Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Öztürk, Temel , Göktaş, Melahat and Hazer, Bakí(2011) 'Synthesis and Characterization of Poly(methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) Block Copolymers by Reversible Addition-Fragmentation Chain Transfer Polymerization', Journal of Macromolecular Science, Part A, 48: 1, 65 — 70

To link to this Article: DOI: 10.1080/10601325.2011.528310

URL: http://dx.doi.org/10.1080/10601325.2011.528310

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2011) **48**, 65–72
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2011.528310

Synthesis and Characterization of Poly(methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) Block Copolymers by Reversible Addition-Fragmentation Chain Transfer Polymerization

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Received March 2010, Accepted June 2010

Synthesis of poly(methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) triblock copolymers by reversible addition–fragmentation chain transfer (RAFT) by using a novel dual macro initiator (RAFT-agent) is reported. RAFT-agent is obtained from potassium salt of the ethyl xanthegonate and the terminally brominated poly(ethylene glycol) (Br-PEG-Br) which is synthesized by the reaction of poly(ethylene glycol) [PEG] with $M_n = 3000$ Dalton and 3-bromopropionyl chloride. The principal parameters such as monomer concentration, initiator concentration, and polymerization time that affect the polymerization reaction are evaluated. The characterization of the products is achieved using Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), gel-permeation chromatography (GPC), thermogravimetric analysis (TGA), and fractional precipitation (γ) techniques. Molecular weights of the polymers obtained from GPC agreed with the theoretical values. RAFT polymerization is used to control the polymerization of MMA over a broad range of molecular weights.

Keywords: Reversible addition-fragmentation chain transfer, macro initiator, poly(ethylene glycol), poly (methyl methacrylate), triblock copolymer; fractional precipitation

1 Introduction

Block copolymers have great important in recent years (1–8). Block copolymers are one of the most important polymeric materials in technological applications and theoretical research because of their exceptional properties due to the micro phase separation (9–11). A variety of synthetic methods for the preparation of block copolymers with various architectures such as linear diblock (AB), triblock (ABA or ABC), pentablock (ABABA), multiblock or segmented copolymers have been proposed (12–22). The synthesis of block copolymers, with a controlled molecular weight, and a better-designed macromolecular structure and composition, is one of the most meaningful and challenging works in the field of polymer chemistry (23). Block copolymers have been the subject of intense experimental and theoretical interest for more than two decades because of their practical applications as adhesives, surfactants, compatibilizers and thermoplastic elastomers (24, 25).

Polymers of a well defined structure and molecular weight are desired and can be prepared by controlled radical polymerization methods, the most used include nitroxide-mediated polymerization (26, 27), atom transfer radical polymerization (28–34), and reversible addition-fragmentation chain transfer (RAFT) polymerization (35–37). RAFT polymerization represents the most recently developed controlled radical polymerization method and is a powerful technique for macromolecular synthesis of a broad range of well-defined polymers. The versatility of the method is demonstrated by its compatibility with a very wide range of monomers and reaction conditions. Reversible chain transfer involves homolytic substitution or addition fragmentation, or some other transfer mechanisms (35–47). It is possible to take RAFT polymerizations to high conversion and achieve commercially acceptable polymerization rates and several solvents (40). Perrier et al. (41) showed that the ionic liquids can be used as efficient solvent for the RAFT polymerization of methacrylate, acrylate and styrene, in the limit of their solubility.

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Macrointermediates such as macroinitiators, macromonomers and macrocrosslinkers have been widely used for preparing various block/graft copolymers and their networks via a radical initiated process (48–56). Poly(ethylene glycol) [PEG] macro monomers are soluble in a large variety of solvents including water and benzene (57). Block/graft copolymers having PEG units have been very attractive for chemical, industrial and biomedical applications, because PEG has unique properties such high hydrophilicity, flexibility and ion absorbability, and a high degree of biocompatibility (58–64). The preparation of (co)polymers using PEG units has been reported using the RAFT process (65–72).

In an earlier study, we report the synthesis of a new macromonomer initiator, methacryloyl oxy polyethylene glycol ethyl xanthogenate, for RAFT polymerization to obtain cross-linked copolymers (45). In this study, we report the synthesis of a new dual macromonomer initiator (RAFT-agent) obtained from potassium salt of the ethyl xanthegonate and the terminally brominated poly (ethylene glycol) (Br-PEG-Br) for RAFT polymerization which is a method of controlled living polymerization. The copolymerization with methyl methacrylate (MMA) is studied and the principal parameters such as monomer concentration, initiator concentration, and polymerization time that affect the polymerization reaction are evaluated.

2 Experimental

2.1 Materials

The potassium salt of ethyl xanthogenate, PEG (3000 Dalton), THF, triethylamin, and methanol were supplied by Merck and used as received. N,N-dimethylformamide (DMF) was received from Fluka. 3-bromopropionyl chloride, 2,2′-azobisisobutyronitrile (AIBN), petroleum ether, and diethyl ether were received from Aldrich and used as received. MMA was supplied by Aldrich, which is purified as follows: It is washed with a 10 wt.% aqueous NaOH solution, dried over anhydrous $CaCl_2$ overnight, and distilled over CaH_2 under reduced pressure before use. All other chemicals are reagent grade and used as received.

2.2 Instrumentation

The molecular weights were measured with an Agilent 1100 HPLC System. A calibration curve was generated with four polystyrene green standards: 162, 2960, 50400, and 696500 Da, of low polydispersity. FTIR—attenuated total reflectance (FTIR-ATR) spectra were recorded using a Nicolet-520 model FTIR spectrometer. ^{1}H-NMR spectra of the samples in $CDCl_3$as the solvent, with tetra methylsilane as the internal standard, were recorded using a Bruker DPX-400, 400 MHz high performance digital FT-NMR spectrometer. TGA of the obtained polymers was carried out under nitrogen using a Seiko II Exstar 6000 TG/differential thermal analyzer to determine thermal degradation. A dried sample was heated from 30°C to 650°C at a rate of 20°C min^{-1}.

2.3 Synthesis of the Terminally Brominated PEG (Br-PEG-Br)

Br-PEG-Br is obtained by the reaction of PEG with M_n = 3000 Dalton with 3-bromopropanoyl chloride. Typically, a 20.00 g (6.67 mmol) sample of PEG in 30 mL of dry dichloromethane is mixed with 1.35 g (13.34 mmol) of triethylamin. The solution is transferred into a 250 mL schlenk flask with a magnet and an argon gas inlet. The reaction flask is cooled down to 0°C and then argon gas is purged into the flask. To this solution is added 2.28 g (13.34 mmol) of 3-bromopropionyl chloride in 30 mL of dry dichloromethane in half an hour. The reaction mixture is stirred for 1 h at 0°C. After that, the solution is slowly warmed to room temperature for a day. The solution is filtered. Solvent is partially evaporated and precipitated in cold diethyl ether:petroleum ether (1:1) solution. The product is dissolved in absolute ethanol and kept in a refrigerator overnight. Then, the precipitated triethylamin hydrochloride crystals are removed. The solvent is then evaporated; the product is washed with cold diethyl ether, and dried under vacuum at room temperature.

2.4 Synthesis of the Novel Dual Initiator (RAFT-Agent)

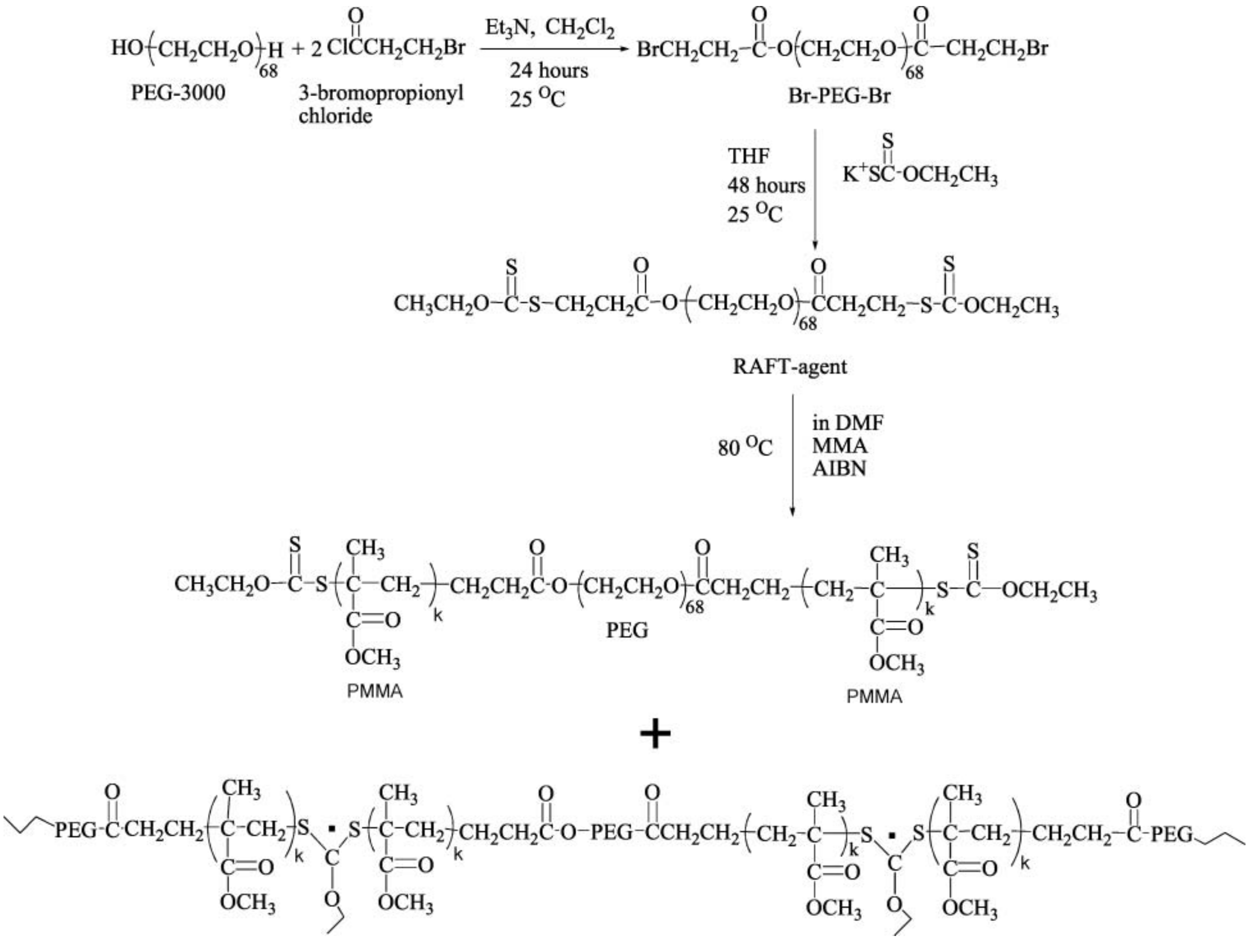
A fixed quantity (17.10 g or 5.23 mmol) of Br-PEG-Br is reacted with 10.04 g (31.39 mmol) of the potassium salt of ethyl xanthogenate in THF at 30°C for 48 h ([Cl]/[K] = 1/6, mol/mol). The solution is filtered to remove the unreacted xanthate, and the solvent is removed by a rotary evaporator. The RAFT-agent is precipitated in cold diethyl ether:petroleum ether (1:1) solution and dried under vacuum at room temperature for four days.

2.5 RAFT Polymerization of the RAFT-Agent with MMA

A given amount of MMA, AIBN, the RAFT-agent and DMF as solvent is charged separately into a Pyrex tube, and then argon is purged into the tube through a needle. The tube, tightly capped with a rubber septum, is put into an oil bath thermostated at 80°C. After the required period of polymerization, the reaction mixture is poured into excess methanol to separate the of poly (methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) triblock (ABA) copolymer. The yield of the polymer is determined gravimetrically.

2.6 Fractional Precipitations of the Polymers

Fractional precipitations of the polymers are carried out according to the procedure cited in literature (73, 74).



Sch. 1. Synthetic route for PEG-based block copolymer.

Vacuum-dried polymer sample (approximately 0.5 g) is dissolved in 10 mL of THF. Petroleum ether is added dropwise as a nonsolvent to the solution with stirring until completion of the first precipitation. After decantation, the upper layer of solvent is treated by adding the nonsolvent for the second fractionation. The same procedure is repeated until no more precipitation is observed. The gamma (γ) values are calculated as the ratios of the total volume of petroleum ether used for each fraction to the volume of THF used for the same. The polymer fractions are subsequently dried under vacuum.

3 Results and Discussion

3.1 Synthesis of the RAFT-Agent

The goal of this work is to synthesize novel dual macromonomeric initiators and copolymerization with MMA by RAFT method in view of the effect of some different polymerization conditions. The RAFT-agent based on PEG having two ethyl xanthogenate ends is synthesized by the reaction of bis (bromo propionate) polyethylene glycol (Br-PEG-Br) with potassium salt of ethyl xanthogenate. The yield of the products is over 85 wt%. The basic outline for the synthesis of the novel dual initiator is shown in Scheme 1. In the ^{1}H-NMR spectrum of the RAFT-agent, and its halide precursor (Fig. 1a and b), the signal of $-\mathbf{CH_2}-Br$ (2.9 ppm) is nearly diminished, and new signals appear at 4.1 ppm for $-\mathbf{CH_2}$-S-; 5.2 ppm for $-O\mathbf{CH_2}-CH_3$; and 1.1 ppm for $-OCH_2-\mathbf{CH_3}$. The FTIR spectrum of the polymer (Fig. 2a, b and c) also indicates the characteristic signals of $-C{=}O$ at 1726 cm^{-1}(poly-MMA) and 1674 cm^{-1} (RAFT-agent), $-$CH(poly-MMA) at 2997 cm^{-1}. The signals of $-C{=}O$ (1726 cm^{-1}) and $-$CH(2997 cm^{-1}) at the spectrum of the copolymer (Fig. 2c) are not observed at the spectrum of the RAFT-agent, and PEG (Figs. 2 a and b).

3.2 RAFT Polymerization of MMA Initiated by RAFT-Agent

The RAFT polymerization of MMA initiated by the novel macromonomeric initiator provided poly(methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) triblock (ABA) copolymers. This process creates two active sites on the thiocarbonate groups for RAFT polymerization. The effects of polymerization time, initiator

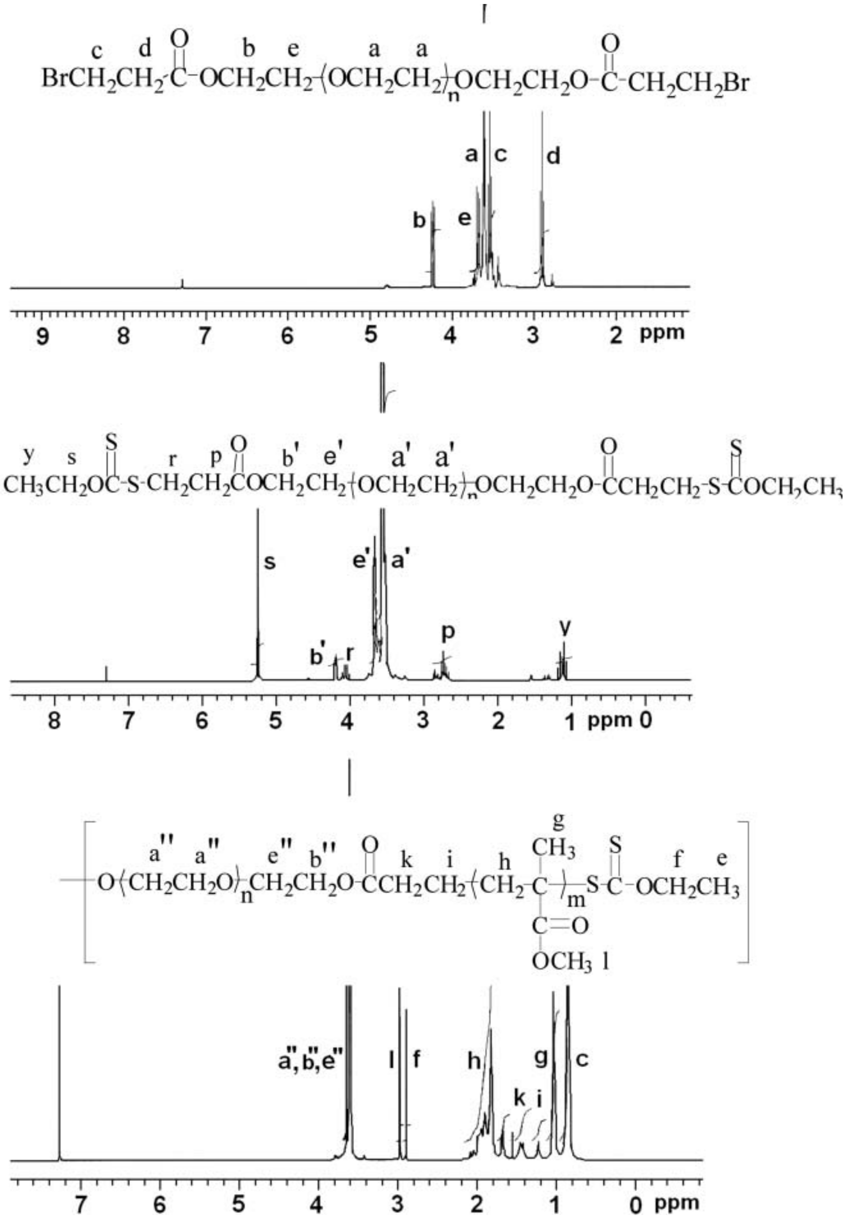


Fig. 1. ^{1}H-NMR spectra of Br-PEG-Br (a), of RAFT-agent (b), and of the copolymer (c).

Table 1. The effects of the polymerization time, amount of the RAFT-agent, and amount of the monomer on the copolymerization. Polym. temp.= 80°C; *nonsolvent (petroleum ether, mL)/solvent (THF, mL); DMF = 4 mL

Code	*RAFT-agent (g)*	*AIBN (g)*	*MMA (g)*	*Time (min.)*	*Yield (g)*	*Conv. (w%)*	$\gamma*$	$M_{n,th}$	$M_{n,GPC}$	*f (initiator efficiency)* $M_{n,fh}/M_{n,GPC}$
KG-1	0.103	0.001	2.808	90	1.258	43.22	0.76	39495	22704	1.74
KG-3	0.422	0.004	2.808	90	1.595	49.38	0.68	11014	20881	0.53
KG-4	0.511	0.005	2.808	90	1.685	50.77	0.64	9352	11876	0.79
KH-2	0.305	0.003	2.340	90	1.046	39.55	0.66	10171	16524	0.62
KH-3	0.318	0.003	3.276	90	1.704	47.41	0.70	16372	18117	0.90
KH-4	0.303	0.003	4.412	90	2.289	48.55	0.64	23697	24464	0.97
KD-8	0.320	0.003	2.808	55	1.023	32.70	0.80	9618	9914	0.97
KD-10	0.310	0.003	2.808	110	1.597	51.22	0.72	15643	11007	1.42
KD-12	0.312	0.003	2.808	180	1.829	58.62	0.90	17684	11937	1.48
KD-13	0.313	0.003	2.808	210	2.119	67.89	0.72	20416	22479	0.91
KD-1	0.318	0.003	2.808	240	2.237	71.56	1.20	21181	22560	0.94

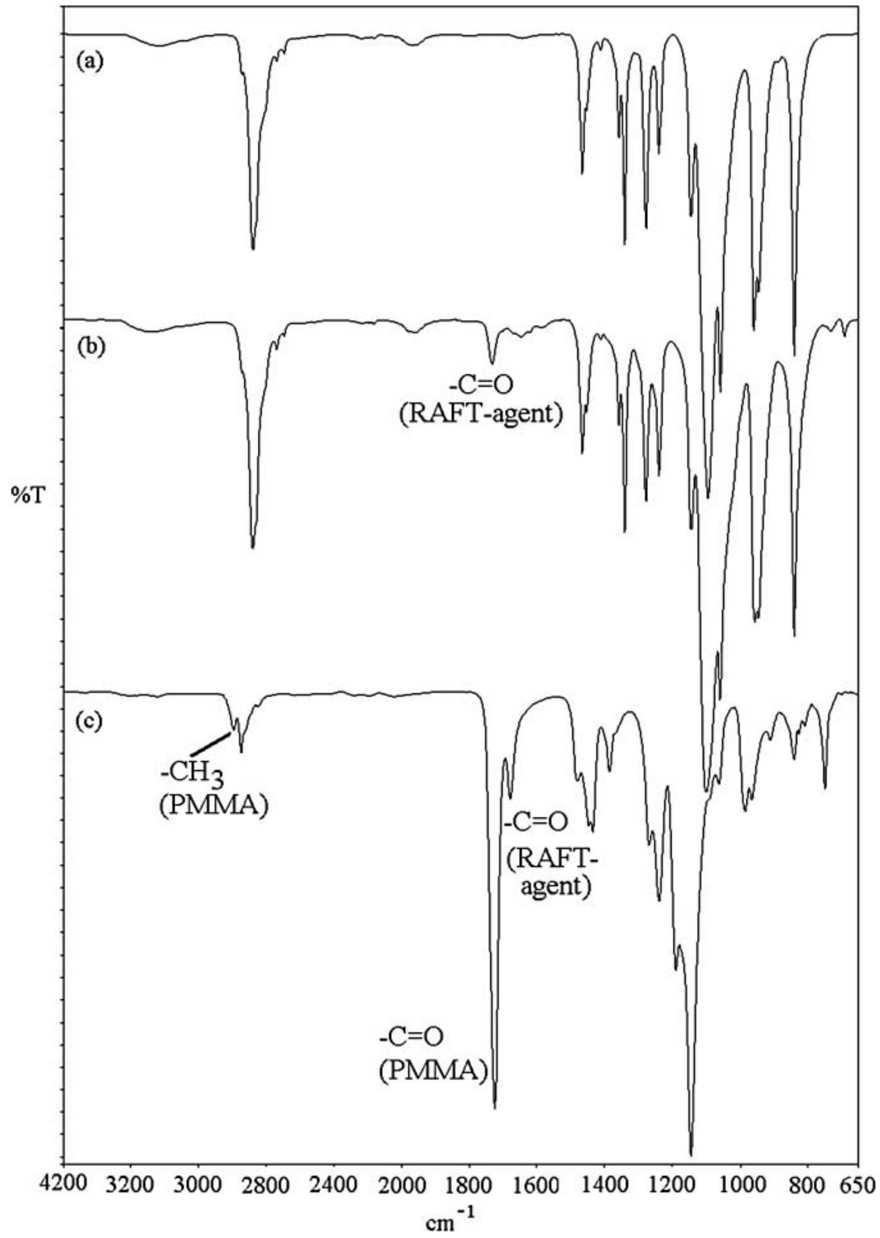


Fig. 2. FTIR spectrum of PEG (a), of RAFT-agent (b), and of poly (methyl methacrylate-b-ethylene glycol-b-methyl methacrylate) (c).

concentration, and monomer concentration on the copolymerization in the presence of the RAFT-agent by the application of RAFT processes have been studied (Table 1). High conversion of MMA is obtained by the polymerization of MMA initiated with the novel macroinitiator (RAFT-agent). For polymerizations of longer durations, polymers of higher molecular weights are obtained. Longer polymerization times cause higher polymer yields. Increased amounts of initiator in the reaction mixture lead to the formation of a higher number of active centers. Consequently, increased numbers of growing macroradicals are formed in the system. Hence, it may be expected that they have shorter poly-MMA segments, which is confirmed by a decrease in the molecular weights of the triblock copolymers. The results show that when the initial MMA feed increased, the molecular weights of the triblock copolymers also increased. Increasing the amount of monomers also causes an increase in the yield of the block copolymers as expected.

Typical ^{1}H-NMR spectra of the block copolymer is shown in Figure 1c. The signals at 1.0 ppm (signal g), 1.9 ppm (signal h), and 3.0 ppm (signal l) corresponding to $-\mathbf{CH}_3$, $-\mathbf{CH}_2$, and $-\mathrm{O}\mathbf{CH}_3$ protons of poly-MMA units appear in the ^{1}H-NMR spectra of the block copolymer, respectively. The signals of $-\mathrm{O}\mathbf{CH}_2$ in the PEG units appear nearly at 3.7 ppm in the all of ^{1}H-NMR spectrum (Fig. 1). Thermal analysis of the samples is carried out

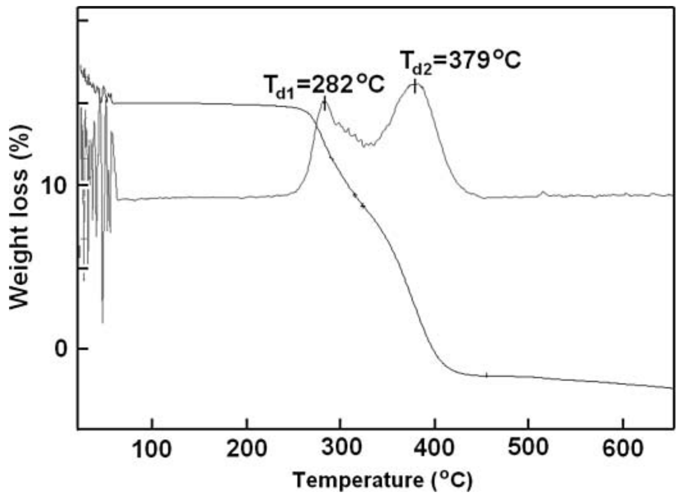


Fig. 3. TGA curve of poly(methyl methacrylate-b-ethylene glycol-b-methyl methacrylate) triblock copolymers.

using TGA and analysis of the curves obtained (Fig. 3). The TGA showed the individual decomposition temperatures (T_d) of the PEG and poly-MMA blocks (ca. 282 and 379°C, respectively). The molecular weights obtained GPC of the block copolymers agreed the theoretical value which can be a proof to control the polymerization of MMA over a broad range of molecular weights. The initiator efficiency of block copolymers is between 0.53 and 1.74, as shown in Table 1. All GPC chromatograms are unimodal, which can be attributed to the fact that any the homopolymer is formed. For example, Figure 4 shows the unimodal GPC curves of the copolymers (KG series in Table 1).The GPC chromatograms of the copolymers (KG series) are shown in Figure 5.

Based on the assumption that one molecule of RAFT-agent generated one polymer chain, the theoretical molecular weight ($M_{n,th}$) for controlled radical polymerization methods is calculated according to Equation 1 (25), where $[M]_o$ and $[RAFT\text{-}agent]_o$ represent the initial concentrations of the monomer and RAFT-agent, $(MW)_o$ is the molecular weight of the monomer and 3352 is the molecular weight of RAFT-agent.

$$M_{n,th} = 3352 + \{([M]_o/([RAFT - agent]_o)\} \times (MW)_o \times \text{conversion} \tag{1}$$

As seen in the literature (65, 75), the existence of the xanthate groups at the chain ends and the intermediate radical compounds in the dormant block copolymer after complete polymerization as shown in Scheme 1 should be considered. Figure 6 shows the photo images of the KH-4 before and after chain-end modification process using excess AIBN as described in the literature (65, 76). The yellowish color appears because of a chromophore of the xanthate group located in the chain and at the chain ends as shown in Scheme 1. The conclusion of the chain-end

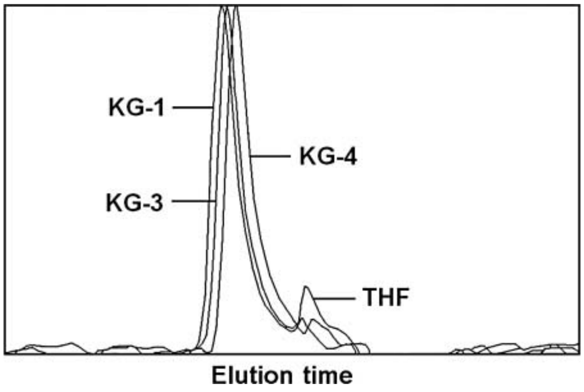


Fig. 4. GPC profiles of the copolymers (KG series in Table 1) with elution time.

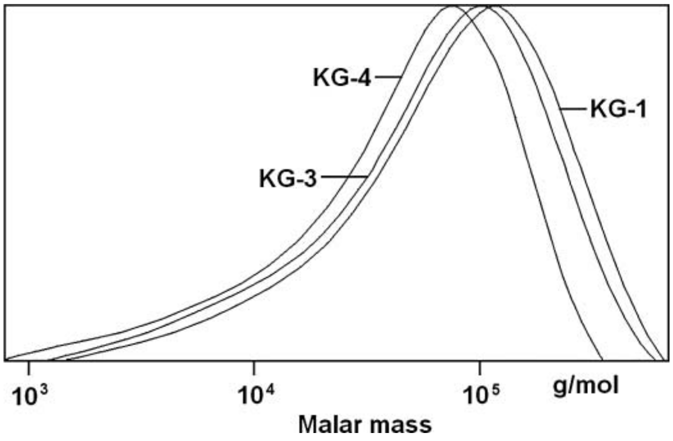


Fig. 5. GPC chromatograms of KG series in Table 1.

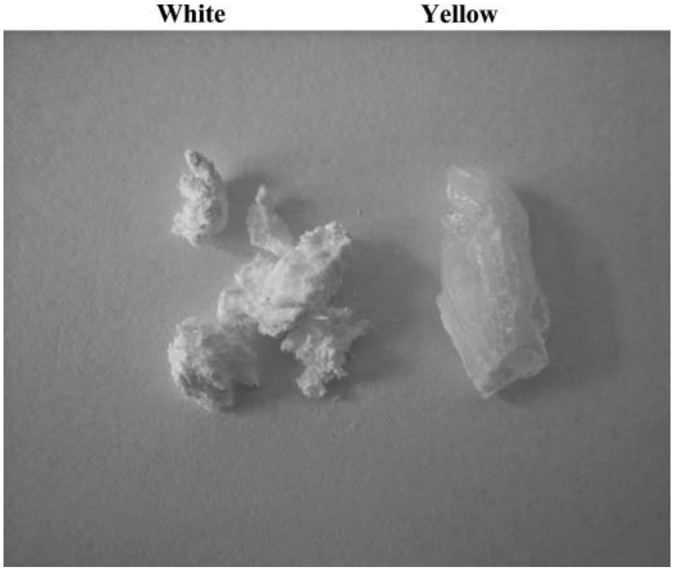


Fig. 6. Photo images of crude KH-4 (yellow) and chain-end modified KH-4 (white) using AIBN.

modification of the block copolymer led to the formation of a white color.

3.3 Fractional Precipitations of the Triblock Copolymers

Fractional precipitation experiments also provided the evidence for formation of block copolymers. The gamma values (γ) of poly (methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) triblock copolymers are between 0.64 and 1.20, as shown in Table 1, when the solvent is THF and the nonsolvent is petroleum ether. In this solvent-nonsolvent system, the γ-values are found to be 0.50–0.55 for homo-PMMA and 1.30–1.58 for homo-PEG. The γ values of the block copolymers are ranged between those of homo-PMMA and homo-PEG and are higher value than that of homo PMMA because of PEG segments. Fractional precipitation behavior provides evidence for the formation of block copolymer. It can also be concluded that homopolymer formation is not present because no polymer precipitation is observed at the γ values of the related homopolymers.

4 Conclusions

In this article, the block copolymers were synthesized with the desired molecular weight by changing the polymerization conditions. The proposed procedure for the preparation of block copolymers is simple and efficient. The block length can be adjusted by varying the monomer and initiator concentrations.

Acknowledgments

This work was supported by the Scientific Research Projects Commission (KAU-BAP) of Kafkas University (Grants#2009FEF02) and TUBITAK (Grants#108T981).

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