polymers with thiol functionalities has increased in different areas, such as optics, microelectronics, and biotechnology, since the mercapto group establishes specific interactions with metals as gold, silver, and cadmium.[13,34−40] Moreover, the development of the thiol−ene "click" chemistry[14,41,42] has improved the potential of this kind of polymers because this reaction shows nearly quantitative yield, short reaction times, mild conditions, and high selectivity, which allows obtaining easily innovative functionalized polymers and macromolecular structures.

Taking into account the actual importance of thiol-functionalized polymers and the contrasted versatility of ATRP, in this contribution we show a new and easy methodology to convert the bromine end group into a thiol group in (meth)acrylic polymers synthesized by ATRP. To the best of our knowledge, this is the first time that this transformation is reported. Therefore, in the first place, two reactions using ATRP initiators as model molecules were carried out to show that this strategy can be applied to acrylic and methacrylic compounds without hydrolysis of the ester group. Then, several bromine end-functionalized homopolymers of poly(methyl methacrylates), P(MMA)s, synthesized in a controlled way by ATRP, were modified in two steps to obtain thiol end-functionalized P(MMA)s. Nevertheless, it is well-known that this thiol end group tends to cyclize through "backbiting" to form a thiolactone end group in P(MMA)s.[18] Therefore, and in order to prove the unequivocal existence of thiol end group in the polymers, the second reaction was done in the presence of an alquene-fluorescent molecule synthesized previously and a source of radicals. This *in situ* thiol−ene "click" reaction[14] is almost quantitative and therefore colored, and fluorescent end-functionalized P(MMA)s are going to be obtained. As a result, it is

Received: December 13, 2010
Revised: January 25, 2011
Published: February 14, 2011

Table 1. Experimental Synthetic Conditions and Characterization of P(MMA)s Synthesized by ATRP and Their Corresponding BODIPY End-Modified Polymers

	P(MMA)-Br					P(MMA)-BODIPY
entry	time (min)	convn (%)	$M_{n,theor}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	M_w/M_n	ε (M^{-1} cm^{-1})
1	2	11.6	7 150	7 944	1.19	2560
2	10	35.3	21 375	21 560	1.06	1370
3	15	44.5	26 900	30 224	1.05	900
4	20	52.8	31 880	32 900	1.05	870

possible, on the one hand, to verify the formation of thiol groups in the polymers and quantify them by absorption measurements and, on the other hand, to demonstrate that this methodology can be use together with a thiol−ene "click" reaction to construct a new range of advanced polymers.

EXPERIMENTAL DETAILS

Materials. For the preparation of the polymers: MMA (99%, Fluka) was passed through an alumina column and distilled prior to use to remove the inhibitor. *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was purified by vacuum distillation. Ethyl 2-bromoisobutyrate (EBrIB, 99%, Aldrich), CuBr (99.999%, Aldrich), and the solvents *n*-hexane and chloroform (99.6%, Panreac) were used as received. For the model reactions: EBrIB, methyl 2-bromopropionate (MBrP, 99%, Aldrich), potassium thioacetate (98%, Aldrich), and sodium methoxide (95%, Aldrich) were employed without previous modification. For the synthesis of the BODIPY−alquene compound and the "click" reaction with the thiol end-functionalized polymers pentenoyl chloride (98%, Aldrich), 3-ethyl-2,4-dimethylpyrrole (97%, Aldrich), triethylamine (99%, Fluka), boron trifluoride diethyl etherate (Fluka), and 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%, Across) were employed as received. The BODIPY derivate 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (PM567, laser grade from Exciton, Dayton, OH) used as reference in the measurement of the photophysical properties was also used without previous purification.

Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$ at room temperature. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Mass spectroscopy was made in an Agilent HPLC/MS 1100. UV−vis absorption and fluorescence spectra were recorded on a Perkin-Elmer Lambda-16 and on a Perkin-Elmer LS5OB spectrophotometer, respectively. The fluorescence quantum yield (Φ) was evaluated relative to the PM567 dye in ethanol solution (Φ = 0.86).[43] Molecular weights (M_n) and molecular weight distributions (MWD) were determined by SEC with a GPC Perkin-Elmer (DMF with LiBr (0.1 wt %) as mobile phase at 0.3 mL min^{-1} and 70 °C using P(MMA) standards for the calibration) provide with a Waters 410 differential refractometer detector.

Synthesis of Bromine End-Functionalized P(MMA)s, [P(MMA)-Br]. ATRPs of MMA were carried out in bulk at 100 °C, using EBrIB as initiator, CuBr/PMDETA as catalyst system, and a constant monomer/initiator concentration ratio of 600:1. The polymerization times, shown in Table 1, were established to obtain moderated conversions to ensure a high bromine end-functionalization degree in the chains. A typical polymerization procedure was as follows: Amine ligand (PMDETA, 80 mg, 5 × 10^{-4} mol) and degassed monomer (10 g, 0.1 mol) were added to dry Pyrex tube ampules with CuBr (72 mg, 5 × 10^{-4} mol). Next, the polymerization mixtures were carefully degassed by bubbling dry argon for 20 min, and then the initiator (32.5 mg, 1.67 × 10^{-4} mol) was introduced into the sealed ampules using degassed syringes to start the polymerization. The ampules were immediately placed in a thermostatic oil bath at 100 °C. When the desired time was up, the reaction mixture was quenched with chloroform. Then, the solution was passed through a neutral alumina column to remove the catalyst. The solution was concentrated by rotary evaporation, and the polymer precipitated by pouring the solution into a large excess of *n*-hexane (600 mL). The precipitated products were filtered and dried until an invariable weight was reached. Total monomer conversions were measured gravimetrically. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.69−1.30 (3H, CH_3) 1.68−2.18 (2H, CH_2), 3.46−3.88 (3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 16.34−17.47 and 18.84−19.57 (CH_3), 44.51−45.72 (*C*), 51.93−52.58 (OCH_3), 52.74−55.17 (CH_2), 178.80−177.14 (COO). IR: ν (cm^{-1}) 3000, 2963, 1740, 1490, 1455, 1445, 1390, 1280, 1245, 1195, 1155, 1060, 990, 845, 755.

Synthesis of Thio-Ester End-Functionalized P(MMA)s, [P(MMA)-SCOCH$_3$]. The bromine end-functionalized P(MMA)s (1 g) and potassium thioacetate (3 equiv) were stirred in acetone (25 mL) and refluxed for 4 h. Then, the acetone was removed, and the crude was redissolved in dichloromethane, washed with water, and dried with sodium sulfate. The resulting thio-ester end-functionalized P(MMA)s were obtained as a pale-yellow solids. Yield: 99%.

Synthesis of BODIPY End-Functionalized via Thiol End-Functionalized P(MMA)s, [P(MMA)-BODIPY]. The former thio-ester end-functionalized P(MMA)s (1 g), sodium methoxide (3 equiv), 2,2′-azobis(2-methylpropionitrile (AIBN) (10 equiv), and alquene-BODIPY (**5**) (1.1 equiv) were stirred in anhydrous dichloromethane (25 mL) and refluxed overnight. The crude of reaction was precipitate into cold *n*-hexane (250 mL), and the solid was filtered and washed with *n*-hexane. The resulting BODIPY end-functionalized P(MMA) was obtained with high yields as pink solids.

Synthesis of 2-Acetylsulfanyl-2-methylpropionic Acid Ethyl Ester (1). EBrIB (0.43 g, 2.2 mmol) and potassium thioacetate (0.276 mg, 2.4 mmol) were stirred in 25 mL of acetone for 2 h at reflux. The work-up of the reaction involved removing the acetone on a rotary evaporator, redissolving the orange solid in dichloromethane, washing with water several times, and drying over sodium sulfate. The resulting thioacetate was obtained as a yellow liquid. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.18 (q, J = 7.1 Hz, 2H, CH_2CH$_3$), 2.26 (s, 3H, CH_3CO), 1.57 (s, 6H, (CH_3)$_2$C), 1.25 (t, J = 7.1 Hz, 3H, CH_3CH$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 194.94 (COS), 173.66 (COO), 61.66 (CH_2O), 51.32 (*C*(CH$_3$)$_2$), 30.12 (CH_3CO), 25.84 (CH$_3$)$_2$),14.01 (CH_3CH$_2$). MS (EI): m/z (%): 190 (5), 148 (26), 87 (18), 75 (44), 59 (48), 43 (100), 31 (51). IR: ν (cm^{-1}) 3000, 2950, 2885, 1743 (COO), 1700 (COS), 1475, 1370, 1265, 1165, 1130, 1030, 960 (CS), 640 (CSC).

Synthesis of 2-Mercapto-2-methylpropionic Acid Ethyl Ester (2). The former thioacetate (200 mg, 1.05 mmol) and sodium methoxide (62.5 mg, 1.15 mmol) were stirred in 25 mL of methanol for 4 h at room temperature. When the reaction is completed the solvent was removed, and the residual was dissolved in dichloromethane, washed with water three times, and dried over sodium sulfate. The resulting liquid, 150 mg (99%), was a mixture (1:1) of thiol and disulfide. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.17 (q, J = 7.3 Hz, 2H, CH_2CH$_3$ disulfide), 4.15 (q, J = 7.3 Hz, 2H, CH$_2$CH$_3$ thiol), 1.58 (s, 6H, CH_3C disulfide), 1.45 (s, 6H, CH_3C thiol), 1.28 (t, J = 7.3 Hz, 3H,

CH_3CH_2 disulfide) 1.26 (t, J = 7.3 Hz, 3H, CH_3CH_2 thiol). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 174.02 (COO disulfide), 172.61 (COO, thiol), 60.46 (CH_2O), 52.39 (C sulfide), 43.85 (C, thiol), 29.92 ($(CH_3)_2C$, sulfide), 24.51 ($(CH_3)_2C$, thiol), 13.06 (CH_3CH_2). MS (ES) m/z: 147 ($M_{thiol}^+ - 1$); 317 ($M_{disulfide}^+ + Na$). IR: ν (cm^{-1}) 2985, 2945, 2885, 2580 (SH), 2265, 1740 (COO), 1470, 1390, 1265, 1030.

Synthesis of 2-Acetylsulfanylpropionic Acid Methyl Ester (3). Procedure described for synthesis of **1**. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.22 (q, J = 7.3 Hz, 1H, $CHCH_3$), 3.71 (s, 3H, CH_3O), 2.33 (s, 3H, CH_3CO), 1.48 (d, J = 7.3 Hz, 3H, CH_3CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 194.19 (CH_3COS), 172.85 ($COOCH_3$), 53.11 (CH_3O), 41.12 (CH), 30.55 (CH_3COS), 18.06 (CH_3CH). MS (EI) m/z (%): 162 [nominal mass, M^+] (7), 149 (2), 120 (24), 88 (8), 59 (22), 43 (100). IR: ν (cm^{-1}) 2990, 2945, 2865, 1750 (COO), 1710 (COS), 1470, 1385, 1265, 1170, 1130, 1020, 960 (CS), 630 (CSC).

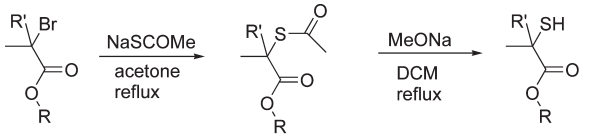
Synthesis of 2-Mercaptopropionic Acid Methyl Ester (4). The hydrolysis of **3** was made using the procedure for compound **2** and with a similar yield. In this case, a mixture (2:1) of thiol and disulfide was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.69 (s, 3H, CH_3O), 3.56 (q, J = 7.1 Hz, 1H, CH thiol), 3.55 (q, J = 7.1 Hz, 1H, CH disulfide), 1.43 (d, J = 7.1 Hz, 3H, CH_3−CH, disulfide), 1.41 (d, J = 7.1 Hz, 3H, CH_3−CH, thiol). MS (ES) m/z: 119 ($M_{thiol}^+ - 1$); 179 ($M_{thiol}^+ + CH_3COO^-$); 261 ($M_{disulfide}^+ + Na$). IR: ν (cm^{-1}) 2970, 2945, 2870, 1745 (COO), 1465, 1380, 1265, 1230, 1130.

Synthesis of 4-(2′,6′-Diethyl-1′,3′,5′,7′-tetramethyl-4′,4′-difluoro-4′-bora-3′*a*,4′*a*-diaza-*s*-indacen-8′-yl)but-1-ene (5). A mixture of 3-ethyl-2,4-dimethylpyrrole (1.0 mL, 8.1 mmol) and pentenoyl chloride (0.45 mL, 4.05 mmol) in 1,2-dichloroethane (50 mL) was refluxed under argon for 30 min. Triethylamine (2 mL, 15.4 mmol) was then added at room temperature, and the mixture stirred for 30 min. Then, boron trifluoride diethyl etherate (2 mL, 16 mmol) was added, and it was refluxed for 2 h. The subsequent work-up yielded a red residue that was purified by flash column chromatography (silica gel, *n*-hexanedichloromethane 9:1 as eluent). Red crystals were obtained. Yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.04−5.84 (m, 1H, CH=CH_2), 5.15 (dd, J = 24.7, 1.5 Hz, 1H, CH_2=CH), 5.11 (dd, J = 17.9, 1.5 Hz, 1H, CH_2=CH), 3.16−3.05 (m, 2H, CH_2−Ar), 2.50 (s, 6H, CH_3−$Ar_{3,5}$), 2.35−2.45 (m, 6H, CH_2CH_3 and CH_2−CH), 2.33 (s, 6H, CH_3−$Ar_{1,7}$), 1.04 (t, J = 7.6 Hz, 6H, CH_3CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.25 (C3/C5), 143.67 (C7a/C8a), 136.64 (CH_2=), 135.66 (C1/C7), 132.64 (C2/C6), 130.84 (C8), 115.44 (CH=), 35.22 (CH_2CH), 27.13 (CH_2CH_2), 17.15 (CH_2CH_3), 14.79 (CH_3−Ar), 13.28 (CH_3−Ar), 12.38 (CH_3CH_2). MS (EI): m/z (%): 358 [nominal mass, M^+] (100), 343 (60), 329 (14), 317 (82), 302 (39), 287 (48). IR: ν (cm^{-1}) 3010, 1550, 1480, 1190, 980. UV/vis ($CHCl_3$) $\lambda_{max}(\varepsilon)$ 525 nm (59 000 M^{-1} cm^{-1}).

RESULTS AND DISCUSSION

Several bromide end-functionalized P(MMA) were synthesized in a controlled way by ATRP employing similar experimental conditions as those used previously by our research group.[44] Thus, the polymerizations were carried out in bulk at 100 °C using EBrIB as initiator and CuBr/PMDETA as catalyst system. The polymerization times, shown in Table 1, were established to obtain moderated conversions to ensure the high bromine end-functionalization of the chains. As expected, the number-average MWs obtained by SEC ($M_{n,SEC}$) were very close to those calculated theoretically from the conversion ($M_{n,theo}$). Moreover, the polydispersity indeces (M_w/M_n) were low (∼1.05−1.19), which indicates that the obtained polymers possessed well-defined structures. From the ^{1}H NMR and IR analyses, it was possible to verify the macromolecular structure of

Scheme 1. Model Reactions for the Transformation of Bromine Groups into Thiol Groups



EBrIB R' = Me; R = Et
MBrP R' = H; R = Me

1 R' = Me; R = Et
3 R' = H; R = Me

2 R' = Me; R = Et
4 R' = H; R = Me

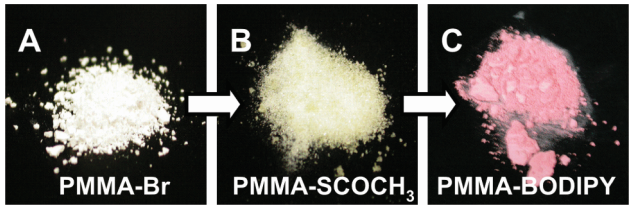


Figure 1. Pictures of sample **1** before and after end-modifications.

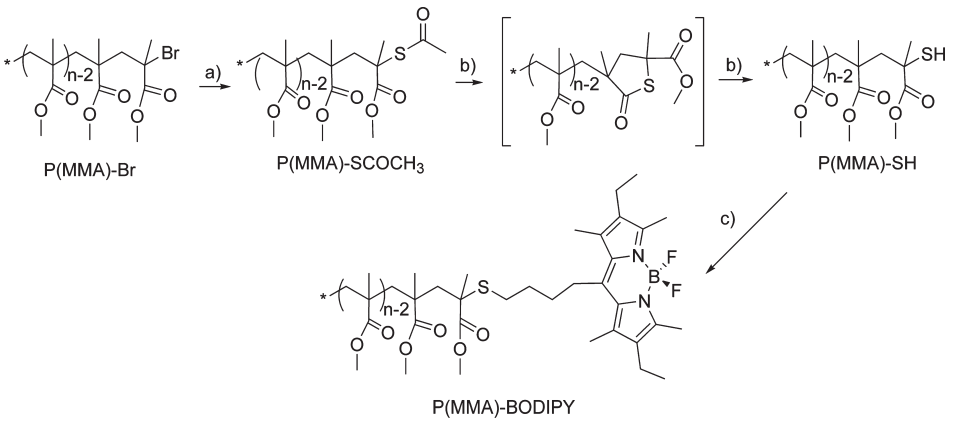
the polymers, but it was difficult to quantify with precision the chain end-functionality. This fact is due to the overlapping of the signals corresponding to the protons of both the initiator fragment and the ultimate monomeric unit in the MW range of the obtained polymers. However, the adequate functionality of these bromine-terminated polymers has been well confirmed in the literature through different analysis techniques and/or by chain extension reactions.[44,45]

A well-known method to convert an alkyl halide into a thiol involves the reaction of a halide with postassium thioacetate to give the corresponding thioester. Subsequent hydrolysis of this compound establishes the formation of the corresponding thiol.[46] Before trying this methodology in the synthesized P(MMA)-Br polymers, two model reactions with analogues molecular compounds (Scheme 1) were investigated in order to corroborate this synthetic strategy. Thus, the ATRP initiators EBrIB and MBrP were chosen as model molecules to show that, on the one hand, the methodology can be employed for methacrylic or acrylic polymers and, on the other hand, the hydrolysis does not affect the ethoxy or methoxy groups of these compounds, respectively. In both cases, the reactions yields were nearly quantitative and the desired molecules were easily obtained, as it is observed from their respective yields and characterizations included in the Experimental Details section. Therefore, it was proved that this synthetic strategy is available.

The successfully reactions used in the molecular models were applied to the bromide end-functionalized P(MMA)s. The formation of the thioester end functional group was easily carried out. Initially, the bromine end-functionalized P(MMA)s were converted into thio-ester end-functionalized P(MMA)s employing practically the same experimental conditions than in the model reactions. However, more drastic conditions were used to ensure complete transformation. Thus, the polymer/potassium thioacetate ratio was 1:3, and the reaction solution was at reflux for 4 h. Although the SEC determinations did not show evidence of changes in the molecular weigh of the samples, the modification could be observed by ^{1}H and ^{13}C NMR (overall in the sample with lower M_w) with the appearance of new weak signals at 2.01 ppm in ^{1}H NMR and 31.32 and 206.90 ppm in ^{13}C NMR corresponding to the $SCOCH_3$ group. In addition, in the IR

dx.doi.org/10.1021/ma102829s |*Macromolecules* 2011, 44, 1335–1339

Scheme 2. Synthetic Route for the Formation of BODIPY End-Functionalized P(MMA)s: (a) Thio-Ester End-Functionalization, (b) Hydrolysis and Thiol End-Functionalization (in Parentheses Possible "Backbiting" Side Reaction), and (c) Thiol−Ene "Click" Reaction and BODIPY End-Functionalization



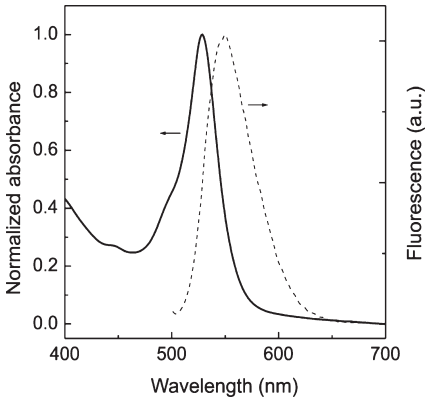


Figure 2. UV−vis normalized absorption (solid lines) and fluorescence (dashed lines) spectra of sample **1** in chloroform at room temperature.

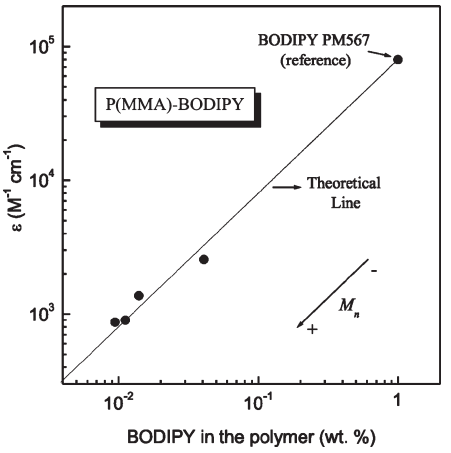


Figure 3. Absorption extinction coefficient versus percentage in weight of BODIPY moieties in the P(MMA).

analysis, an increment of the width of the band of the C═O stretching occurred. Last, the change of color of the samples, which become yellow-pale as is shown in Figure 1b, is other proof that corroborates the modification.

It is well-known that thiol-polymers are susceptible to further oxidation to disulfide, leading to bimodal polymer populations composed of thiol and disulfide functional polymers.[29] Moreover, Xu et al.[18] reported that the thiol end group generated during the aminolysis of P(MMA) synthesized by RAFT tends to cyclize thought "backbiting" to form a thiolactone end group. Although our hydrolysis method should be able of hydrolyze this thiolactone, the second reaction of the proposed synthetic methodology was made in the presence of an alquene−BODIPY molecule (**5**), previously synthesized, and AIBN as radical initiator (see Scheme 2). This *in situ* formation of the thiol end-functionalized polymers in the present of thiol-reactive compounds was done to lead simultaneous protection/functionalization of the created thiols. The thiol−ene reaction[14] is almost quantitative, and therefore, dye end-functionalized P(MMA)s were obtained as orange-pink powder (Figure 1c). As a result, it was possible to verify the formation of thiol groups in the polymers through their reactivity. As an example, Figure 2 shows the absorption and emission spectra of a chloroform solution of sample 1. Samples present a maximum of absorption at around 528 nm and a maximum of emission at 549 nm (excited at 490 nm), which are the typical values for BODIPY-based dyes.[43]

The introduction of a fluorescence dye let us to quantify the number of these groups by absorption measurements using as a reference the absorption extinction coefficient (ε) of the commercial BODIPY dye PM567 in the same solvent (ε = 80 000 M^{-1} cm^{-1}). Logically, the intensity of emission (and absorption) depends on the number of BODIPY dyes (see Table 1) and, therefore, on the molecular weight. Thus, the shorter the macromolecular chain is, the higher the number of BODIPY tethered molecules per gram and the higher absorption value, as is shown in Figure 3. From this figure, it is observed that the experimental results fit quite well with the theoretical line calculated from the BODIPY dye used as reference. Therefore, and taking into account the molecular weights, it was possible to estimate that the degree of BODIPY end-functionalization, and subsequently, the degree of the thiol end-functionalization in the precursor is nearly quantitative for all polymers under study.

■ CONCLUSIONS

In this work, it has been demonstrated that the bromine end-functional group of (meth)acrylic polymers synthesized by

ATRP can be easily transformed into thiol groups in only two steps. The methodology was applied for well-defined P(MMA)s of different molecular weight and synthesized by ATRP. The correct thiol end-functionalization of the polymers was corroborated by a thiol−ene "click" reaction, introducing a fluorescent moiety that allows us to quantify the thiol functionalization. Moreover, two model reactions were employed in order to show that this methodology can be also applied to other methacrylic and acrylic polymers.

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ACKNOWLEDGMENT

Authors thank the financial support of the Consejo Superior de Investigaciones Científicas (CSIC) and Ministerio de Ciencia e Innovación (MICINN) through the Project CTQ2008-03229. R.P. thanks MICINN for a Juan de la Cierva contract and M.L. thanks CSIC for a JAE-Doc contract. Moreover, authors are very grateful to Dr. A. Muñoz-Bonilla for her assistance in the SEC measurements.

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