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Poly(methyl methacrylate)-*block*-polysulfide-*block*-poly(methyl methacrylate) copolymers obtained by free-radical polymerization combined with oxidative coupling

Mircea Teodorescu[a] (✉), **Constantin Draghici**[b]

[a] Department of Polymer Science and Engineering, Polytechnic University, 149 Calea Victoriei, 010071 Bucharest, Romania
[b] "C. D. Nenitzescu" Institute of Organic Chemistry, 202B Splaiul Independentei, 060023 Bucharest, Romania

E-mail: mirceat@tsocm.pub.ro, Fax: +40 214023844

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Summary

Poly(methyl methacrylate)-*block*-polysulfide-*block*-poly(methyl methacrylate) copolymers were synthesized for the first time through a new method involving the free radical polymerization of MMA in the presence of a thiocol oligomer as a chain transfer agent, followed by chemical oxidation of the remaining SH end-groups. The chain transfer constant of the SH end-groups of the thiocol was estimated from the rate of consumption of the thiol groups versus the rate of consumption of the monomer ($C_T = 0.67$). The triblock copolymers synthesized were characterized by SEC and ^{1}H NMR measurements.

Keywords

Thiocol, polysulfide, methyl methacrylate, free radical polymerization, chain transfer agent, triblock copolymer

Introduction

Block copolymers are valuable materials with a large range of applications deriving from the possibility to tailor their properties through the combination of monomers that form the blocks, and the length of the polymeric sequences. Thus, one can obtain adhesives and sealants, thermoplastic elastomers, or amphiphilic copolymers with applications as hydrogels, stabilizers, compatibilizers for polymer blends, surface-modifying agents, etc [1-3].

The most used procedures for the synthesis of block copolymers are based on the ionic polymerization mechanisms, as they afford an excellent control over the molecular weight, polydispersity, functionality and architecture of the resulting polymers [1,2]. However, the reaction conditions are very demanding, as the synthesis requires complete absence of moisture and acidic impurities, inert atmosphere, high purity of monomers and solvents, etc. Almost similar control over the characteristics of the block copolymers has been recently afforded by the controlled/living radical polymerization techniques, but under milder reaction conditions [4]. Nevertheless, even in this latter case, the polymerization process may be complicated by the necessity to employ some special and/or expensive initiators or deactivating agents, or to remove the catalyst from the final product. That is why, in some cases, conventional radical polymerization is still advantageous to use due to its simplicity.

Two methods are described in literature for the synthesis of block copolymers by conventional radical polymerization: i) by means of multifunctional free radical initiators, either micromolecular or polymeric; ii) by means of chain transfer processes [1,3]. In the latter case, an oligomer with end-groups able to act as free radical chain transfer sites is synthesized in the first step, followed by conventional radical polymerization of the second monomer [3,5-7].

Many functional groups display chain transfer ability in the radical polymerization [8]. Amongst them, the thiol group is one of the most efficient and also, used, functional group for the synthesis of end functional oligomers [9,10], as well as block [5,6] and graft copolymers [11].

The present paper deals with the synthesis of poly(methyl methacrylate)-*block*-polysulfide-*block*-poly(methyl methacrylate) copolymers by the free radical polymerization of methyl methacrylate (MMA) in the presence of a polysulfide oligomer (thiocol), taking advantage of both chain transfer ability and chemical oxidation sensitivity of the mercaptan groups located at both ends of the thiocol. To the best of our knowledge, this is the first report on the synthesis of such triblock copolymers, although the modification of the thiocol SH end-groups and the polymerization of the resulting species have been already described in literature [12].

Experimental

Materials

MMA (commercial grade) was washed with 2% aqueous NaOH solution and then with water until neutral, dried over anhydrous $CaCl_2$, and distilled under vacuum. Azobisisobutyronitrile (AIBN) was recrystallized from methanol at 50ºC. Thiocol (Akcros, G1) was used as received. Its SH group content was 0.56 mmol/g (1.85 wt.-%), as determined by iodometry, which corresponds to a number-average molecular weight (M_n) of 3550, calculated assuming two SH groups/molecule. The same result was obtained by acetylation determinations. All other chemicals, of reagent grade, were used without further purification.

Polymerization

A stock solution was prepared in a 250 mL volumetric flask from 22.19 g (12.5 mmol SH groups) thiocol, 75.0 g (0.75 mol) MMA, 0.1231 g (0.75 mmol) AIBN and benzene. Samples of 40 ml each were transferred from the stock solution to five glass ampoules and bubbled with nitrogen for 30 min to remove any dissolved oxygen. The glass ampoules were then flame-sealed and placed in a thermostatted bath at 60ºC. After appropriate time intervals, ampoules were removed from the heating bath, cooled in an ice-water bath and opened. The contents were diluted with benzene and added dropwise to a large excess of petroleum ether. The polymer precipitates were collected and dried under vacuum at room temperature, to constant weight. The MMA conversions were determined gravimetrically, as follows:

$$C_{MMA}(\%) = \frac{m_p - m_{thiocol,0}}{m_{MMA,0}} \times 100 \qquad (1)$$

where m_p is the amount of polymerization solid product (mixture of block copolymers and unreacted thiocol), recovered from each glass ampoule (g), while $m_{thiocol,0}$ and $m_{MMA,0}$ are the amounts of thiocol and MMA, respectively, introduced into each glass ampoule (g).

Chemical oxidation of the SH end-groups contained by the polymerization solid product

The oxidation procedure was similar to that employed for the titrimetrical determination of the SH end-group content of the polymers (see below). Thus, about 3 g of the polymerization solid product were dissolved in 20 ml benzene, and 50 ml of water were added. Then 0.1 N aqueous I_2/KI solution was added in 3 ml portions until the brown color of the organic phase lasted for 5 min. Excess I_2 was then neutralized by adding 0.1 N $Na_2S_2O_3$ solution until the mixture became colorless. Further, the organic layer was separated, dried over anhydrous Na_2SO_4, filtered and poured into a large excess of petroleum ether. The polymer precipitated was recovered by filtration and dried.

Determination of the SH end-group content

The SH end-group content of both thiocol G1 and polymerization solid products were determined iodometrically. Thus, the polymer sample (0.7-1.2 g) was accurately weighed into a 250 ml flask and dissolved in benzene (20 ml), with stirring, followed by the addition of 50 ml of water. Then 0.1 N aqueous I_2/KI solution was added in 2-3 ml portions, under stirring, waiting after each addition until the brown color of the mixture has disappeared. The addition of the iodine solution was stopped when the brown color of the organic layer persisted for more that 5 minutes. Further, 10 ml of a starch solution were added, and excess iodine was titrated with 0.1 N aqueous $Na_2S_2O_3$ solution until the blue color of the aqueous layer disappeared and did not come back after 2-3 min stirring. A blank titration was carried out separately. The SH end-group content (*F*) was calculated with eq.2:

$$F(mol/g) = \frac{(V_0 - V) \times 0.1}{1000 \times m} \qquad (2)$$

where V_0 and V are the volumes of 0.1 N aqueous $Na_2S_2O_3$ solution used in the blank experiment and for titrating the polymer sample, respectively, while m is the amount of polymer sample (g) employed in the analysis.

The F values obtained were used to calculate the SH end-group content (N_{SH}, eq. 3) of the polymer products resulted from each polymerization ampoule, and the conversion of the thiol groups (C_{SH}, eq. 4*)* as follows:

$$N_{SH}(mol) = F \times m_p \qquad (3)$$

$$C_{SH}(\%) = \frac{N_{SH,0} - N_{SH}}{N_{SH,0}} \times 100 \qquad \textbf{(4)}$$

where m_p is the amount of polymerization solid product (mixture of block copolymers and unreacted thiocol), recovered from each glass ampoule (g), while $N_{SH,0}$ is the mole number of SH groups contained initially by each polymerization ampoule.

Instruments

Size-exclusion chromatography (SEC) measurements were performed at 25ºC on a Waters 510 chromatograph equipped with a refractive index detector and four μ-Styragel columns (10^5, 10^3, 500 and 100 Å). THF was employed as the solvent, at a flow rate of 1 ml/min. PolyMMA samples were used for calibration. ^{1}H NMR spectra were recorded on a 300 MHz Varian Gemini 300 BB spectrometer, using deuterated chloroform as the solvent.

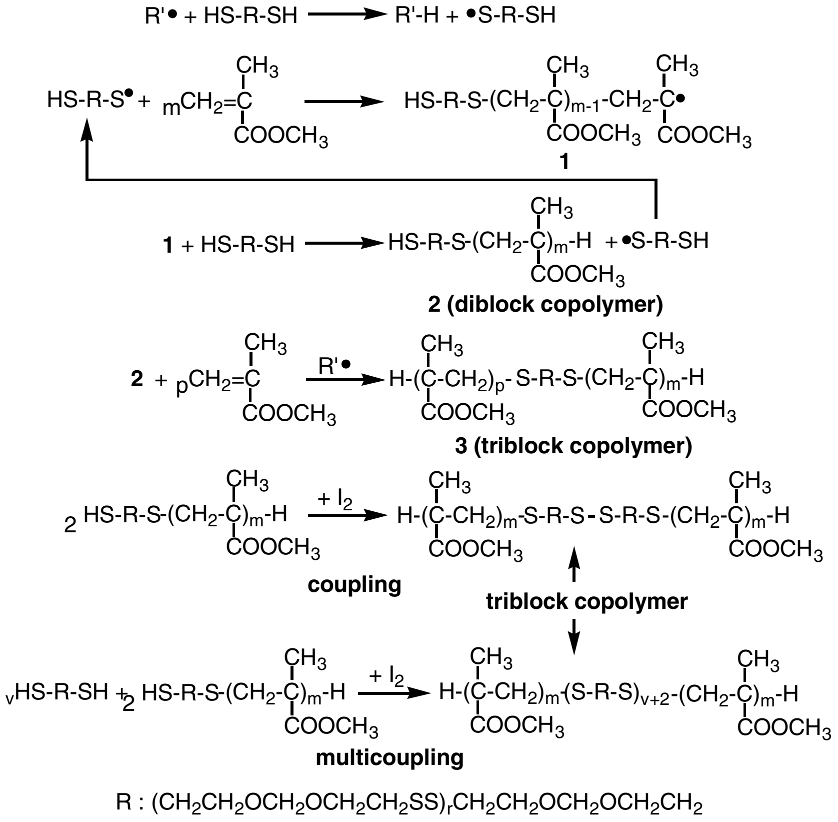
Results and discussion

The employed thiocol $H(SCH_2CH_2OCH_2OCH_2CH_2S)_{21}H$ contains two types of groups active in radical chain transfer: SH groups, located at both ends of the oligomer, and disulfide (S-S) groups, located within the oligomer chain. However, based on the chain transfer constants (C_T) of similar low molecular weight compounds in the radical polymerization of MMA at 60ºC, i. e. C_T = 0.60 [13] or 0.62 [14] for 2-mercaptoethanol, and $C_T = 6.5\times10^{-4}$ for $(EtOOCCH_2S)_2$ [8], one may assume that in the case of MMA polymerization in the presence of thiocols the transfer reactions take place almost entirely at the SH end-groups, while the chain transfer to the S-S groups (about 21 S-S groups/thiocol molecule in our case) may be neglected.

As the chain transfer constant of the thiol groups in MMA polymerization is less than unity, their conversion can not reach completion during the polymerization process [15], and therefore, it is not possible to fully convert the thiocol to polyMMA-thiocol-polyMMA triblock copolymer by means of MMA radical polymerization only. Depending on MMA conversion, the reaction mixture will contain triblock copolymer along with diblock copolymer polyMMA-thiocol-SH and unreacted thiocol in various ratios. To fully convert the polymerization product mixture to triblock copolymer, one can use the SH end-group ability to couple through chemical oxidation (for example with iodine), resulting in disulfide linkages [16-18]. Triblock copolymer molecules may form either by the coupling of two diblock copolymer molecules resulted directly from the polymerization process, or from a multicoupling reaction among diblock copolymer molecules and unreacted thiocol molecules, the diblock copolymer acting in this case as a chain stopper [19]. The mechanism of the synthesis of polyMMA-thiocol-polyMMA triblock copolymers is shown in Scheme 1.

To prove the above theoretical assumptions, a conversion - time polymerization experiment, followed by the chemical oxidation of the polymerization products was carried out (Table 1).

The thiol group consumption was slower than that of MMA monomer indicating that, under the experimental conditions employed, the chain transfer constant of the SH end-groups is lower than unity, as expected.



Scheme 1. Mechanism of polyMMA-*block*-thiocol-*block*-polyMMA copolymer synthesis

Table 1. Synthesis of polyMMA-thiocol-polyMMA triblock copolymers[a]

Time	C_{MMA}	C_{SH}	triblock copolymer[b]			
			M_n	M_w/M_n	MMA content[c]	MMA content[d]
h	%	%			wt %	wt %
10	39	34	22500	1.81	64	57
15	53	47.5	17100	1.71	69	64
23	70	59	15700	1.81	74	70
28	78	64	12000	1.81	76	73

[a] $[MMA]_0=3$ mol/l, $[SH]_0=5\cdot10^{-2}$ mol/l, $[AIBN]_0=3\cdot10^{-3}$ mol/l, 60°C, benzene;
[b] after chemical oxidation with iodine;
[c] determined by ^{1}H NMR.
[d] calculated based on mass balance.

In the case of effective chain transfer agents, such as thiols in MMA radical polymerization, the chain transfer constant can be determined from the following equation [9]:

$$\ln\frac{[transfer\ agent]_0}{[transfer\ agent]} = C_T \times \ln\frac{[monomer]_0}{[monomer]} \qquad (5)$$

By plotting ln[SH]$_0$/[SH] as a function of ln[MMA]$_0$/[MMA], a straight line resulted, whose slope is the chain transfer constant of thiocol SH groups in the radical polymerization of MMA (Figure 1). The value obtained (C_T = 0.67) was very close to the reported chain transfer constant of 2-mercaptoethanol in MMA polymerization (C_T = 0.60 [13], 0.62 [14]), which may be considered as a low molecular weight model of the thiocol SH end-groups. This implies that the chain transfer properties of the thiol group are practically unaffected by its location on the thiocol chain, which agrees with the finding of Reghunadhan Nair *et al* [5] for the case of styrene polymerization in the presence of a SH-terminated polyMMA oligomer. However, a different outcome has been reported in the case of poly(ethylene oxide) chain transfer macroagents, i.e. a lower chain transfer constant by comparison with the corresponding low molecular weight model [6,7]. These different results found in literature may be explained by differences in the compatibility between the transfer macroagent and the forming polymer, which is influenced by both nature and molecular weight of the two different polymer species involved in the chain transfer process.

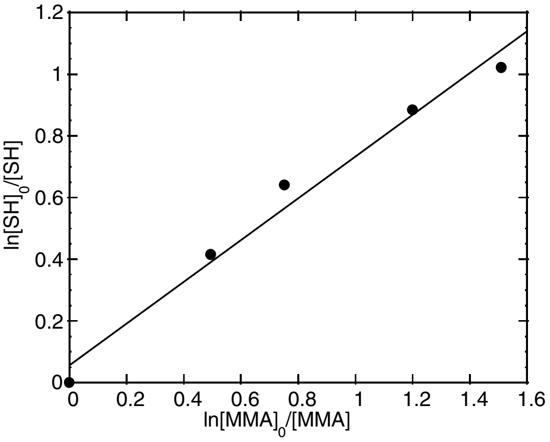


Figure 1. Determination of the chain transfer constant of thiocol SH end-groups in MMA polymerization. [MMA]$_0$=3 mol/l, [SH]$_0$=$5\cdot10^{-2}$ mol/l, [AIBN]$_0$=$3\cdot10^{-3}$ mol/l, 60°C, benzene

During the polymerization process, the composition of the reaction mixture changed, so that the polymerization products obtained at different polymerization times contained triblock copolymer along with diblock copolymer and unreacted thiocol in various ratios. The evolution of the mole fractions of triblock copolymer, diblock copolymer and unreacted thiocol with MMA conversion (Figure 2) can be calculated on the basis of the determined SH end-group conversions, and assuming that the thiol end-groups are independent each other from the chain transfer reactivity point of view. This assumption is true taking into account the length of the thiocol chain. Thus, by applying the principles of probability [21] it results that $(C_{SH})^2$, which represents the probability that both SH end groups of the thiocol molecule have reacted, equals the triblock copolymer (disubstituted thiocol) fraction, while $(1\text{-}C_{SH})^2$, representing the probability that none of the SH end groups of the thiocol oligomer have reacted, equals the fraction of unreacted thiocol (unsubstituted thiocol). The probability that only one thiocol SH end group has reacted, $2C_{SH}\cdot(1\text{-}C_{SH})$, equals the fraction of diblock copolymer (monosubstituted thiocol) formed. As expected, the triblock copolymer and thiocol fraction monotonously increased, respectively decreased, with MMA conversion, while the fraction of diblock copolymer increased at the beginning of the polymerization and then decreased.

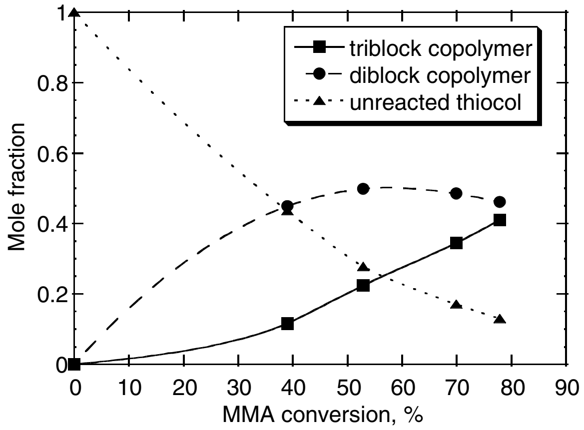


Figure 2. Evolution of the composition of the polymerization product with MMA conversion

The solid polymerization products obtained at different reaction times were treated with an iodine solution in order to convert the SH groups to S-S linkages. The SEC analyses of the oxidation products showed monomodal MW distributions in all cases (Figure 3), indicative for the complete conversion of the thiocol oligomer to triblock copolymer. Unfortunately, we were not able to obtain accurate SEC traces of the original (unoxidized) polymerization products, due to some oxidation processes occurring during the SEC analysis. The same oxidation processes seemed to affect the shape of the SEC trace of the thiocol, which should have been monomodal, as well [12].

The M_n of the triblock copolymers was higher for lower SH group conversions (Table 1). This can be ascribed mainly to an increased contribution of the multicoupling reactions due to the presence of higher amounts of unreacted thiocol, while the amount of diblock copolymer (chain stopper) was approximately constant (Figure 2), leading to the formation of higher molecular weight triblock copolymers through oxidation, with longer thiocol sequences. As MMA conversion increased, the polyMMA block length decreased due to the chain transfer constant being less than unity, but this decrease was small [13], and it can not be responsible for the large molecular weight difference observed. Indeed, by applying equation 6 [20] for the experimental conditions employed in this work, i.e. $[MMA]_0 = 3$ mol/l, $[SH]_0 = 5\cdot 10^{-2}$ mol/l, $C_T = 0.67$, the overall M_n decrease of the polyMMA block was calculated to be about 1400 Dalton (700 Dalton/SH end-group) for a MMA conversion increase from 39% to 70%, much lower than the experimentally measured decrease of M_n ($\Delta M_n = 6800$) in the case of the oxidized products.

$$DP_n = \frac{C_{MMA}}{\frac{[SH]_0}{[MMA]_0}[1-(1-C_{MMA})^{C_T}]} \tag{6}$$

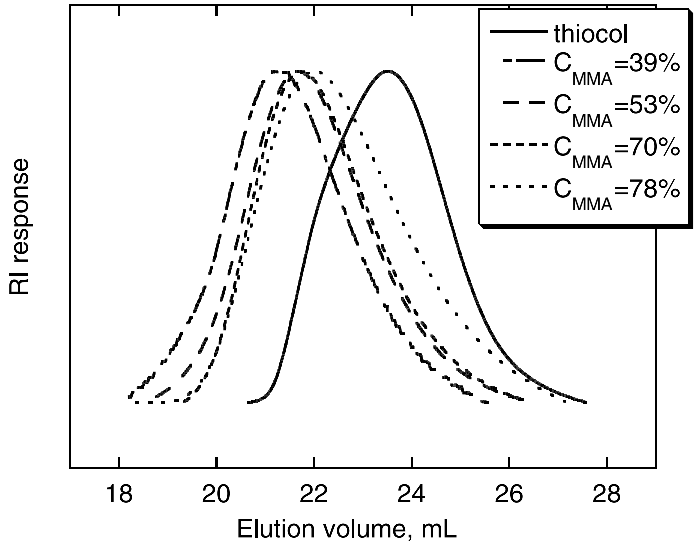


Figure 3. SEC traces of the thiocol and triblock copolymers prepared. $[MMA]_0$=3 mol/l, $[SH]_0$=5·10^{-2} mol/l, $[AIBN]_0$=3·10^{-3} mol/l, 60°C, benzene

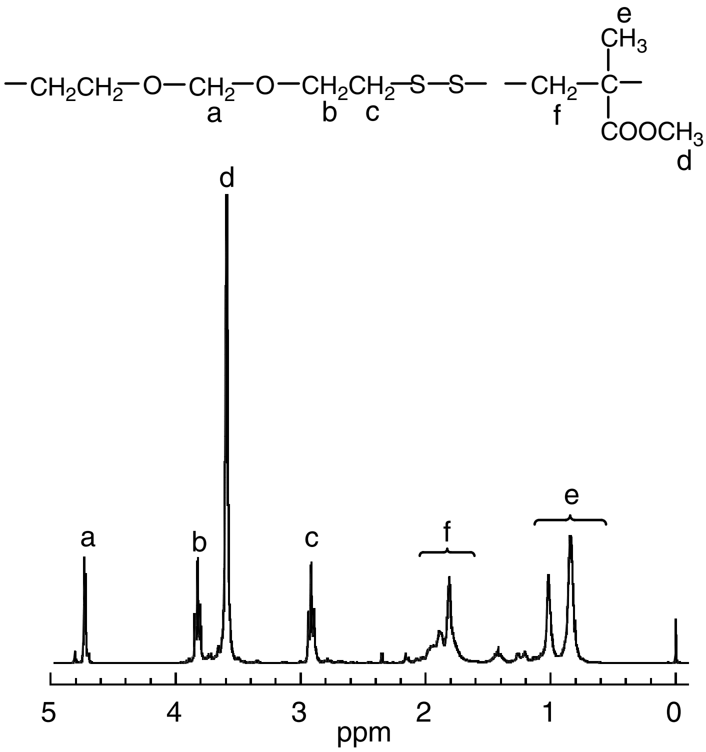


Figure 4. ^{1}H NMR spectrum of polyMMA-*block*-thiocol-*block*-polyMMA copolymer (C_{MMA} = 78%)

Also, the concentration of the polymerization-resulted triblock copolymer, that has a lower M_n than the products formed through oxidation, was higher at higher conversions (Figure 2), contributing to a lower M_n of the oxidized product, as well. The ^{1}H NMR spectra of the oxidized products contained peaks for both polyMMA and thiocol blocks (Figure 4). By comparing the areas of the peaks at $\delta = 3.6$ ppm (-COOC**H**$_3$) and $\delta = 4.74$ ppm (-OC**H**$_2$O-), respectively, the composition of the triblock copolymers was established (Table 1). As expected, the MMA content of the block copolymers increased with MMA conversion.

Conclusions

The paper describes for the first time the preparation of some polyMMA-*block*-thiocol-*block*-polyMMA copolymers by radical polymerization of MMA in the presence of a commercial thiocol as chain transfer agent, followed by chemical oxidation of the remaining SH end-groups. The procedure employed for the synthesis of the triblock copolymers is a new one, and it can be applied for any linear oligomer with SH groups at both ends, in conjunction with a monomer that displays a C_T smaller than unity in reaction with mercaptans. The method allows to control the length of the blocks, as by varying the monomer/SH groups ratio, the length of the monomer block can be predetermined, while by adding SH-functionalized oligomer to the polymerization mixture before the chemical oxidation step, the M_n of the oligomer block may be adjusted as well.

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