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Synthesis and Characterization of a Novel Macromonomer Initiator for Reversible Addition Fragmentation Chain Transfer (RAFT). Evaluation of the Polymerization Kinetics and Gelation Behaviors

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Reversible addition fragmentation chain transfer, RAFT, self condensing a novel macromonomer initiator polymerization and copolymerization with methyl methacrylate, MMA, in the presence of 2,2′-azobisisobutyronitrile, AIBN, has been reported. RAFT-MIM was obtained from potassium salt of the ethyl xanthegonate and the terminally brominated poly (ethylene glycol) methacrylate (v-PEG-Br) which was synthesized by the reaction of poly (ethylene glycol) methacrylate, v-PEG-OH with $M_n = 526$ Dalton and 3-bromopropionyl chloride. Self condensing RAFT-MIM polymerization and copolymerization with MMA gave highly branched and cross-linked amphiphilic copolymers. The kinetic parameters were evaluated by changing some polymerization conditions such as monomer, initiator and solvent concentration, polymerization time and polymerization temperature. The plots of ln (M_0/M) versus reaction time are linear, corresponding to first-order kinetics. The overall polymerization rate constant, k, was calculated as 7.9×10^{-5} s^{-1}. The products were characterized by ^{1}H-NMR and TGA. Swelling ratio values of the crosslinked products in $CHCl_3$ were also determined.

Keywords: Reversible addition fragmentation chain transfer, macromonomeric initiator, self condensing polymerization, swelling ratio

1 Introduction

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 (1). 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 (2). Macromonomeric initiators, also referred to as macroinimers (MIM), which behave as initiator, monomer and crosslinker, have recently been synthesized by end-capping the reaction of either methacryloyl chloride, 4-vinyl benzyl chloride, or isocyanatoethyl methacrylate with the hydroxyl end groups of polyazoesters containing PEG units (3). Synthesis of macromonomer initiators containing polytetrahydrofuran, polycaprolactone, polydimethyl siloxane, polypropylene glycol were also reported and used in the preparation of the branched and crosslinked block copolymers (4). In a conventional radical polymerization (ca. 60°C) at the beginning, a small amount of MIM decomposes into macromonomer radicals for the free radical copolymerization of styrene with undecomposed MIM, and a crosslinked copolymer is formed. In that case, undecomposed MIM behaves as a macrocrosslinker leading to branching. Azo groups remaining continue to cleave to produce radical ends, and the hyperbranched structure gradually turns to crosslinked moities as polymerization proceeds (5).

Polymers of a well defined structure and molecular weight are desired and can be prepared by controlled radical polymerization methods, the most used of which include nitroxide-mediated polymerization (6), atom transfer radical polymerization (7), and reversible addition fragmentationchain transfer (RAFT) polymerization (8). RAFT polymerization represents the most recently developed controlled radical polymerization method and is

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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 (9).

The introduction of branching into a polymer can dramatically alter its properties, so the preparation of these types of macromolecules is of interest to the polymer/materials community. A recent subject in polymer/materials synthesis is the preparation of hyperbranched polymers via self-condensing vinyl polymerizations (SCVP) (10). Homo- and co-polymerization of a halogenated and chain transfer agent functionalized initiator having a vinyl group can initiate controlled living polymerization leading to hyper branched polymers. In this manner, self condensing ATRP of poly(tert-butyl acrylate) macroinimer ($M_n = 3060$ Dalton) (11), methacryloyl oxypolyoxyethlene 2-bromo propionate ($M_n = 600$ Dalton) (12), 2-((bromoacetyl)oxy)ethyl acrylate as inimer (13) and PEG-Polystyrene macroinitiator (14) led to hyperbranched or highly branched polymers. Similarly, self condensing vinyl (SCV) co-polymerization (15), self condensing group transfer (16), and self condensing nitroxy mediated (17) living radical polymerizations of monomeric initiators (inimers), in order to obtain higher branched polymers or dendrimers, have also been used successfully.

To the best of our knowledge, macromonomeric initiators for RAFT polymerization have not been reported. For the first time, we report the synthesis of a new macromonomer initiator, methacryloyl oxy polyethylene glycol ethyl xanthogenate, for RAFT polymerization which is a method of controlled living polymerization. Gelation behavior of the self condensing RAFT-MIM polymerization and copolymerization with methyl methacrylate (MMA) was studied and the polymerization kinetic results were evaluated.

2 Experimental

2.1 Materials

Poly(ethylene glycol) methacrylate (also called methacryloyl oxy-polyoxyethlene glycol, v-PEG-OH, M.W. 525 g/mol), AIBN, and 3-bromopropionyl chloride were received from Aldrich and used without further purification. Triethylamine and potassium salt of ethyl xanthogenate were supplied from Merck and used as received. THF, toluene, and dichloromethane were received from Merck and purified by conventional procedures. MMA was supplied from Aldrich and washed with a 10% aqueous NaOH, water dried over $CaCl_2$, respectively, and was then distilled on CaH_2 under reduced pressure before use.

2.2 Polymer Characterization

FT-IR spectra were recorded using a Perkin-Elmer 1600 Series FT-IR Spectrometer. ^{1}H-NMR of the products was recorded using Bruker DPX-400, 400 MHz High Performance Digital FT-NMR Spectromete, in $CDCl_3$ solvent having tetra methylsilane as the internal standard. Thermogravimetric analysis (TGA) of the obtained polymers was performed on a PL TGA 1500 instrument to determine thermal degradation.

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

v-PEG-Br was obtained by the reaction of methacryloyl PEG, (v-PEG-OH) with 2-bromopropanoyl chloride according to the procedure reported in our recent paper (12). Typically, a 19.4 g (36.95 mmol) sample of v-PEG-OH in 30 mL of dry dichloromethane was mixed with 4.55 g (45 mmol) of triethylamine. The solution was transferred into a 250 mL schlenk flask with a magnet and an argon gas inlet. The reaction flask was cooled down to 0°C and then argon gas was purged into the flask. To this solution was added 7.71 g (45 mmol) of 3-bromopropionyl chloride in 30 mL of dry dichloromethane in half an hour. The reaction mixture was stirred for 1 h at 0°C. After that, the solution was slowly warmed to room temperature for a day. The solution was filtered. Solvent was partially evaporated and precipitated in cold diethyl ether. The product was dissolved in absolute ethanol and kept in a refrigerator overnight. Then, the precipitated triethylamin hidrochloride crystals were removed. The solvent was then evaporated, the product was washed with cold diethyl ether, and dried under vacuum at room temperature.

2.4 Synthesis of RAFT-Macromonomeric Initiator (RAFT-MIM)

The mixture of 9.93 g (15 mmol) of v-PEG-Br and 9.60 g (60 mmol) of potassium salt of ethyl xanthogenate in THF was stirred at 25°C for 24 h ($[Br]/[K] = 1/4$, mol/mol), then precipitated in diethyl ether and dried under vacuum at room temperature. The purification of crude RAFT-MIM was performed as described below. It was dissolved in toluene, filtered to remove unreacted xanthate and precipitated in cold diethyl ether.

2.5 Self-Initiated Polymerization of the RAFT-MIM

A given amount of the RAFT-MIM, AIBN and toluene as solvent was weighed into a Pyrex tube. Argon was purged into a Pyrex tube through a needle. The tube tightly capped with a rubber septum was put into an oil bath thermostated at varied temperatures. After the required period of polymerization, the content of the tube was put into 50 mL of chloroform, stirred for one day, and filtered to separate the crosslinked polymer. The crosslinked polymer was dried, first in air at room temperature, and then in a vacuum oven at 40°C.

2.6 RAFT Polymerization of the RAFT-MIM with MMA

A given amount of MMA, AIBN, the RAFT-MIM and toluene as solvent was charged separately into a Pyrex tube, and then argon was purged into the tube through a needle. The tube, tightly capped with a rubber septum, was put into an oil bath thermostated at various temperatures. After the required period of polymerization, the reaction mixture was poured into excess methanol to separate the PEG-g-PMMA graft copolymer. For sol-gel analysis, the graft copolymers were extracted with chloroform to separate gel fractions. The yield of the polymer was determined gravimetrically. Kinetic studies were evaluated for the polymerization of MMA initiated by RAFT-MIM at 80°C.

2.7 Measurement of Swelling Ratio

The swelling ratio (q_v) of the crosslinked copolymers (18) was carried out by storing 0.2 g of the samples in 50 mL of $CHCl_3$ for 24 h at 20°C. The q_v of the crosslinked copolymers were calculated by the following equations:

q_v = volume of swollen polymer/volume of dry polymer

$$A = \frac{\text{Swollen gel(g)} - \text{Dry gel(g)}}{\text{Dry gel(g)}}$$

$$q = 1 + \frac{A}{d_{\text{solvent}}}$$

The density of dry polymer is taken as 1 gmL^{-1}.

3 Results and Discussion

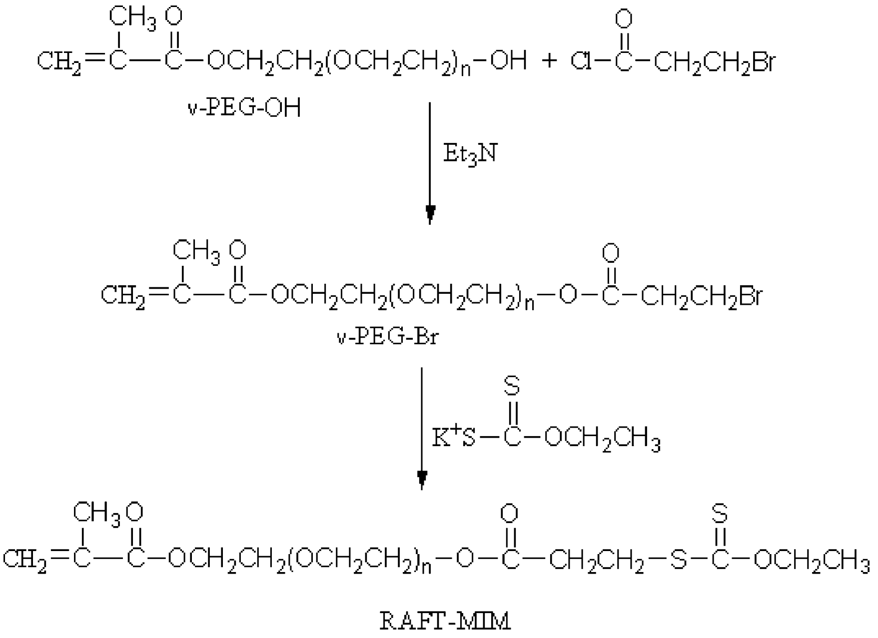
3.1 Synthesis of the RAFT-MIM Initiator

Macromonomeric initiators in a conventional free radical polymerization combine the properties of macroinitiators, macromonomers and macrocrosslinkers. The goal of this work was to synthesize novel macromonomeric initiators and to evaluate kinetic parameters of self condensing polymerization and copolymerization with methyl methacrylate by reversible addition chain transfer method in view of the effect of some different polymerization conditions.

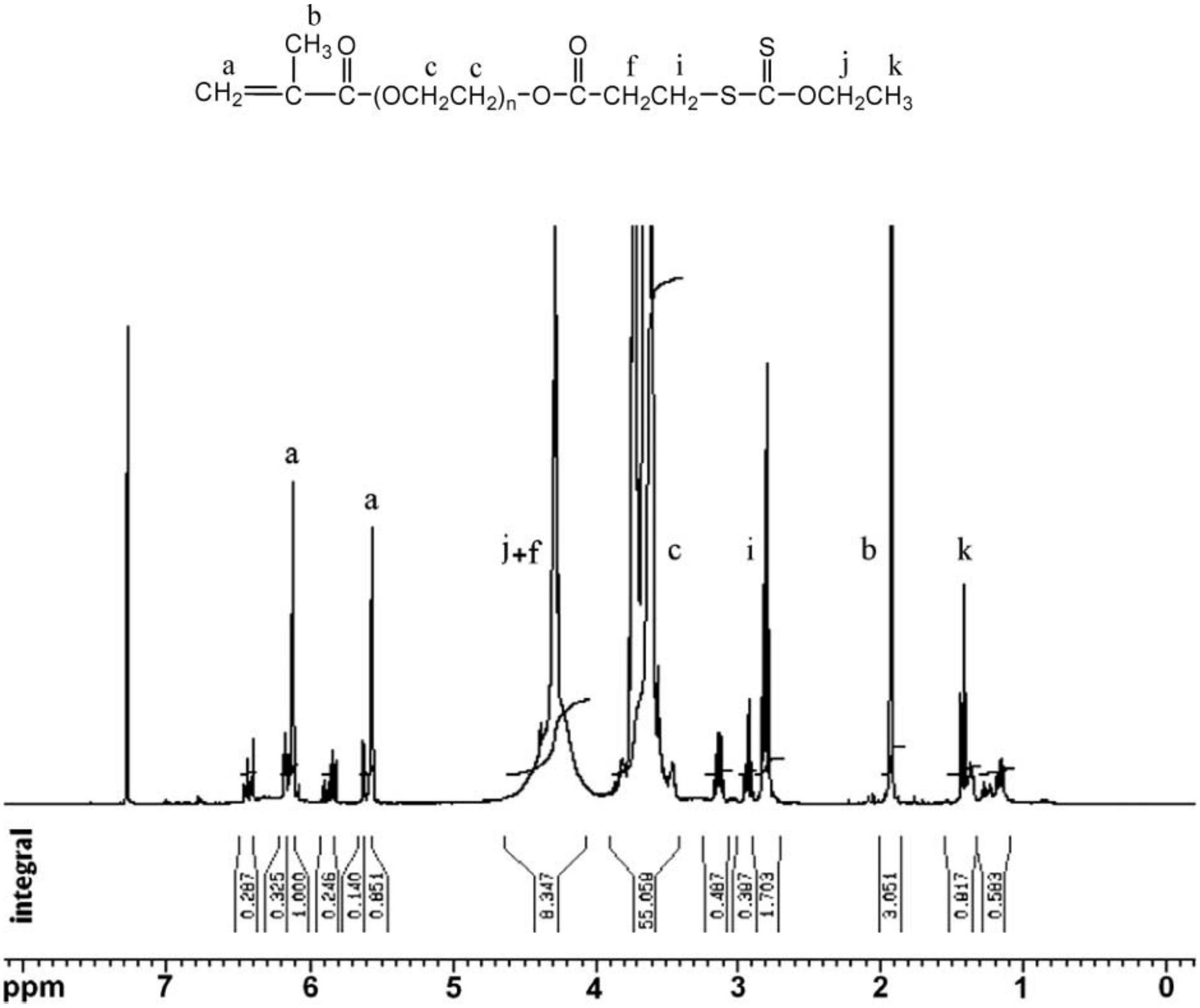
The RAFT-MIM based on PEG having one ethyl xanthogenate and one methacryloyl end was synthesized by the reaction of methacryloyl oxy polyethylene glycol-bromo propionate (v-PEG-Br) with potassium salt of ethyl xanthogenate. The yield of the products was over 80 wt%. The basic outline for the synthesis is shown in Scheme 1. ^{1}H-NMR spectra of the RAFT-MIM is shown in Figure 1. The characteristic signals of the novel macromonomer initiator at 2.8 ppm for –$\mathbf{CH_2}$-S-(i), 1.4 ppm for –O-CH_2-$\mathbf{CH_3}$,4.25 ppm for –O-$\mathbf{CH_2}$-CH_3were observed in ^{1}H-NMR spectrum of RAFT-MIM in Figure 1.

3.2 Self condensing RAFT-MIM Polymerization (Homopolymerization of RAFT-MIM)

The new macromoer initiator, RAFT-MIM, was used in self condensing solution polymerization (homopolymerization). The polymerization process creates two new active sites arising on the second carbon atom of the double bond and on the CH_2 bonding S-C formed by the RAFT catalyst as shown in Scheme 2a. Therefore, homopolymerization of

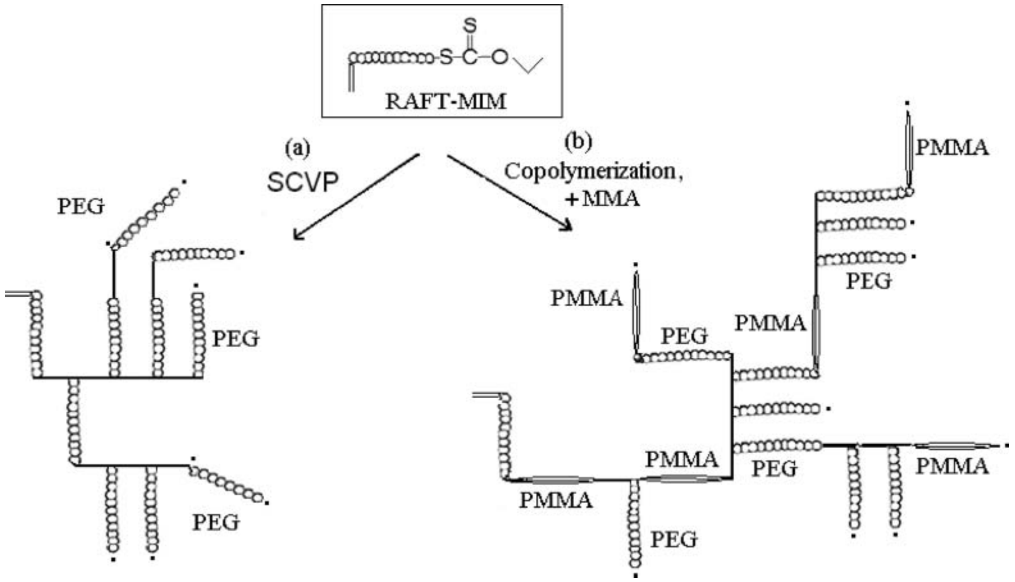


Scheme 1. Reaction pathways in the synthesis of the macromonomer initiator (RAFT-MIM).



$CH_2{=}C(CH_3){-}C({=}O){-}(OCH_2CH_2)_n{-}O{-}C({=}O){-}CH_2CH_2{-}S{-}C({=}S){-}OCH_2CH_3$

Figure 1. ^{1}H-NMR spectra of the RAFT-MIM.



Scheme 2. Self condensation polymerization of the RAFT-MIM (a); polymerization of MMA mediated by RAFT-MIM (b).

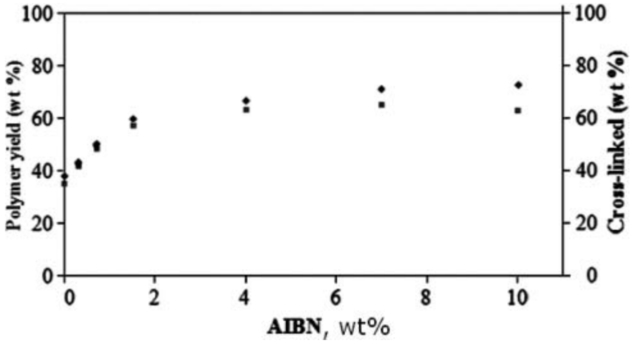


Figure 2. Self condensation RAFT polymerization of the macromonomer initiator (RAFT-MIM) in toluene at 80°C. Dependance of the polymer yield on the amount of AIBN {(AIBN/RAFT-MIM)×100} ♦: total polymer yield, ■: crosslinked polymer fraction, wt%.

the RAFT-MIM leads to branching and then crosslinking via self terminations of the growing radicals. RAFT-MIM is a kind of methacrylate monomer having a PEG side chain with a RAFT agent. Poly (MMA-co-PEG) copolymer was obtained by this way in high yield as a mixture of a branched and cross linked polymer depending on the polymerization temperature, polymerization time and the concentration of the radical source (AIBN). Self condensing RAFT-MIM polymerization was carried out in the presence of AIBN in a range from 0.3 to 10 wt% of RAFT-MIM. Increasing radical source increased the polymer yield with a high crosslinked fraction which is simply separated by sol-gel analysis as we discuss below (Fig. 2). Similarily, increased temperature from 40°C to 80°C also caused an increase in the polymer yield and crosslinked fraction (Fig. 3). We have not observed any noticeable amount of polymer at around under 30°C for 7 h polymerization time because AIBN starts to decompose at a higher temperature than this at around 40°C in order to produce radicals. Lower polymerization temperature (ca. 50°C) causes a lower polymer yield. The swelling degrees of the crosslinked polymers in chloroform were measured to evaluate the crosslinking process in different concentration of the radical source (AIBN). Swelling degrees of the crosslinked polymers were at around 10 for the runs the radical source (AIBN) between from 1 to 10 wt%, while those of runs using less than 1 wt% of AIBN were found to be 20. It is important to say that the crosslinked density of the polymer was changed by the AIBN concentration used in feeding. Because of inverse proportionality of swelling degree and crosslinking density, we can say crosslinking density increases as AIBN wt% increases up to 1.5. The higher concentration of AIBN than 1.5 wt% does not influence on the crosslinking density.

3.3 Polymerization of MMA initiated by RAFT-MIM

The RAFT polymerization of MMA initiated by this novel macromonomeric initiator provided highly branched and crosslinked polymers as in the case of conventional free radical polymerization indicating the characteristic behavior of a macromonomeric initiator as shown in a previous study (5). Crosslinked polymers fraction increases with the increase in the initial macromonomeric initiator. Sol-gel analysis of the graft copolymers was performed by using chloroform extraction. RAFT-MIM concentration and polymerization time were effective to obtain polymers from highly branched to crosslinked. Additionally, the reactivity of the MA end-groups increases the degree of branching and lead to crosslinked polymers. The reaction chart shown in Scheme 2b indicates a typical polymerization by a macromonomer initiator. High conversion of MMA was obtained by the polymerization of MMA initiated with the novel macromer initiator (RAFT-MIM). Figure 4 shows the amount of total and crosslinked polymer formed as a function of polymerization time. As polymerization time increases, cross linked polymer yield increases. After 3 h, 80 wt% of polymer yield was obtained. After this time,

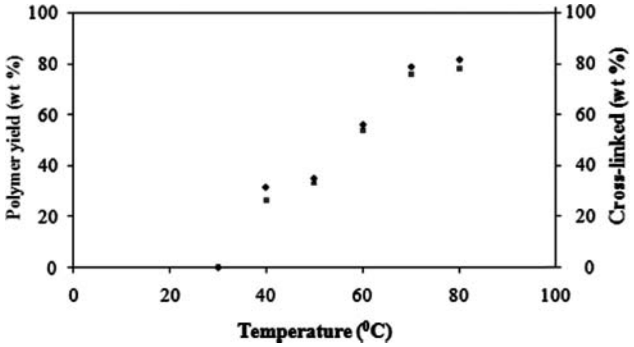


Figure 3. Self condensation RAFT polymerization of the macromonomer initiator (RAFT-MIM). Dependance of the polymer yield on the temperature. (Polym. Time: 7 h, RAFT-MIM: 1.0 g, AIBN: 0.015 g, toluene: 5 mL). ♦: total polymer yield, ■: crosslinked polymer fraction, wt%.

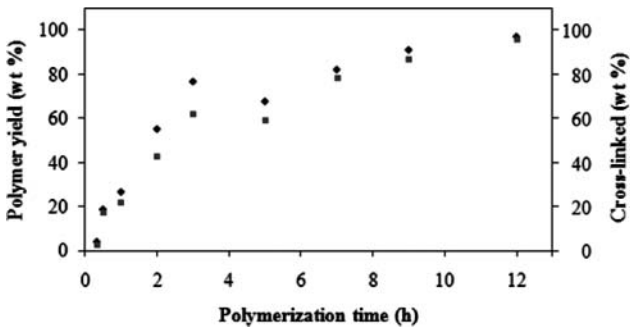


Figure 4. RAFT copolymerization of MMA mediated by the RAFT-MIM in toluene at 80°C. Dependance of the polymer yield on the polymerization time. (RAFT-MIM: 0.3 g, AIBN: 0.007 g, MMA: 2.0 mL (1.87 g), polym. temp: 80°C, toluene: 5 mL). ♦: total polymer yield, ■: crosslinked polymer fraction, wt%.

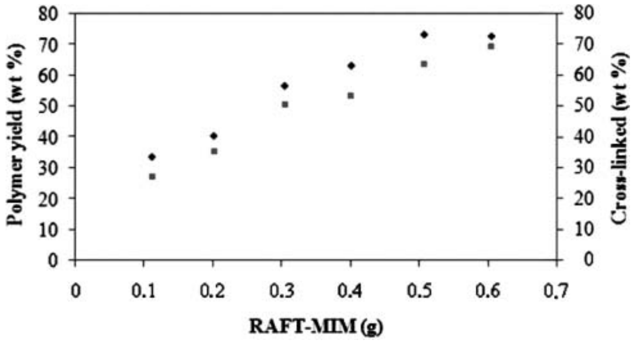


Figure 5. RAFT copolymerization of MMA mediated by the RAFT-MIM in toluene at 80°C. Dependance of the polymer yield on the amount of the macromonomer initiator (RAFT-MIM. (RAFT-MIM/AIBN: 10/1 mol/mol, MMA: 2.0 mL (1.87 g), polym. temp: 80°C, polym. time: 7 h, toluene: 5 mL).♦: total polymer yield, ■: crosslinked polymer fraction, wt%.

polymer yield and crosslinked part gradually increased and after 12 h, the polymer obtained was completely crosslinked (98 wt%). An increase in polymerization time causes an increase in crosslinked fraction.

Keeping the temperature 80°C, solution polymerization of MMA (2 mL) was initiated by RAFT-MIM in range from 0.1 g to 0.6 g. A low amount of initiator caused low polymer yield with a low crosslinked part (Fig. 5). The increased amount of macroinitiator in the reaction mixture leads to the formation of a higher number of active centers. For this reason, more growing macro radicals are formed in the system leading to a high polymer yield containing a high crosslinked part.

To study the effect of monomer concentration on the polymerization kinetics, keeping the amount of RAFT-MIM 0.30 g, polymerization of MMA in changing concentration was carried out. The increasing amount of MMA caused an expected increase in the yield of the graft copolymers (Fig. 6). At higher amounts of MMA, a deviation from normal behavior was observed, which may be attributed to the increase in viscosity of the medium. As the solvent amount increases, the polymer yield decreases, which may be attributed to the decrease in viscosity of the medium (Fig. 7). The polymerization of MMA started at around 50°C; any polymer under this temperature for 7 h polymerization, was not determined (Fig. 8). Higher temperature gave higher yields of crosslinked polymers as expected. Interestingly, the highest soluble-branched polymer fraction was only observed at lower polymerization temperatures. For example, at 50°C, 25 wt% of crosslinked polymer together with 40 wt% of total polymer yield was obtained. Reactive methacrylate end group and a high polymerization temperature (ca. 80°C) could be affective on the crosslinked polymers rather than highly branching PEG-g-PMMA graft copolymers.

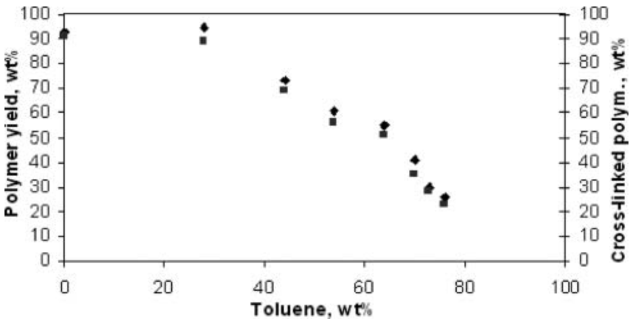


Figure 7. . Solvent effect on the copolymerization of MMA mediated by RAFT-MIM at 80°C. (RAFT-MIM: 0.30 g, AIBN: 0.007 g). ♦: total polymer yield, wt% ■: crosslinked polymer fraction, wt%.

3.4 Kinetic Studies of RAFT Polymerization of MMA

Figure 9 shows a linear relationship between ln (M_0/M) and polymerization time. The plot of ln (M_o/M) vs. reaction time is linear, as expected from a living system,

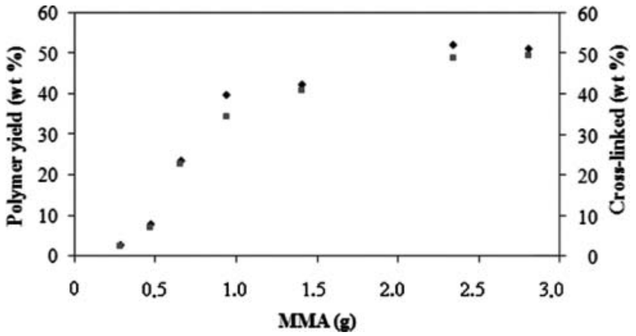


Figure 6. RAFT copolymerization of MMA mediated by the RAFT-MIM in toluene at 80°C. Dependance of the polymer yield on the amount of the MMA. (RAFT-MIM: 0.30 g, AIBN: 0.007 g, polym. time: 7 h, toluene: 5 mL). ♦: total polymer yield, ■: cross-inked polymer fraction, wt%.

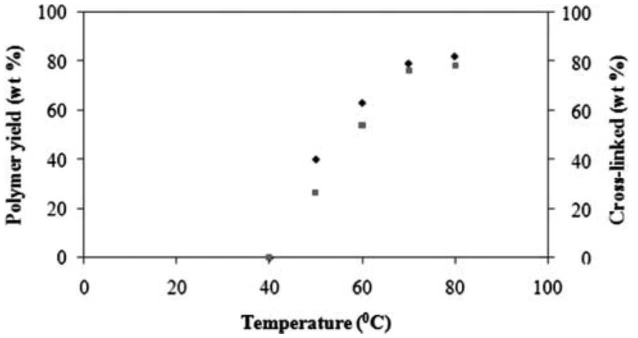


Figure 8. Temperature dependence of polymer yield on the RAFT copolymerization of MMA mediated by RAFT-MIM at 80°C. (RAFT-MIM: 0.30 g, AIBN: 0.007 g, MMA: 2.0 mL (1.87 g), polym. time: 7 h, toluene: 5 mL).♦: total polymer yield, ■: crosslinked polymer fraction, wt%.

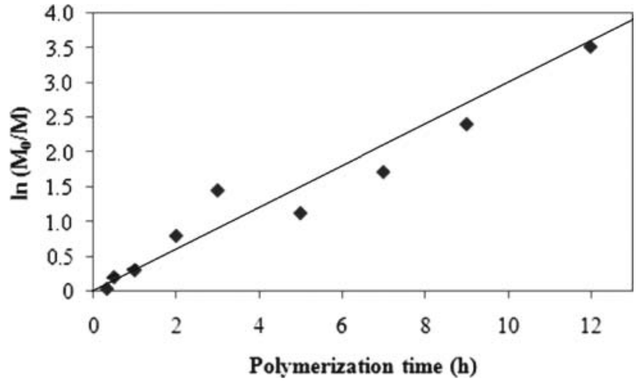


Figure 9. Time dependence of ln (Mo/M) for the RAFT polymerization of MMA mediated by RAFT-MIM at 80°C. (AIBN: 0.07 g, MMA: 2 mL (1.87 g), toluene: 5 mL).

corresponding to first-order kinetics. In the RAFT polymerization, it is well known that k is given in the following equation.

$[M_0]$ and $[M]$ are the total concentrations of the monomer in the beginning and after a polymerization time (t), respectively; k, is the overall rate constant. The overall rate constant, k, was calculated as 7.9×10^{-5} s^{-1} by using the linear part of the plot in Figure 9. It is important to note that the overall polymer yield always follows very closely the crosslinked polymer yield. Perhaps, it can be explained why the yield of hyperbranched polymer are not obtained rather than that of crosslinked polymers in particular for low RAFT-MIM concentration.

3.5 Thermal Analysis of the poly(RAFT-MIM) and PEG-g-PMMA

Thermal analysis of the samples was carried out by taking TGA curves. Thermo gravimetric analysis showed interesting properties of the poly (RAFT-MIM) indicating continuous weight loss starting from 300°C to nearly 430°C with a derivative at 411°C (Fig. 10). This can be attributed to the high miscibility of the polymerizable methacrylate groups of the RAFT-MIM and PEG moities of the crosslinked poly (RAFT-MIM). Whereas, in the case of the crosslinked PMMA-g-PEG graft copolymers, PEG and PMMA blocks had the individual decomposition temperatures as shown in Table 1 (ca. 300°C and 400°C, respectively).

Table 1. Thermal properties of the crosslinked polymers obtained by RAFT-MIM

Polymer Code	*Initial feeding of the RAFT-MIM, wt%*	*Decomp. temp., °C*	
		T_{d1}	T_{d2}
KB-4	21	299	406
KC-1	40	300	394
KC-2	25	295	385
KC-3	18	300	385
KC-4	11	295	385
KC-5	10	295	380
KC-6	52	292	380
KC-7	32	295	375
LB-4	100	-	411

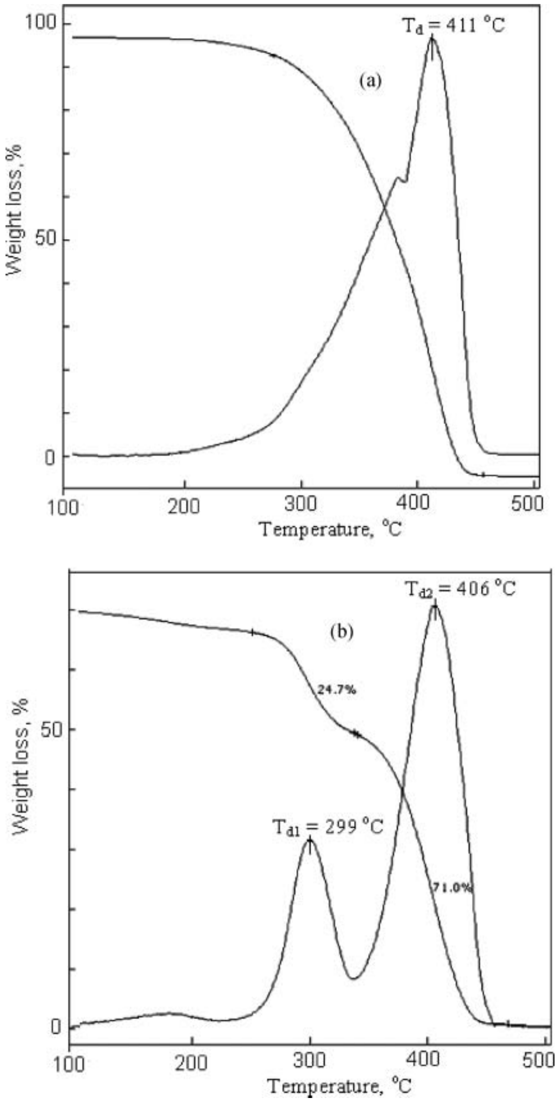


Figure 10. TGA curves of (a) crosslinked polyRAFT-MIM obtained by self condensing polymerized RAFT-MIM (LB-4 in Table 1) and (b) crosslinked poly (MMA-g -RAFT-MIM) (KB-4 in Table 1).

4 Conclusions

A novel RAFT macromonomer, RAFT-MIM is a kind of methacrylate monomer having a PEG side chain with a RAFT agent-xhantegonate unit. RAFT-MIM having very reactive methacrylate end group leads to crosslinked polymers rather than highly branching PEG-g-PMMA graft copolymers. Gelation behavior and kinetics of the RAFT–MIM were studied. RAFT-MIM initiators can be useful to obtain one pot synthesis of gel polymer materials based on PEG for the medical and industrial applications. Basically, controlling the polymerization parameters such as RAFT-MIM concentration and polymerization temperature, RAFT macromonomeric initiators can be promising materials in order to obtain PMMA-co-PEG hyper branched amphiphiles.

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