

Synthesis of Poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) Block Copolymer by Redox Polymerization and Atom Transfer Radical Polymerization

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ABSTRACT

Poly(methyl methacrylate)-b-poly(N-isopropylacrylamide) [PMMA-b-PNIPAM] block copolymers were obtained by a combination of redox polymerization and atom transfer radical polymerization (ATRP) methods in two steps. For this purpose, PMMA macroinitiator (ATRP-macroinitiator) was synthesized by redox polymerization of methyl methacrylate and 3-bromo-1-propanol using Ce(NH₄)₂(NO₃)₆ as a catalyst. The synthesis of PMMA-b-PNIPAM block copolymers was carried out by means of ATRP of ATRP-macroinitiator and NIPAM at 60 °C. The block copolymers were obtained in high yield and high molecular weight. The characterization of products was accomplished by using multi instruments and methods such as nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, gel permeation chromatography, and thermogravimetric analysis.

Keywords: atom transfer radical polymerization; redox polymerization; macroinitiator; block copolymer; methyl methacrylate

ABSTRAK

Kopolimer blok poli(metil metakrilat)-b-poli(N-isopropilakrilamina) [PMMA-b-PNIPAM] telah didapatkan dalam dua tahap melalui kombinasi metode polimerisasi redoks dan polimerisasi radikal transfer atom (atom transfer radical polymerization, ATRP). Dalam hal ini, makroinisiator PMMA (makroinisiator ATRP) disintesis melalui polimerisasi redoks antara metil metakrilat dan 3-bromi-1-propanol menggunakan Ce(NH₄)₂(NO₃)₆ sebagai katalis. Sintesis kopolimer blok PMMA-b-PNIPAM dilakukan dengan menggunakan makroinisiator ATRP dan NIPAM pada 60 °C. Kopolimer blok diperoleh dengan rendemen dan masa molekul yang tinggi. Karakterisasi produk menggunakan berbagai metode meliputi spektroskopi resonansi magnetik inti, spektroskopi infra merah, kromatografi permeasi gel, dan analisis termogravimetri.

Kata Kunci: polimerisasi radikal transfer atom; polimerisasi redoks; makroinisiator; kopolimer blok; metil metakrilat

INTRODUCTION

Recently, many research groups have been working on living-controlled radical polymerization techniques, such as Nitroxide-Mediated Polymerization (NMP) [1], Atom Transfer Radical Polymerization (ATRP) [2] and Reversible Addition/Fragmentation Chain Transfer (RAFT) Polymerization [3]. Controlled radical polymerization techniques are based on radical closing mechanisms and agents [4-6,]. After intensive studies on ionic-living polymerization techniques, it has recently become important to develop free-radical polymerization that can demonstrate the characteristics of living polymerization techniques [7]. Controlled/"living" radical polymerization (CRP) has been enabled the synthesis of polymers which have narrow molecular weight distribution and a well-defined structure because all chains are growing at equal rate, or in other words, the

molecular weight increases linearly with conversion [8-9].

Since Wang and Matyjaszewski suggested the idea of ATRP [10] in 1995, the polymers with low polydispersity index, including poly (methyl) acrylates, styrene, acrylonitrile etc. have been synthesized by using the Cu-based catalytic system ATRP that has many advantages as compared with other CRPs [11-12]. The diversity of the ATRP is proved by its compatibility with a very wide range of monomers and reaction conditions [13-14]. Many redox pairs containing organic and inorganic components as polymerization initiator have been successively used. In these redox initiation systems, free radicals are produced by the oxidation of the substrate, which in turn initiate the polymerization. A kind of redox initiation system, salt of Ce(IV) oxidized a primary alcohol leading to radical formation [15-17].

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The well-defined synthesis of block copolymers is a significant topic in macromolecular chemistry [18]. Block copolymers that provide particular combinations of physical properties are the nearly appropriate materials for different purposes [19]. Macroinitiators have been broadly used for designing diverse block copolymers via a radical set off process [20-21]. Synthesis of block copolymers have recently been successful in the by the combination of different techniques. Block copolymers that have excellent physical properties are some of the most important polymeric materials used in technological applications and theoretical research because of their exceptional properties based on micro-phase separation [22-26]. Block copolymers are largely used as resistant material. There are largely number of superior articles published on this subject [27-30].

We have reported RAFT-ROP and ATRP-ROP in our previous studies. They are combination of different techniques for synthesis of block and graft copolymers. In this work, 3-bromo-1-propanol initiator was used, which allows different steps for both redox polymerization and ATRP polymerization. For this purpose, PMMA macroinitiator (ATRP-macroinitiator) was synthesized by redox polymerization of methyl methacrylate (MMA) and 3-bromo-1-propanol. Ammonium cerium(IV) nitrate, $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$, was used as a catalyst for the redox polymerization. The synthesis of poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) PMMA-*b*-PNIPAM block copolymers was carried out by means of ATRP of ATRP-macroinitiator and NIPAM at 60 °C. Characterizations of the products are discussed in detail.

EXPERIMENTAL SECTION

Materials

3-Bromo-1-propanol, methyl methacrylate (MMA), *N*-isopropylacrylamide (NIPAM) and copper(I) bromide (CuBr) were obtained from Aldrich. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA) was supplied by Fluka. Methanol, *N,N*-Dimethylformamide (DMF) were obtained from Sigma-Aldrich and used as received. All other chemicals were reagent grade and used as received.

Instrumentation

The molecular weights and molecular-weight distributions were measured with Polymer Labs PL-GPC 220 and Malvern Viscotek RI-UV-GPC max gel-permeation chromatography (GPC) with THF as the solvent. A calibration curve was generated with three

polystyrene standards: 2960, 50400, and 696500 Da, of low polydispersity. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded with a PerkinElmer Spectrum 100 Model FTIR spectrometer in transmissive mode and scan rate from 4000 to 650 cm^{-1} . ^1H -nuclear magnetic resonance (^1H -NMR) spectra of the samples were recorded using a Bruker Ultra Shield Plus, ultra-long hold time 400 MHz NMR spectrometer in CDCl_3 as the solvent, with tetra methylsilane as the internal standard. Thermal analysis measurements of the polymers were carried out under nitrogen using a Perkin Elmer Pyris 1 TGA and Spectrum thermal analyzer to determine thermal degradation. Differential scanning calorimetry (DSC) measurements were carried out by using a Perkin Elmer Diamond DSC series thermal analysis system. Dried sample was heated at a rate of 10 °C/min under nitrogen atmosphere.

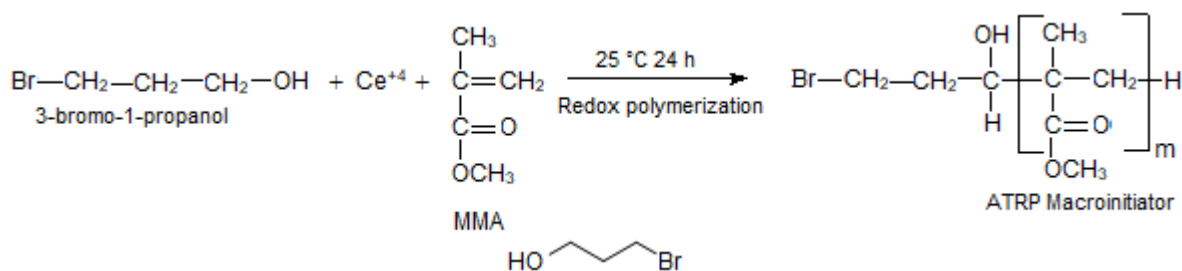
Procedure

Synthesis of ATRP-macroinitiator by redox polymerization

For redox polymerization of MMA, 30 mL of MMA, 0.5 g of 3-bromo-1-propanol, and 2 g of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (as a catalyst) were placed into a 100 mL of flask equipped with a magnetic stirrer. Argon was subsequently purged into the tube through a needle. The flask was placed in water bath at 25 °C for 24 h. After the reaction, the reaction mixture was poured into an excess of methanol to precipitate ATRP-macroinitiator (PMMA-Br). ATRP-macroinitiator was dried under vacuum at room temperature for three days and was defined gravimetrically.

Atom Transfer Radical Polymerization for PMMA-*b*-PNIPAM block copolymers

PMMA-*b*-PNIPAM block copolymers were prepared by atomic transfer radical polymerization (ATRP) using the previously prepared PMMA-Br as the initiator. NIPAM, ATRP-macroinitiator, PMDETA and CuBr were charged separately into a Pyrex tube and were dissolved in DMF (The amounts of chemicals used in the polymerization are shown in Table 1 and 2). Next, argon was purged into the tube through a needle. The tube was tightly capped with a rubber septum and was placed in an oil bath at 60 °C for 16 h. After the polymerization, the reaction mixture was poured into an excess of methanol to precipitate PMMA-*b*-PNIPAM block copolymer. The polymers were dried at 40 °C under vacuum for three days. The yield of the copolymer was determined gravimetrically.



Scheme 1. Reaction pathways in the synthesis of ATRP macroinitiator

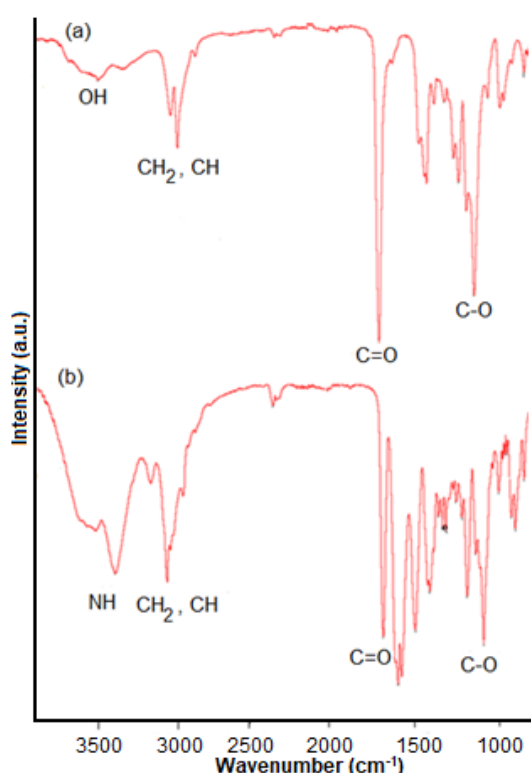


Fig 1. FTIR spectra of (a) ATRP-macroinitiator, and (b) PMMA-*b*-PNIPAM block copolymers

RESULT AND DISCUSSION

Synthesis of ATRP-Macroinitiator

ATRP-macroinitiator was synthesized by redox polymerization of MMA, and 3-bromo-1-propanol using $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ as a catalyst. The gravimetric conversion obtained from the weight of ATRP-macroinitiator was approximately 50 wt.%. The basic outline for the synthesis of ATRP macroinitiator is shown in Scheme 1.

The FTIR spectrum of ATRP-macroinitiator in Fig. 1(a) shows 3434 cm^{-1} for $-\text{OH}$ groups, 2890 cm^{-1} for aliphatic $-\text{CH}_2$ and $-\text{CH}$ groups, 1728 cm^{-1} for $-\text{C}=\text{O}$ groups, and 1060 cm^{-1} for $-\text{O}-\text{C}$ groups.

The $^1\text{H-NMR}$ spectrum of ATRP-macroinitiator in Fig. 2(a) shows the 3.6 ppm for $-\text{OCH}_3$ protons of PMMA

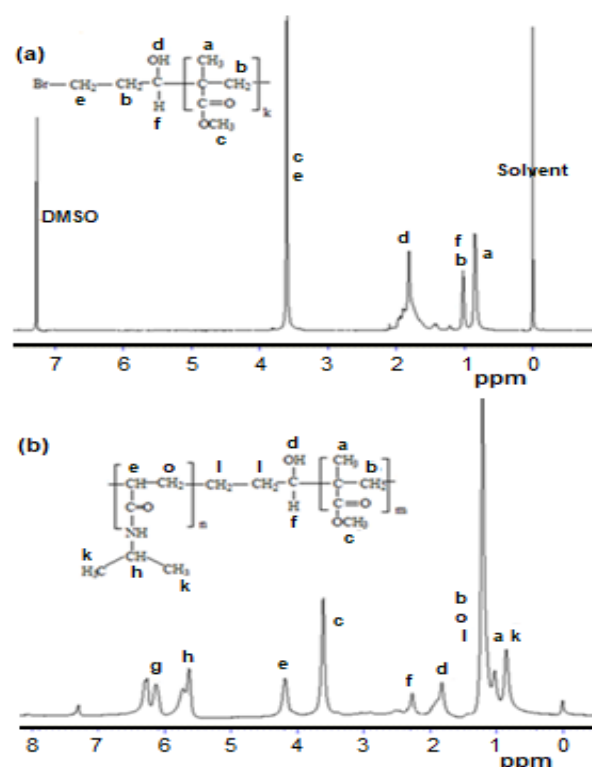


Fig 2. $^1\text{H-NMR}$ spectra of (a) ATRP-macroinitiator, and (b) PMMA-*b*-PNIPAM block copolymers

segment and for $-\text{BrCH}_2$ protons of 3-bromo-1-propanol segment, 1.8 ppm for $-\text{OH}$ protons of 3-bromo-1-propanol segment, 1.0 ppm $-\text{CH}_2$ protons of PMMA segment, $-\text{CH}$ protons of 3-bromo-1-propanol segment, and 0.8 ppm $-\text{CH}_3$ protons of PMMA segment.

Atom Transfer Radical Polymerization for PMMA-*b*-PNIPAM block copolymers

Atom Transfer Radical Polymerization of NIPAM initiated by ATRP-macroinitiator provided PMMA-*b*-PNIPAM block copolymers. The basic outline for the synthesis of block copolymer is shown in Scheme 2. The effect of monomer and initiator concentration on the block copolymerization in the presence of ATRP macroinitiator by the application of ATRP process have

been studied. The results of the copolymerization of NIPAM are shown in Table 1 and Table 2. The monomer conversion was calculated from the weight of recovered polymer. The conversion of the monomer was between 19.08 and 84.98 wt.%. Increase in the molecular weights of the copolymers as compared with molecular weight of the initiator can confirm block copolymer formation.

FTIR spectrum of PMMA-*b*-PNIPAM block copolymer in Fig. 1(b) shows the signals at 3800 cm^{-1} for -NH groups, 2890 cm^{-1} for aliphatic -CH₂, -CH groups, 1728 cm^{-1} for -C=O groups, 1060 cm^{-1} for -O-C groups.

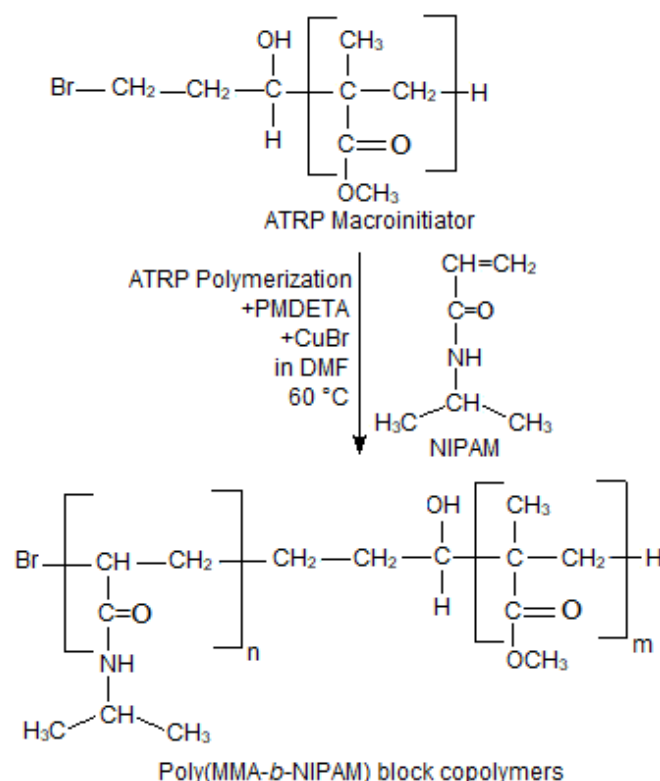
The ¹H-NMR spectrum of the block copolymers in Fig. 2(b) shows 0.8 ppm for aliphatic -CH₃ protons of PNIPAM and PMMA segment, 1.2 ppm for aliphatic -CH₂ protons of PMMA segment, -CH₂ protons of 3-bromo-1-propanol segment and -CH₂ protons of PNIPAM segment, 1.8 ppm for -OH protons of 3-bromo-1-propanol segment, 2.2 ppm -CH protons of 3-bromo-1-propanol segment, 3.6 ppm for -OCH₃ protons PMMA segment, 4.3 ppm for -CH of PNIPAM segment, 5.7 ppm -CH of PNIPAM segment, and 6.3 ppm for -NH protons PNIPAM segment.

Dependence of NIPAM concentration on number average molecular weight (M_n) for the copolymerization is shown in Table 1. Relatively, increasing the amount of monomers also causes an increase in both the yield and the molecular weights of the copolymers as expected (Table 1).

Dependence of ATRP macroinitiator concentration on number average molecular weight (M_n) for the block copolymerization is shown in Table 2. Increasing the amount of ATRP macroinitiator causes an increase in the molecular weights of the copolymer. Interestingly, the value of M_n can only decrease if new chains are generated. However, that is not in accordance with a controlled polymerization. Increased amounts of initiator in the reaction mixture lead to the formation of a higher number of active centers. Consequently, increased numbers of growing radicals are formed in the system. Hence, it may be expected that they have shorter PNIPAM segments, which is confirmed by a decrease in the molecular weights of the block copolymers, as shown in Table 2. The same situation was also observed

in our previous articles [9,11]. Furthermore, dependence of ATRP macroinitiator concentration on conversion (wt.%) for the block copolymerization is also shown in Table 2. Higher amounts of ATRP macroinitiator cause higher polymer yield as expected.

The Mw/Mn values of the block copolymers are between 2.03 and 2.17 (Table 1 and 2). Because of the use of a macroinitiator having very broad molecular weight distribution, Mw/Mn values of the block copolymers are relatively higher than expected. All the block copolymers have GPC chromatograms. Fig. 3



Scheme 2. Reaction pathways in the synthesis of PMMA-*b*-PNIPAM block copolymers

Table 1. The effect of the amount of the monomer on copolymerization for PMMA-*b*-PNIPAM block copolymers

Code	Poly(MMA) (g)	NIPAM (g)	CuBr (g)	PMDETA (g)	Yield (g)	Conv. (wt.%)	M _{n,GPC}	M _w /M _n
MG-1	0.012	0.50	0.016	0.08	0.334	65.23	57,500	2.14
MG-2	0.012	0.75	0.016	0.08	0.540	70.86	59,800	2.13
MG-3	0.012	1.00	0.016	0.08	0.860	84.98	57,700	2.17

Table 2. The effect of the amount of ATRP macroinitiator on polymerization for PMMA-*b*-PNIPAM block copolymers

Code	Poly(MMA) (g)	NIPAM (g)	CuBr (g)	PMDETA (g)	Yield (g)	Conv. (wt.%)	M _{n,GPC}	M _w /M _n
M-1	0.024	0.50	0.016	0.08	0.100	19.08	65,700	2.04
M-2	0.048	0.50	0.032	0.16	0.180	32.85	67,500	2.03
M-3	0.096	0.50	0.064	0.32	0.200	34.00	58,300	2.16

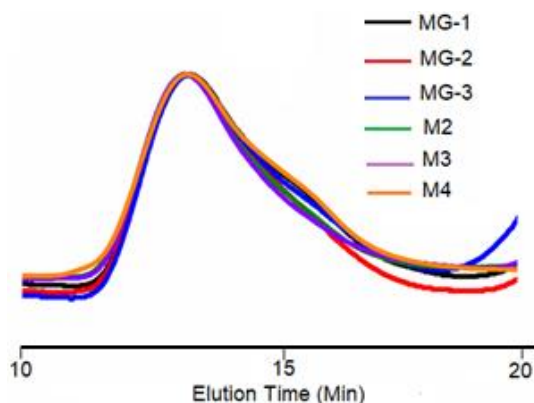


Fig 3. GPC curve of PMMA-*b*-PNIPAM block copolymers

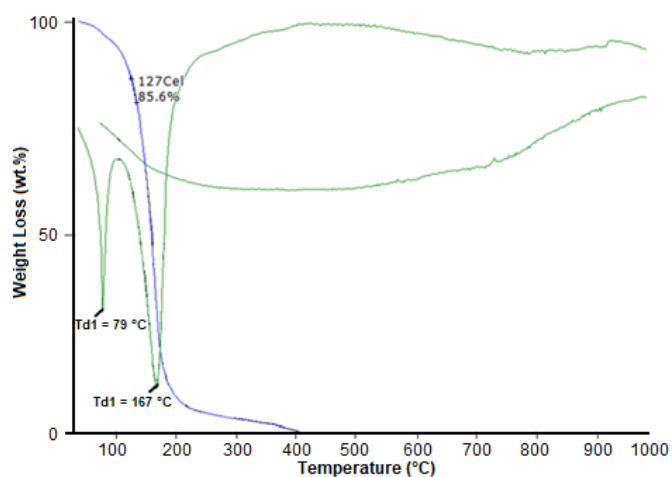


Fig 4. TGA curves of PMMA-*b*-PNIPAM block copolymers (MG-2 in Table 1)

shows the unimodal GPC curves of the graft copolymers (MG-1, MG-2, and MG-3 in Table 1, and M-2, M-3 and M-4 in Table 2).

Thermal analysis of the samples was carried out by taking TGA curves. TGA showed interesting properties of the block copolymer indicating continuous weight loss starting from 10 °C to 500 °C. In the case of PMMA-*b*-PNIPAM block copolymer (MG-2), PNIPAM, PMMA blocks had the individual decomposition temperatures as shown in Fig. 4 [ca. 79 and 167 °C, respectively].

CONCLUSION

A macromonomer initiator (ATRP macroinitiator) was synthesized by redox polymerization. ATRP macroinitiator was used as initiator for ATRP polymerization which is one of the controlled radical polymerization methods. Block copolymers synthesized by methods such as ATRP, RAFT and NMP have applied in various medical and biomedical processes. Macro ATRP initiator including poly-MMA has

demonstrated the characteristic macroinitiator behavior in the copolymerization of NIPAM. A set of synthesis, ATRP polymerization conditions of the block copolymers poly(MMA-*b*-NIPAM), were obtained. The block copolymers were relatively obtained in high yield and molar weight. In this study, poly(MMA-*b*-NIPAM) block copolymers have added via ATRP and Redox polymerization techniques. The proposed procedure for the preparation of block copolymers is simple and efficient than conventional free radical polymerization. The synthesized macroinitiator, as an initiator for different polymerization techniques such as RAFT polymerization and "CLICK" Chemistry, can be used to synthesize block copolymers.

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