

**SYNTHESIS AND CHARACTERIZATION OF DIBLOCK COPOLYMERS  
CONTAINING MONOTHIO-ORTHOESTER FUNCTIONS USING RAFT  
POLYMERIZATION**

S. Hadjout, R. Haraoubia and Z. Benabdelghani\*

Laboratory of Macromolecular and Thio-macromolecular Chemistry, Faculty of  
Chemistry, University of Sciences and Technology, P.O.Box 32, El Alia, Algiers 16111,  
Algeria. (USTHB)

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**ABSTRACT**

The acyclic and cyclic monothio-orthoester monomers were synthesized by modification of aromatic monomers containing dithioester function in the side chain. Reversible addition-fragmentation chain transfer (RAFT) polymerization was employed for the preparation of polymers containing a dithioester end as macro-chain transfer agents (macro-CTA) using 4-benzyl methylthiobenzoate (BMDTB) as chain transfer agent (CTA) and 2,2-azobisisobutyronitrile (AIBN) as initiator. A series of diblock copolymers were prepared by RAFT copolymerization of MVDTB, MMMS and MVPOCO, using the different macro-chain transfer agents (macro-CTA) and AIBN as initiator. All polymerizations were carried out at 60 °C for 24 or 30 hours in dry THF. Homopolymers and diblock copolymers are characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, SEC, DSC and TGA.

**Keywords:** Dithioesters, monothio-orthoesters, RAFT polymerization.

Author Correspondence, e-mail: [author@mail.com](mailto:author@mail.com)

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**1. INTRODUCTION**

Over the last two decades, the living radical polymerization has been the subject of much academic and industrial research [1]. Compared to the classic radical process, these methods



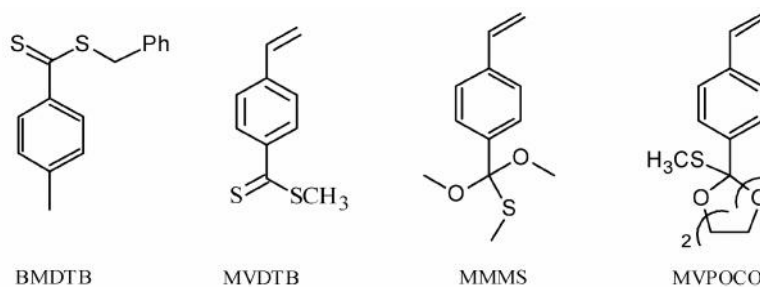
allowed the synthesis of homopolymers and copolymers with predictable molecular weight and low polydispersity of the molecular weight distribution ( $M_w / M_n < 1.5$ ). Recently, the living radical polymerization techniques have received greatest attention such as: nitroxide-mediated polymerization (NMP) [2] atom-transfer radical polymerization (ATRP) [3] and as special case “macromolecular design via the interchange of xanthates” (MADIX) [4]. Thus, the NMP and ATRP free-radical polymerization techniques have certain disadvantages; in particular, they are applicable at a limited range of monomers and required expensive reagents, which there are difficult to remove. Besides, the use of these methods in the synthesis of block copolymers, stars and other structures of complex architecture is limited. The recent controlled radical polymerization process “reversible addition-fragmentation chain transfer” polymerization (RAFT) has been discovered by Rizzardo et al [5]. The process of chain transfer RAFT has received much attention and becomes one of the most versatile methods to prepare block copolymers using a variety of functionalized monomers at a large range of temperatures and solvents [6,7]. Generally, it offers homopolymers and block copolymers with predetermined molecular weight and a very narrow polydispersity (usually very close to unity 1.2). These polymerizations can be carried out in bulk, solution, emulsion, mini-emulsion and dispersion, using standard reaction conditions to give blocks, diblock, triblock, and star polymers, as well as complex architectures [8, 9].

It is well known that the dithioesters are widely used in RAFT technique due to their large chain transfer constant compared to trithiocarbonates. Many studies have shown that the effectiveness of CTA agent whose radical  $R=CH_2Ph$  and  $Z=Ph$  is appropriate for the polymerization of styrene [6, 10-14]. Radical polymerization by addition-fragmentation chain transfer of 2VPy and 4VPy is made by a transfer agent where  $R=(CH_3)_2Ph$  and  $Z=Ph$  [15]. It has been shown that the chain-transfer coefficients decrease in the series as follows: dithibenzoates > trithiocarbonates > dithioalkanoates > dithiocarbonates > dithiocarbamates.

On the other hand, the synthesis of dithiocarboxylic esters has been the subject of intense research owing to the interest provided to their structures and their large wide range of industrial applications. Moreover, the dithioesters and dithioesters containing vinyl group

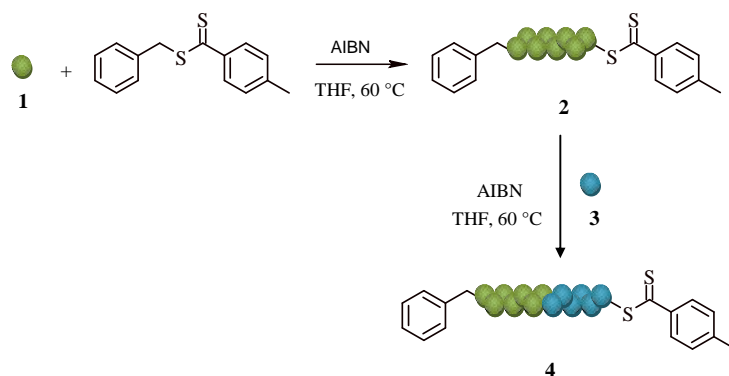
have been prepared in high yield using the Grignard reagent and copper (I) bromide [16-18]. It is important to note that only few examples of acyclic monothio-orthoesters have been described in the literature [19, 20]. Previously, we have treated the dithioesters with an excess of sodium alkyl oxides and alkylated by addition of an alkyl halide in THF at room temperature [21]. The formation of new polymers and copolymers containing the functional groups in the side chain opens new ways of several chemical reactions (grafting, reticulation...etc). Their chemical modifications allow us to obtain new polymers having a large scale of chemical and physical properties [22].

In this contribution, we will describe, firstly, the synthesis of a new chain transfer agent such as the benzyl-4-methyldithiobenzoate (BMDTB), the monomer, methyl-4-vinyldithiobenzoate (MVDTB) and modification of MVDTB in acyclic monothio-orthoesters (MMMS) and cyclic monothio-orthoesters (MVPOCO) (see Figure 1).



**Fig.1.** Chemical structures of the main reagents used for the synthesis of homopolymers and diblock copolymers: BMDTB (Benzyl 4-methyldithiobenzoate), MVDTB (methyl-4-vinyldithiobenzoate), MMMS (Acyclic monothio-orthoester) and MVPOCO (cyclic monothio-orthoester)

Our second aim in this work is to prepare the homopolymers and the diblock copolymers by the RAFT method using the synthesized monomers such as styrene standard (S), 2-vinylpyridine (2VP), and 4-vinylpyridine (4VP) (see Figure 2). The synthesized polymers are listed in Table 1.



**Fig.2.** Synthetic route of RAFT polymerization

**Table 1.** Identification of polymers and block copolymers synthesized by RAFT polymerization

1	2	3	4
MVDTB	PMVDTB	-	-
MMMS	PMMMS	-	-
MVPOCO	PMVPOCO	-	-
S	PS	MVDTB	PS-PMVDTB
2VP	P2VP	MVDTB	P2VP-PMVDTB
4VP	P4VP	MVDTB	P4VP-PMVDTB
S	PS	MMMS	PS-MMMS
2VP	P2VP	MMMS	P2VP-MMMS
S	PS	MVPOCO	PS-MVPOCO
2VP	P2VP	MVPOCO	P2VP-PMVPOCO
4VP	P4VP	MVPOCO	P4VP-PMVPOCO

## 2. EXPERIMENTAL

### 2.1. Reagents and solvents

4-bromostyrene (Acros, 96%), styrene (Acros, 99%), 2-vinylpyridine (Aldrich, 99%), and 4-vinylpyridine (Acros, 95%) were distilled twice under reduced pressure and stored at temperature lower than 0°C. 2,2'-Azobis(isobutyronitrile) (AIBN) (Aldrich, 97%) was recrystallized from methanol. 4-bromotoluene (Acros, 99%), benzyl bromide (Acros, 98%),

methyl iodide (Acros, 99%) and carbon disulfide (Acros, 99.9), methanol (Acros, 99.9%), diethylene glycol (Acros, 99%) were used as received. Sodium hydride (Acros, 60% in oil) was washed by pentane. THF (Fluka, 99%) was distilled from a complex Na benzophenone.

## 2.2. Instrumentation

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, measurements were carried out on a Fourier Bruker AC 250 MHz spectrometer using  $\text{CDCl}_3$  as solvent and TMS as reference. UV-visible spectra of a new RAFT agent and the dithioesters monomers were recorded on a Beckman DU-7 spectrophotometer using  $\text{CH}_2\text{Cl}_2$  as solvent. Fourier transform spectroscopy (FTIR) was performed on a Perkin Elmer ATR spectrophotometer using thin film for liquids and thin pallet for solids. The number-average molar mass ( $M_n$ ), the weight-average molar mass ( $M_w$ ), and the polydispersity index ( $M_w/M_n$ ) were determined by the size exclusion chromatography (SEC) using THF or DMF as eluent. The SEC system is an apparatus equipped with a Viscotek VE 5200 automatic and was calibrated using a PS standard or PMMA standard. Differential scanning calorimetric (DSC) measurements were performed using Perkin-Elmer DSC 7. All Tg measurements were carried out at a heating rate of 10 °C/min under nitrogen flow in the temperature range 0-200 °C. The Tg value was taken as the mid point of the transition of the second scan. Thermo gravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 instrument under a nitrogen atmosphere. The temperature was elevated from 100 °C to 600 °C a rate of 20°C/min under nitrogen.

## 2.3. Synthesis of aromatic dithioesters

Aromatic dithioesters BMDTB and MVDTB were prepared by combine the procedures as mentioned in references [14-16].

An ice-bath Grignard solution was prepared under nitrogen atmosphere from magnesium (1.15 equiv) and aromatic halides (1 equiv) in dry THF. The mixture was vigorously stirred for 4 h at 0 °C. A small amount of CuBr (5 mol %) is added to the solution at (-50 °C) and subsequently, a solution of carbon disulphide (1.1 equiv) in dry THF was added drop wise at -50 °C. After stirring the reaction mixture for 30 mn at -50°C, a solution (1.1 equiv) of alkyle halide in 30 ml of dry THF is added and the solution was stirred a period of 30 min reaction at 0 °C. The mixture was concentrated and the product is isolated by washing with the mixture

of HCl at 10 % / pentane. The organic phases were dried on MgSO<sub>4</sub> and concentrated under vacuum. The red compound was purified by chromatography on silica gel column using the cyclohexane as eluent.

### 2.3.1. Benzyl 4-methyldithiobenzoate (BMDTB)

The RAFT agent was obtained by reaction of 4-bromotoluene (30 m.mol), Mg (34.5 m.mol), CuBr (1.5 m.mol), CS<sub>2</sub> (33 m.mol), and benzyl bromide (39 m.mol) for 5 h. The product consists of red crystals. Yield: 60 %, mp: 53 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 2.30 (s, 3H, CH<sub>3</sub>Ph), 4.52 (s, 2H, SCH<sub>2</sub>), 7.25 and 7.87 (2d, 4H, A<sub>2</sub>B<sub>2</sub>, J= 8.31 Hz), 7.35-7.70 (m, 5H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 227.1 (C=S), 42.1 (SCH<sub>2</sub>), 21.5 (CH<sub>3</sub>Ph), FT-IR (film) (cm<sup>-1</sup>): 1596 (C=C, Ar), 1245 (C=S).

### 2.3.2. Methyl 4-vinyldithiobenzoate (MVDTB)

MVDTB was obtained by reaction of 4-bromostyrene at (54.6 m.mol), magnesium (62.8 m.mol), copper bromide (2.73 m.mol), carbon disulphide (60.1 m.mol), and methyl iodide (71.0 m.mol) for 5h. The product consists of red crystals. Yield: 78 %, mp: 34 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 2.7 (s, 3H, SCH<sub>3</sub>), 5.3 (d, 1H, J<sub>AX</sub>=10.6, =CH<sub>2</sub>), 5.79 (d, 1H, J<sub>BX</sub> = 17.3, =CH<sub>2</sub>), 6.66 (d, 1H, J<sub>AB</sub> = 6.7, CH=) 7.33 and 7.94 (2d, 4H, A<sub>2</sub>B<sub>2</sub>, J= 8.47 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 20.5 (SCH<sub>3</sub>). 116.3 and 135.9 (CH=CH<sub>2</sub>), 228.1 (C=S). FT-IR (film) (cm<sup>-1</sup>): 1598 (C=C, Ar), 1625 (C=C, vinyl), 1238 (C=S).

## 2.4. Synthesis of aromatic acyclic and cyclic monothio-orthoesters

The sodium hydride at (60 % wt, 3.0 equiv) was placed in a three-necked flask of 250 ml, a solution of alcohol (3.0 equiv) or diethylene glycol (1.2 equiv) in dry THF at 0°C. The mixture was vigorously stirred under nitrogen atmosphere for 2 h at 0°C. A solution of dithioester monomer (1 equiv) in dry THF was added drop wise on the mixture réaction at 0 °C. After 4 h of stirring, a solution of methyl iodide (3.2 equiv) in dry THF was added. The mixture was stirred (18 h) at room temperature and the solvent removed. A light yellow product was obtained after filtration and evaporation of solvent under vacuum. The monomers were purified by flash chromatography on silica gel with cyclohexane or a mixture of cyclohexane / ethyl acetate as eluent.

### 2.4.1. 4-[1,1-dimethoxy-1-methylthiomethyl] styrene (MMMS)

MMMS was obtained by reaction of sodium hydride at 60 % (15.5 m.mol), methanol (0.65 g, 15.5 m.mol), methyl 4- vinyl dithiobenzoate (5.15 m.mol) and methyl iodide (16.5 m.mol). The monomer was purified by flash chromatography on silica gel with cyclohexane as eluent. The product obtained is a yellow crystal at cold temperature. Yield: 82 %  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) (ppm): 1.60 (s, 3H,  $\text{SCH}_3$ ), 3.20 (s, 6H,  $\text{OCH}_3$ ), 5.20 (d, 1H,  $\text{CH}_2=\text{CH}$ ),  $J = 10.8$  Hz), 5.7 (d, 1H,  $\text{CH}_2=\text{CH}$ ,  $J = 17.6$  Hz), 6.7 (m, 1H,  $\text{CH}_2=\text{CH}$ ,  $J = 6.8$  Hz), 7.33 and 7.48 (2d, 4H,  $\text{A}_2\text{B}_2$ ,  $J_{\text{AB}} = 8.41$  Hz).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) (ppm): 12.3 ( $\text{SCH}_3$ ), 50.2 ( $\text{OCH}_3$ ), 112.7 (C quart), 114.4 ( $=\text{CH}_2$ ), 136.5 ( $\text{CH}=\text{}$ ). FT-IR (film) ( $\text{cm}^{-1}$ ): 1608 (C=C, Ar), 1630 (C=C, vinyl), 1235 (C-O).

#### 2.4.2. 2-(methylthio)-2-(4-vinylphenyl)-1,3,6-trioxacycloctane (MVPOCO)

MVPOCO was synthesized by reaction of sodium hydride at 60 % (15.5 m.mol), diethylene glycol (6.13 m.mol), methyl 4-vinyl dithiobenzoate (5.15 m.mol) and methyl iodide (16.5 m.mol). The product is a yellow viscous liquid. Yield: 51.3 %.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) (ppm): 1.63 (s, 3H,  $\text{SCH}_3$ ), 3.63-3.71 (2m, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 5.20 (d, 1H,  $\text{CH}_2=\text{CH}$ ),  $J = 10.94$  Hz), 5.70 (d, 1H,  $\text{CH}_2=\text{CH}$ ,  $J = 16.96$  Hz), 6.72 (m, 1H,  $\text{CH}_2=\text{CH}$ ,  $J = 6.71$  Hz), 7.31-7.53 (2d, 4H,  $\text{A}_2\text{B}_2$ ,  $J_{\text{AB}} = 8.34$  Hz).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) (ppm): 65.1-72.2 ( $\text{OCH}_2\text{CH}_2\text{O}$ ), 13.0 ( $\text{SCH}_3$ ), 112.7 (C quart), 114.8 ( $=\text{CH}_2$ ), 136.7 ( $\text{CH}=\text{}$ ). FT-IR (film) ( $\text{cm}^{-1}$ ): 1607 (C=C, Ar), 1630 (C=C, vinyl), 1229 (C-O).

### 2.5. Preparation of homopolymers

The RAFT polymerization of different homopolymers is as follows: In round-bottom flask, a freshly distilled monomer (1 equiv) is added with BMDTB as CTA (0.34%-2.4%) and AIBN (0.06%-10%) as initiator in dry THF under nitrogen. The solution was degassed by three freeze-vacuum-thaw cycles and stirred 24 h at 60 °C (see Figure 2, Table 1, 2). The polymerization was stopped by liquid nitrogen and produced polymers were retrieved by precipitation in pentane for PMVDTB, PMMMS and PMVPOCO. Similarly, PS was precipitated in methanol, whereas P2VP and P4VP were retrieved by precipitation in ether. After filtration, all obtained polymers of pink color were left to dry under vacuum at 60 °C overnight.

#### 2.5.1. PMVDTB

$^1\text{H RMN}$  ( $\text{CDCl}_3$ ) (ppm): 2.3 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.75 (s, 3H,  $\text{SCH}_3$ ).  $^{13}\text{C RMN}$  ( $\text{CDCl}_3$ )

(ppm): 20.7 (SCH<sub>3</sub>), 228 (C=S). IR (film) (cm<sup>-1</sup>): 1600 (C=C, Ar), 1235 (C=S).

### 2.5.2. PMMMS

<sup>1</sup>H RMN (CDCl<sub>3</sub>) (ppm): 1.66 (s, 3H, SCH<sub>3</sub>), 2.3 (s, 3H, CH<sub>3</sub>Ph), 3.1 (s, 6H, OCH<sub>3</sub>). <sup>13</sup>C RMN (CDCl<sub>3</sub>) (ppm): 12.2 (SCH<sub>3</sub>), 50.0 (OCH<sub>3</sub>), 112.6 (C<sub>quart</sub>). IR (film) (cm<sup>-1</sup>): 1609 (C=C, Ar), 1237 (C-O).

### 2.5.3. PMVPOCO

<sup>1</sup>H RMN (CDCl<sub>3</sub>) (ppm): 1.65 (s, 3H, SCH<sub>3</sub>), 2.4 (s, 3H, CH<sub>3</sub>Ph), 3.6 and 3.7 (m, 8H, OCH<sub>2</sub>). <sup>13</sup>C RMN (CDCl<sub>3</sub>) (ppm): 12.7 (SCH<sub>3</sub>), 64.7-70.2 (OCH<sub>2</sub>), 112.4 (C<sub>quart</sub>). IR (film) (cm<sup>-1</sup>): 1600 (C=C, Ar), 1235 (C=S).

### 2.5.4. PS

<sup>1</sup>H RMN (CDCl<sub>3</sub>) (ppm): 2.4 (s, 3H, CH<sub>3</sub>Ph), 3.8 (s, 2H, SCH<sub>2</sub>). <sup>13</sup>C RMN (CDCl<sub>3</sub>) (ppm): 21.6 (CH<sub>3</sub>Ph). IR (film) (cm<sup>-1</sup>): 1601 (C=C, Ar).

### 2.5.5. P2VP

<sup>1</sup>H RMN (CDCl<sub>3</sub>) (ppm): 2.38 (s, 3H, CH<sub>3</sub>Ph). <sup>13</sup>C RMN (CDCl<sub>3</sub>) (ppm): 22.0 (CH<sub>3</sub>Ph). IR (film) (cm<sup>-1</sup>): 1642 (C=N), 1589 (C=C, Ar).

### 2.5.6. P4VP

<sup>1</sup>H RMN (CDCl<sub>3</sub>) (ppm): 2.35 (s, 3H, PhCH<sub>3</sub>). <sup>13</sup>C RMN (CDCl<sub>3</sub>) (ppm): 21.8 (CH<sub>3</sub>Ph). IR (film) (cm<sup>-1</sup>): 1663 (C=N), 1596 (C=C, Ar).

## 2.6. Preparation of copolymers by polymerization RAFT

The typical procedure of RAFT copolymerization is described as follows: On the PS, P2VP, and P4VP (1 equiv) containing a dithioester end is considered as macro-CTA, the freshly distilled monomers are added (0.8%-4.6% equiv) using AIBN as initiator (1.7% - 7.9%) in anhydrous THF. The reaction mixture was degassed by freezing in liquid nitrogen and vacuum suction and is then stirred at 60 ° C for 24 hours (see Figure 2, Table 1, 3). The copolymerization was stopped in liquid nitrogen and well defined copolymers: PS-PMVDTB, PS-PMMMS and PS-PMVPOCO, were obtained by precipitation in methanol. Similarly, P2VP-PMVDTB and P2VP-PMMMS were obtained by precipitation in pentane, whereas P4VP-PMVDTB, P2VP-PMVPOCO and P4VP-PMVPOCO were retrieved by precipitation in THF. After precipitation, all polymers were left to dry under vacuum at 60°C.



**2.6.1. PS-PMVDTB**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 2.70 (s, 2H,  $\text{SCH}_3$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 20.7 ( $\text{SCH}_3$ ), 228.2 (C=S). IR (film), ( $\text{cm}^{-1}$ ): 1601 (C=C, Ar), 1238 (C=S).

**2.6.2. P2VP-PMVDTB**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 2.67 (s, 3H,  $\text{SCH}_3$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 20.5 ( $\text{SCH}_3$ ), 227.8 (C=S). IR (film), ( $\text{cm}^{-1}$ ): 1590 (C=C, Ar) 1235 (C=S).

**2.6.3. P4VP-PMVDTB**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 2.72 (s, 3H,  $\text{SCH}_3$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 20.5 ( $\text{SCH}_3$ ), 228.0 (C=S). IR (film), ( $\text{cm}^{-1}$ ): 1597 (C=C, Ar), 1220 (C=S).

**2.6.4. PS-PMMMS**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 2.33 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 3.38 (s, 3H,  $\text{OCH}_3$ ), 3.83 (s, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 12.2 ( $\text{SCH}_3$ ), 51.0 ( $\text{OCH}_3$ ), 112.1 ( $\text{C}_{\text{quart}}$ ). IR (film) ( $\text{cm}^{-1}$ ): 1602 (C=C, Ar), 1240 (C-O).

**2.6.5. P2VP-PMMMS**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 2.24 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 3.2 (s, 3H,  $\text{OCH}_3$ ), 3.8 (s, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 12.2 ( $\text{SCH}_3$ ), 50.0 ( $\text{OCH}_3$ ). IR (film), ( $\text{cm}^{-1}$ ): 1631 (C=N, Py), 1610 (C=C, Ar), 1238 (C-O).

**2.6.6. PS-PMVPOCO**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 3.68-3.78 (2m, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 12.9 ( $\text{SCH}_3$ ), 65.1 and 70.6 ( $\text{OCH}_2$ ), 112.8 ( $\text{C}_{\text{quart}}$ ). IR (film) ( $\text{cm}^{-1}$ ): 1602 (C=C, Ar), 1275 (C-O).

**2.6.7. P2VP-PMVPOCO**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 3.65-3.70 (2m, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 11.6 ( $\text{SCH}_3$ ), 65.7 and 70.7 ( $\text{OCH}_2$ ), 112.6 ( $\text{C}_{\text{quart}}$ ). IR (film), ( $\text{cm}^{-1}$ ): 1635 (C=N, Py), 1229 (C-O).

**2.6.8. P4VP-PMVPOCO**

$^1\text{H}$  RMN ( $\text{CDCl}_3$ ) (ppm): 3.76-3.95 (2m, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ) (ppm): 13.0 ( $\text{SCH}_3$ ), 68.9 and 70.6 ( $\text{OCH}_2$ ), 112.9 ( $\text{C}_{\text{quart}}$ ). IR (film) ( $\text{cm}^{-1}$ ): 1636 (C=N, Py), 1220 (C-O).

### 3. RESULTS AND DISCUSSION

The bloc polymers such as PS, P2VP, P4VP, PMVDTB, PMMMS and PMVPOCO bearing a dithioester functions at the end of the chain, were synthesized by RAFT polymerization at 60 °C using benzyl-4-methyldithiobenzoate (BMDTB), considered as an appropriate CTA for the controlled polymerization. The obtained homopolymers are pink solid confirming the presence of the dithioester end group of CTA (BMDTB).

The homopolymers synthesized in the first step by RAFT, acts as a macro-CTA in the polymerization of the second monomer. On the other hand, the PS, P2VP, P4VP chains were active as RAFT agents to control the synthesis of the diblock copolymers.

**Table 2.** Synthesis of [Macro-CTA]: <sup>d</sup>(PS), <sup>e</sup>(P2VP), <sup>f</sup>(P4VP) as RAFT agent

Homopolymers	[Mono] mol/l	[CTA] <sup>g</sup> mol/l	[AIBN] mol/l	T <sub>g</sub> (°C)
PMVDTB	2.00 <sup>a</sup>	0.022	0.164	105.5
PMMMS	2.00 <sup>b</sup>	0.020	0.200	113.5
PMVPOCO	0.33 <sup>c</sup>	0.008	0.017	84.7
PS	10.0 <sup>d</sup>	0.034	0.006	97.6
P2VP	5.80 <sup>e</sup>	0.029	0.029	146.2
P4VP	4.60 <sup>f</sup>	0.037	0.037	146.5

**Table 3.** Synthesis of diblock copolymers based on PS, P2VP and P4VP by RAFT copolymerization. Monomers: <sup>a</sup>(MVDTB), <sup>b</sup>(MMMS), <sup>c</sup>(MVPOCO)

Diblock copolymers	Macro-CTA] mol/l	[Mono] mol/l	[AIBN] mol/l	C %	T <sub>g</sub> (°C)	
PS-PMVDTB	0.012 <sup>a</sup>	0.26 <sup>d</sup>	0.004	16.0	98	106
P2VP-PMVDTB	0.003 <sup>b</sup>	0.36 <sup>d</sup>	0.018	14.0	146	105
P4VP-PMVDTB	0.007 <sup>c</sup>	0.20 <sup>d</sup>	0.020	10.0	147	106
PS-PMMMS	0.007 <sup>a</sup>	0.16 <sup>e</sup>	0.009	11.5	97	113
P2VP-PMMMS	0.008 <sup>b</sup>	0.18 <sup>e</sup>	0.022	10.2	145	107
PS-PMVPOCO	0.011 <sup>a</sup>	0.41 <sup>f</sup>	0.020	10.6	97	84
P2VP-PMVPOCO	0.004 <sup>b</sup>	0.19 <sup>f</sup>	0.010	18.3	147	85
P4VP-PMVPOCO	0.004 <sup>c</sup>	0.14 <sup>f</sup>	0.007	9.90	145	86

The obtained polymers are characterized using several techniques such as NMR spectroscopy, Fourier Transform-IR, size exclusion chromatography (SEC), differential scanning microscopy (DSC) and thermogravimetric analysis (TGA).

### 3.1. Spectroscopic analysis

#### 3.1.1. RAFT agent and monomers

The chemical structure of BMDTB was confirmed from the proton NMR spectrum where the characteristic peaks at 4.52 ppm and 3.2 ppm are assigned respectively to SCH<sub>2</sub> and CH<sub>3</sub>Ph. A chain transfer agent (CTA) was confirmed from the carbon NMR spectrum when the characteristic peaks at 227.1 nm, 42.1 nm and 21.5 ppm may be assigned to C=S, SCH<sub>2</sub> and CH<sub>3</sub>Ph, respectively.

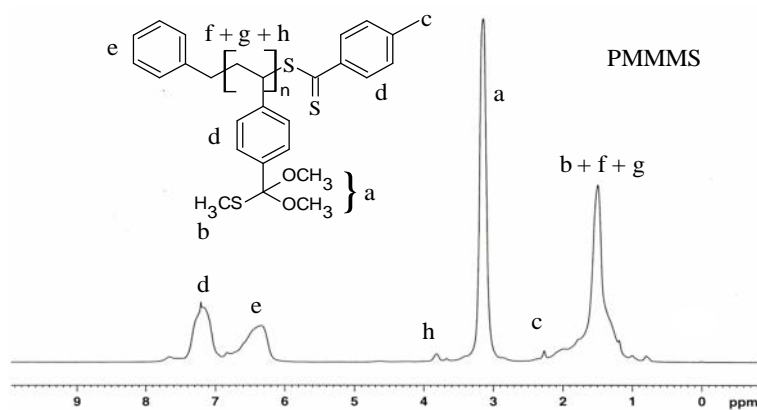
<sup>1</sup>H NMR and <sup>13</sup>C NMR did not reveal of extra peaks, which indicate the presence of impurities that could be accurately quantified. The weak absorption band in the visible range ( $\lambda_{\max} \equiv 470$  nm in CDCl<sub>3</sub>) is due to the n  $\rightarrow$   $\pi^*$  transition of the C=S. The spectroscopic analysis <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, UV-Visible, elemental analysis and spectrometric weight of different monomers confirmed the synthesis of monomers, MVDTB, MMMS and MVPOCO.

### 3.1.2. Homopolymers and diblock copolymers

As can be seen in Figure 3, the  $^1\text{H}$ NMR spectra reveals the presence of several peaks localized, respectively, at 3.1 ppm which can be attributed to methoxy groups of homopolymer PMMMS. While, the peak localized around 1.66 ppm may be assigned to methylthio ( $\text{SCH}_3$ ) groups. The peak observed at 2.3 ppm in block polymer PMMMS is assigned to  $\text{CH}_3\text{Ph}$  of RAFT agent. The polymerization was confirmed by the absence of peak in the chemical shift between 5.2 and 6.7 ppm, regularly attributed of protons of the monomer.

In addition, the signals at 12.1 ppm observed at  $^{13}\text{C}$  spectrum reveal the presence of carbons ( $\text{SCH}_3$ ). While, the peaks localized at 50.0 ppm indicate the presence of carbons  $\text{OCH}_3$  which ascribed, respectively, to PMMMS.

The polymerization of MMMS was confirmed by the absence of peak in the chemical shift at 114.4 and 136.5 ppm, typically assigned for carbons of the unsaturated bond of monomer. The FT-IR spectrum of PMMMS shows the characteristic vibration band of aromatic ( $\text{C}=\text{C}$ ) at  $1609\text{ cm}^{-1}$  and vibration band of  $\text{C}-\text{O}$  at  $1237\text{ cm}^{-1}$  [20-21]. The absence of characteristic vibration band at  $1630\text{ cm}^{-1}$  of the vinyl group ( $\text{CH}=\text{CH}_2$ ) reveals the polymerization of MMMS. Consequently, we can state that these results indicate that the moiety of the RAFT agent was attached to the end of PMMMS.

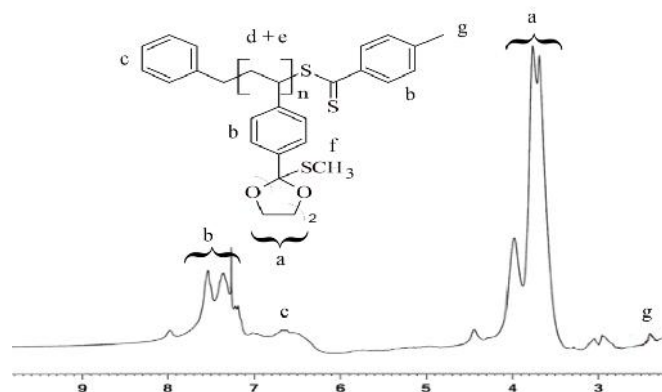


**Fig.3.**  $^1\text{H}$  NMR spectra of PMMMS polymer recorded in  $\text{CDCl}_3$ . The letters indicate the attributed protons

The polymerization of MMMS was confirmed by the absence of peak in the chemical shift at

114.4 and 136.5 ppm, typically assigned for carbons of the unsaturated bond of monomer. The FT-IR spectrum of PMMMS shows the characteristic vibration band of aromatic (C=C) at  $1609\text{ cm}^{-1}$  and vibration band of C-O at  $1237\text{ cm}^{-1}$  [20-21]. The absence of characteristic vibration band at  $1630\text{ cm}^{-1}$  of the vinyl group (CH=CH<sub>2</sub>) reveals the polymerization of MMMS. Consequently, we can state that these results indicate that the moiety of the RAFT agent was attached to the end of PMMMS.

In the NMR spectrum of protons, the peaks at 3.7 ppm were attributed to protons (a) (OCH<sub>2</sub>CH<sub>2</sub>O), of homopolymer PMVPOCO. The peak localized at 1.63 ppm is assigned to the protons (f) of the group (SCH<sub>3</sub>). For the PMVPOCO obtained from the polymerization mediated by BMDTB, the signal at 2.4 ppm in Figure 4 was attributed to the protons (g) of group (CH<sub>3</sub>Ph) of RAFT agent. Such polymerization was confirmed by the absence of peak in the chemical shift range between 5.2 and 6.7 ppm, commonly assigned to proton of the unsaturated bond of the monomer.

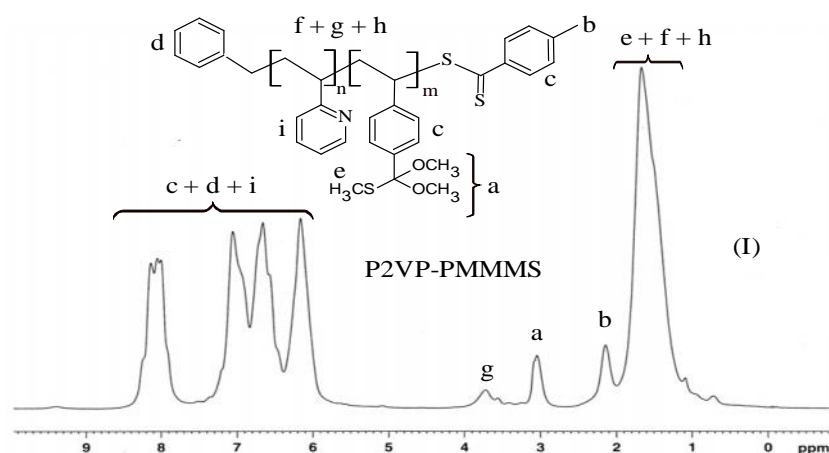


**Fig.4.** <sup>1</sup>H NMR spectra of PMVPOCO polymer recorded in CDCl<sub>3</sub>. The letters indicate the attributed protons

These results indicated that the moiety of the RAFT agent was attached to the end of PMVPOCO. In the carbon RNM spectrum, the signal at 12.7 ppm reveal the presence of carbons (SCH<sub>3</sub>) while the signals at 65-70 ppm reveal the presence of carbons (OCH<sub>2</sub>CH<sub>2</sub>O) which appertained for PMVPOCO. Thus, the polymerization of MVPOCO was confirmed by the absence of peak in the chemical shift at 114.8 and 136.7 ppm, typically corresponding to carbons of the unsaturated bound of monomer. The FT-IR spectrum of PMVPOCO show characteristic vibration band for aromatic (C=C) at  $1605\text{ cm}^{-1}$  and characteristic vibration

band of (C-O) at  $1230\text{ cm}^{-1}$ . The absence of band at  $1630\text{ cm}^{-1}$  attributed to vinyl ( $\text{CH}=\text{CH}_2$ ) group is indicative of the polymerization of MVPOCO.

As can be seen in Figure 5, the presence of three peaks at 6.3-8.2 ppm from protons of P2VP and one peak at 3.2 ppm confirmed the RAFT copolymerization.



**Fig.5.**  $^1\text{H-NMR}$  spectrum of P2VP- PMMMS block copolymer in  $\text{CDCl}_3$ , The letters indicate the attributed protons

The spectroscopic results indicated that the moiety of the RAFT agent was attached to the ends of PS, P2VP, P4VP, PMVDTB, PMMMS and PMVPOCO.

### 3.2 Molecular weight distribution and polydispersity index

Among the analytical methods allowing the determination of the molar mass polymers, size exclusion chromatography (SEC) was chosen as method for the characterization of the homopolymers and copolymers. SEC was used since it gives access to the number-average molecular weights ( $M_n$ ), to the weight-average molar mass ( $M_w$ ) and to the molar mass distribution of the sample polydispersity indexes (PDI) of polymers and copolymers.

Table 2 lists the synthesized homopolymers along with their polymerization yields and molecular characteristics. All polymers were characterized by relatively narrow molecular weight distribution and polydispersity indices ( $\text{PDI} < 1.33$ ) demonstrating the controlled character of RAFT process. Furthermore, the efficiency of agent RAFT (BMDTB) in terms of control can be evaluated by a comparison of the experimentally determined molar masses and

those expected theoretically  $M_n^{th}$  [18], given by :

$$M_n^{th} = \frac{[Monomer]_0 \cdot M_{monomer} \cdot \%conversion}{[CTA_0]} + M_{CTA}$$

As can be seen in **Tables 4**, there is a good agreement between the molecular weight determined by SEC and those calculated from the conversion assuming one dithiocarbonyl group per chains. The correspondence between the experimental and calculated molecular weights indicates complete consumption of the initial RAFT agent.

Generally, one requirement for the formation of narrow polydispersity diblock copolymers is that the first-formed macro-CTA (A block) should have a high transfer coefficient in order to give another block (B block). As can be seen, the molecular weight increased from 12629 g/mol (PDI=1.23) to 18048 g/mol (PDI=1.24, 10.6% conversion) with BDTB-PS as macro-RAFT agent for copolymers PS-PMVPOCO. This result indicates that PS acts as the macro-CTA.

This is due in fact that PS-CTA is a good hemolytic leaving group in polymerization of MMMS and MVPOCO. However, BMDTB considered as the new RAFT agent provides a narrow polydispersity product with the increase of monomer/CTA ratio.

**Table 4.** Molecular weight distribution and polydispersity index of polymers and diblock copolymers

Polymers and diblock copolymères	$M_n^{th}$ (g/mol)	$M_n^{exp}$ (g/mol)	PDI
PS	10352	12629	1.23
PS-PMVDTB	13302	17523	1.18
PS-PMMMS	13218	13849	1.16
PS-PMVPOCO	13680	14555	1.24
P2VP	19868	28434	1.32
P2VP-PMVDTB	31693	31760	1.01
P2VP-PMMMS	28948	29341	1.19
P2VP-PMVPOCO	30746	32118	1.53
P4VP	12567	16406	1.16
P4VP-PMVDTB	16960	17421	1.20
P4VP-PMVPOCO	17356	17646	1.01
PMVDTB	11640	34920	1.67
PMMMS	3999	6552	1.14
PMVPOCO	6512	12498	1.74

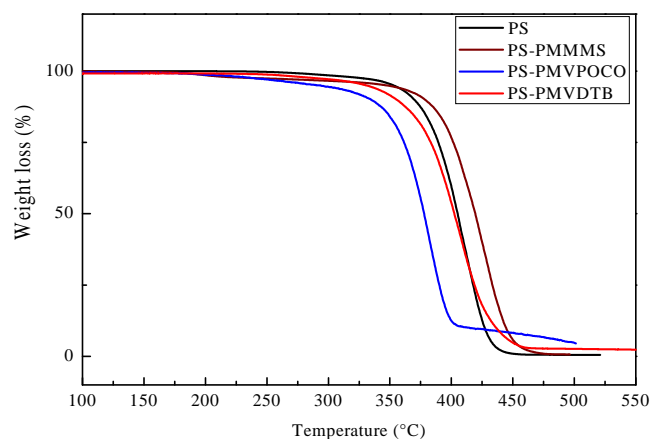
### 3.3. Thermal gravimetric analysis study (TGA)

The thermal stability of polymer materials constitutes is one of the key factors in their application for several sectors. In order to determine the upper temperature limit of the processing and use of polymers, the thermogravimetric analysis (TGA) is widely used to understand the thermal degradation of polymer synthesized and the possibility to form cross-linked structures. In this context, the thermal behavior of PS, PS-PMVDTB, PS-PMMMS and PS-PMVPOCO were studied. The thermogravimetric curves for synthesized polymers are shown in Figure 6. As can be seen, all polymers exhibit one stage degradation processes. It is assigned to the decomposition of the main chain by random scissions. It can be observed that PS-PMMMS shows a good thermal stability until about 350°C. Above this

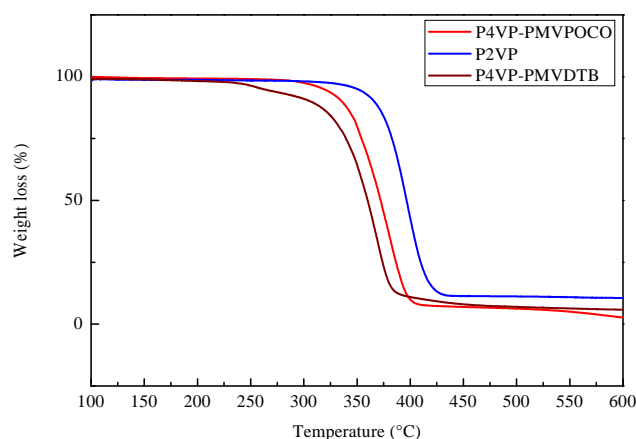


temperature, only one exothermic event corresponding to the decomposition of the polymer was detected. It has been noted that the copolymers based of PS present the same thermal stability that PS.

**Figure 7** showed the thermogravimetric curves of synthesized copolymers such as P4VP-PMVDTB, P4VP-PMVPOCO and P2VP. These polymers present similar behaviors that we have observed with the PS-copolymers. Furthermore, P2VP reveals a good thermal stability until about 340°C compared to 4VP copolymers.



**Fig.6.** Thermogravimetric traces of PS, PS-PMVDTB, PS-PMMS and PS-PMVPOCO



**Fig.7.** Thermogravimetric traces of P4VP-PMVPOCO, P2VP and P4VP-PMVDTB

### 3.4. Differential scanning calorimetric study (DSC)

The transition behaviors observed with the polymers have long been used as a basic criterion in the study of temperature range of applicability of homopolymers and their copolymers. Thus, the study of glass transitions can provide important information about the physical state and morphology of these polymers. These phenomena can also provide important information

about the possible relaxations that occurring at the segments level during the transition. In general, the DSC is the most convenient method to elucidate fundamental characteristic of the physical state, morphology and orientation of the chains. For all these advantages, we have therefore adopted this technique to study our systems. Thus, the thermal characterization of the homopolymers and diblock copolymers was performed by differential scanning calorimetric (DSC) with subsequent heating/cooling program from 100 °C to 200 °C. The results are summarized in Table 2, 3. As can be seen, for all block copolymers, the obtained results reveal that each copolymer presents two temperature transitions in agreement with those obtained previously.

#### 4. CONCLUSION

We have used benzyl 4-methyldithiobenzoate as a new chain transfer agent in the RAFT polymerization process in order to prepare block polymers of PS, 2VP, 4VP, PMVDTB, PMMMS and PMVPOCO. The use of block polymers bearing a dithioester function in termination as a new macro-chain transfer agent in copolymerization of PMVDTB, PMMMS and PMVPOCO allowed us to synthesize diblock copolymers. Therefore, we have obtained, using the RAFT process, a variety of block polymers possessing high molecular weight and the narrow polydispersity index. The TGA thermograms show that the degradation of the obtained polymers and copolymers begins between 200-300 °C and reach 95% to about 400-450°C. The glass transition temperatures of different diblock copolymers are determined by DSC. The experimental molecular weights obtained were in good agreement with those estimated theoretically and revealing that 4-benzyl methyldithiobenzoate has a high transfer coefficient. The RAFT polymerization using the transfer agent BMDTB has proven to be an excellent and versatile method that offers polymers and copolymers with controlled molecular weight and narrow polydispersity indices ( $M_n / M_w < 1.33$ ). Also, the results may open the way for several research projects of new materials such as polymers-surfactants.

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