

Atom Transfer Radical Polymerization of Methyl Acrylate with PVAc-CCl₃ Macroinitiator and a Novel Synthesis of Block Terpolymers of PVAc-*b*-poly(MA-co-MMA)

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ABSTRACT

The atom transfer radical polymerization of methyl acrylate (MA) with poly vinylacetate telomer (PVAc-CCl₃) as a macroinitiator and CuCl/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) as a catalyst was successfully carried out in the bulk. The reaction temperature had a direct effect on the conversion and apparent propagation rate constant (K_p^{app}) of MA polymerization reaction. In this study the apparent enthalpy of activation and enthalpy of equilibrium are 83.68 and 65.98 kJ/mol, respectively, for this polymerization reaction. In a similar polymerization system, PVAc-CCl₃ macroinitiators were used with several molecular weights, it was found that the rate of polymerization was independent of molecular weight of the macroinitiator, but the percentage of telomer used had a direct effect on the K_p^{app} of this polymerization. In all reactions studied the first order kinetics showed a linear dependence, indicating a constant number of propagating species during the polymerization. Kelen-Tüdös and Fineman-Ross linear methods were used to determine monomers chemical reactivity of methyl acrylate and methyl methacrylate in atom transfer radical polymerization. The synthesized block copolymers showed a relatively narrow molecular weight distribution ($1.1 < PDI < 1.3$) specific of the controlled polymerization reactions of ATRP. A broadening trend of PDI in block copolymers was observed with polymerization temperature. This work shows that it is possible to synthesis the novel block terpolymers of PVAc-*b*-poly(MA-co-MMA) with further narrowing in PDI which is shows that there is a chemical selectivity within the mechanism of ATRP.

Key Words:

atom transfer radical polymerization;
methyl acrylate;
macroinitiator;
chemical selective ATRP;
terpolymer.

INTRODUCTION

Controlled/living radical polymerization (CLRP) is the best method for the preparation of polymers with controlled molecular weights, chain architecture, and low polydispersity [1-2]. Among three kinds of CLRP methods, the transition-metal-catalyzed ATRP seems to be the most effective system to control radical polymerization of styrenes,

acrylates, methacrylates, and methacrylamides with transition metals catalyst such as copper, iron, nickel, cobalt, and molybdenum [3-4]. Because of its radical nature, ATRP is a successful method for controlling the degree of branching in vinyl polymerization in order to control the macroscopic properties of polymers [5]. With ATRP, func-

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tionality of final polymers and architecture can be combined resulting in multifunctional polymers such as block copolymers and hyperbranched polymers [6].

Recently, some experiments have been used to produce polymers with well-controlled architecture in the synthesis of several block copolymers by ATRP from macroinitiators which were synthesized by ring opening polymerization (ROP) [7,8], conventional free radical polymerization (CFRP) [9-13], and atom transfer radical polymerization (ATRP) [14-17] methods.

In block copolymers with different monomers, the morphology of the polymer chain is influenced not only by the overall molecular weight and the mole fraction of each block, but also by the sequence of the blocks with different properties, applications, and functionality. For example, synthesis and properties of amphiphilic vinyl acetate triblock copolymers [13], synthesis of poly(ethylene oxide)-block-poly(methyl methacrylate)-block-polystyrene triblock copolymers [7], novel block copolymers of (meth)acrylates with vinyl acetate as macroinitiator [11], tri and penta block copolymers of MMA, nBMA and lauryl methacrylates at ambient temperature [14], and grafting of PMMA from poly(ethylene-co-vinyl acetate) copolymer [12] have been investigated with ATRP.

ATRP has not yet been successful in polymerization of the vinyl acetate (VAc) monomer because of either relatively strong carbon-halogen bonds or low radical reactivity of this monomer [18]. Therefore a combined method of CFRP and ATRP has been applied to synthesis the block copolymers of polyvinyl acetate (PVAc) as a macroinitiator by other monomers such as methylacrylate [9]. Polyvinyl acetate with predictable molecular weight and low polydispersity (1.1-1.3) was synthesized by cobalt-mediated radical polymerization of vinyl acetate monomer [19].

The main purpose of this paper is the atom transfer radical polymerization of PVAc-CCl₃ macroinitiator with methyl acrylate (MA) and methyl methacrylate (MMA). Two linear methods of Kelen-Tüdös and Fineman-Ross are employed for determination of monomers chemical reactivity of MA and MMA. The polymerization temperature effect on the monomer conversion and apparent propagation rate constant of MA monomer with CuCl/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) catalyst was used to determine

the apparent enthalpy of activation and enthalpy of equilibrium. The effect of molecular weight of macroinitiator on ATRP was used to study the chemical selectivity of macroinitiator toward MA monomer. Characterization of molecular structure, number average molecular weight, and molecular weight distribution are also reported for novel terpolymers and several block copolymers by ¹HNMR spectroscopy, FTIR spectrometry, and gel permeation chromatography (GPC) techniques.

EXPERIMENTAL

Materials

Methyl acrylate (MA) (Merck, 99.9%) and methyl methacrylate (MMA) (Merck, 99.9%) were passed from the basic alumina column over calcium hydride (CaH₂). CuCl (Merck, 97%) was purified by washing with glacial acetic acid (three times), ethanol, and diethyl ether in successive. The dried catalysts under nitrogen were used in reactions. PMDETA (Merck, 99.8%) and tetrahydrofuran (THF) were used as received. PVAc-CCl₃ telomer was synthesized by telomerization of VAc monomer with chloroform. After the reaction, unreacted monomer and chloroform were evaporated at room temperature. Tetrahydrofuran was then added to produce the telomer and then, the mixture refluxed for 5 h to decompose traces of unreacted initiator. Finally THF was evaporated and the polymer was dried under vacuum at 50°C up to a constant weight. The dried polymer was used for determination of molecular structure by ¹HNMR, FTIR, and GPC techniques [9].

Characterization

The ¹HNMR spectra of polymer and copolymer were recorded in CDCl₃ with a Bruker DRX500 spectrometer operated at 400 and 500 MHz. Infra-red spectra were obtained on a Bruker IFS 48 Fourier transform infrared (FTIR) spectrometer. Molecular weight and its distribution (MWD) were measured by a Waters 150C gel permeation chromatography (GPC) in THF at 35°C and 1 mL/min equipped with a refractive index detector and a 10⁴, 10³ and 500 Å set of ultrastryrogel columns.

Atom Transfer Radical Polymerization

A required amount of CuCl was introduced to a glass tube equipped with a magnetic stirrer. The glass tube

was sealed with a rubber septum and was cycled between vacuum and nitrogen for three times. The mixtures containing MA or MMA, macroinitiator (PVAc-CCl₃ telomer), and ligand (PMDETA) were degassed by nitrogen purging for 20 min before adding to the glass tube. The freeze-pump-thaw cycle was carried out three times to remove oxygen from the glass tube and sealed under vacuum. The sealed tube was immersed in a pre-heated oil bath at the desired temperature. The tube was then removed from oil bath and reaction mixture was dissolved in THF, filtered and dried under vacuum at 50°C to a constant weight and conversion was determined gravimetrically.

The dried polymer or copolymer was redissolved in THF and passed through a neutral alumina column to remove the remaining copper catalyst. The sample was then dried again under vacuum up to a constant weight and studied by ¹HNMR spectroscopy, FTIR spectrometry and gel permeation chromatography (GPC) techniques.

RESULTS AND DISCUSSION

Preparation of Macroinitiators

Monofunctional initiators were prepared via conventional free radical polymerization of vinyl acetate monomer with chloroform as a solvent or telogen and AIBN as an initiator in solution at 60°C. In this study three kinds of PVAc-CCl₃ as macroinitiator were used in atom transfer radical polymerization of MA, synthesis of AB block copolymers, and chemical selectivity of MA and MMA monomers.

From the results of ¹HNMR spectroscopy and GPC of macroinitiators of No. 1, 2, and 3, the average number molecular weights and polydispersities and telomer percent are 3292 g/mol, 1.92, and 79%; 2432 g/mol, 1.77; and 81%, and 1656 g/mol, 1.7, and 79%, respectively. [9]. The telomere percent of macroinitiators were calculated from the signal intensity of methylene protons of the first vinylacetate unit in the neighbours of CCl₃ functionality (I_a) or C(CH₃)₂CN functionality (I_b) of telomere or polymer and from the eqn (1) [9]

$$\text{Telomer (\%)} = I_a / (I_a + I_b) \quad (1)$$

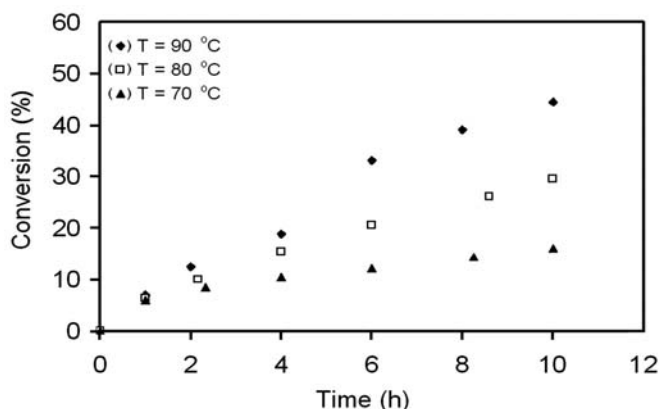


Figure 1. Conversion vs. reaction time in bulk polymerization of MA via ATRP at three temperatures. ([MA]₀ / [Ligand]₀ / [CuCl]₀ / [PVAc-CCl₃]₀ = 100 / 2 / 1 / 1 (M_{n, macroinitiator} = 2432 g/mol, PDI = 1.77))

Effect of Polymerization Temperature

The effects of polymerization temperature on the conversion and apparent rate of propagation of methyl acrylate (MA) monomer in the bulk system catalyzed by CuCl/PMDETA and initiated by PVAc-CCl₃ macroinitiator over a temperatures range of 70-90°C are shown in Figures 1 and 2. The monomer conversions increase with reaction temperature.

The linear kinetic plots of Ln[M]₀/[M] versus time indicate that polymerizations are of first-order with respect to the monomer concentration and suggest that the number of active species is constant. The apparent propagation rate constant (K_p^{app}) of MA monomer in

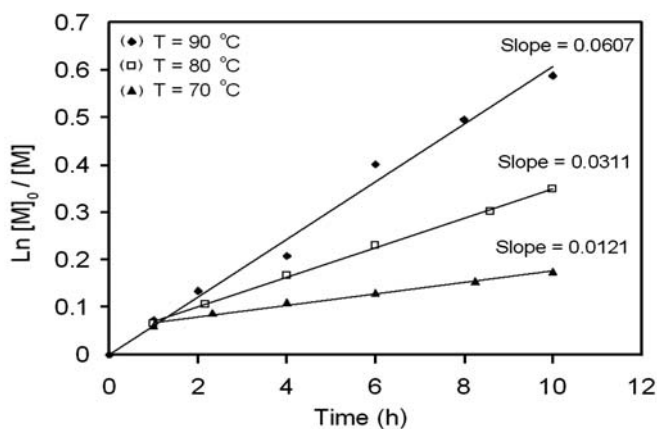


Figure 2. Effect of polymerization temperature on kinetic plots of ATRP of MA in bulk. ([MA]₀ / [Ligand]₀ / [CuCl]₀ / [PVAc-CCl₃]₀ = 100 / 2 / 1 / 1 (M_{n, macroinitiator} = 2432 g/mol, PDI = 1.77))

Table 1. Effect of temperature on the concentration of the propagation radical during the bulk ATRP of MA.

Temperature (°C)	K_p ($\times 10^4$ L/mol.s)	K_p^{app} ($\times 10^{-6}$ s $^{-1}$)	$[P^\circ]$ ($\times 10^{-10}$ mol/L)
90	4.82	16.86	3.5
80	3.64	8.64	2.37
70	2.70	3.36	1.24

$[MA]_0 / [Ligand]_0 / [CuCl]_0 / [PVAc-CCl_3]_0 = 100 / 2 / 1 / 1$, $M_{n, macroinitiator} = 2432$ g/mol, PDI = 1.77

ATRP is calculated by eqn (2) [22].

$$\ln\left(\frac{[M]_0}{[M]}\right) = K_p K_{eq} \frac{[PVAc-CCl_3]_0 \times [CuCl]}{[CuCl_2]} t = K_p^{app} \times t \quad (2)$$

The apparent propagation rate constants (K_p^{app}) increase with reaction temperature [20-21] from 0.0121 to 0.0607. In this process, rate constant for radical propagation and the atom transfer equilibrium constant may have increased [3].

The K_p^{app} values of the ATRP systems at 80 and 70°C are relatively high at the beginning of the reaction but decrease sharply after about 1 h of the reaction. This is probably related to the different reactivity between the PVAc-CCl₂-Cl alkyl halide and acrylic ones (PVAc-CCl₂-MA-Cl) and the different equilibrium constants between the dormant species and their corresponding radical species (tertiary radical and secondary radicals).

Figure 3 shows the Arrhenius plot of $-\ln K_p^{app}$ versus $1/T$ obtained from the experimental results in Figure 2. From the slope of the plot, an apparent enthalpy of activation (E_{app}) of 83.68 kJ/mol was derived. According to eqn (3) [20-21], with $E_{prop} = 17.69$ kJ/mol for MA monomer [23], an enthalpy of equilibrium (E_{eq}^0) of 65.98 kJ/mol was obtained for the ATRP of MA catalyzed with CuCl/PMDETA and PVAc-CCl₃ as a macroinitiator.

$$E_{eq}^0 = E_p^{app} - E_{prop} \quad (3)$$

This value is higher than the corresponding values for St ($E_{eq}^0 = 56.06$ kJ/mol for Cl-mediated) or MMA ($E_{eq}^0 = 40.58$ kJ/mol for Cl-mediated) [24]. It has been suggested that this difference is too large to be attributed to substituent effects on the energy associated with cleavage of the carbon-halogen bonds and may originate in the variation of the catalyst structure with solvent and temperature [24].

The steady state radical concentrations were calculated for ATRP of MA at 70, 80 and 90°C on the basis of eqn (4) [21] and the propagation rate constants of MA at different temperatures [23]. The results are shown in Table 1 which indicates steady state radical concentrations increase with reaction temperature.

$$K_p^{app} = k_p [P^\circ] \quad (4)$$

$$\ln K_p = 20.72 - 3608.4/T \text{ (K)} \quad (\text{for MA monomer [23]}) \quad (5)$$

The theoretical and experimental average number molecular weight, polydispersity, and reaction condition of block copolymers which were synthesized at three temperatures 70, 80 and 90°C are shown in Table 2. In block copolymerization reaction of MA with macroinitiator, the polydispersities of synthesized block copolymers were narrowed from 1.77 in macroinitiator to 1.14-1.26 in block copolymers. A continuous exchange reaction in ATRP has been suggested for this process [3]. Furthermore, we suggest that the equilibrium process within the mechanism of ATRP is perhaps responsible for the selectivity and formation of a monodisperse

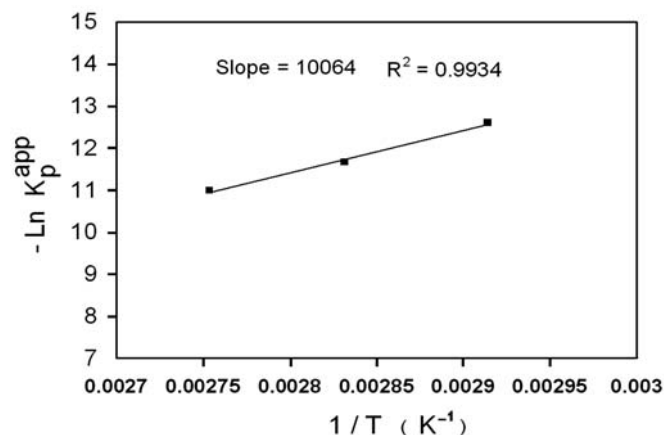


Figure 3. Plot of $-\ln K_p^{app}$ vs. $1/T$ for bulk ATRP of MA. ($[MA]_0 / [Ligand]_0 / [CuCl]_0 / [PVAc-CCl_3]_0 = 100 / 2 / 1 / 1$ ($M_{n, macroinitiator} = 2432$ g/mol, PDI = 1.77))

Table 2. Effects of temperature on ATRP of MA using CuCl as catalyst and PVAc-CCl₃ as macroinitiator.

Reaction temperature (°C)	Time (h)	Conversion (%)	M _{n, theory} ¹	M _{n, GPC} ²	PDI ²
70	10	14.5	3680	3210	1.14
80	10	29.1	4937	3370	1.16
90	10	43	6134	3790	1.26

[MA]₀/[Ligand]₀/[CuCl]₀/[PVAc-CCl₃]₀ = 100 / 2 / 1 / 1, M_{n, macroinitiator} = 2432 g/mol, PDI = 1.77. ⁽¹⁾ Calculated with this equation: M_{n,theory}=M_{n,macroinitiator} + Conversion × M₀, and M₀= 86.09 g/mole. ⁽²⁾ From PS-calibrated GPC.

polymer in this process. Table 2 shows that the average number molecular weights of block copolymers also increase with the increase of temperature and conversion. The polydispersities of block copolymers also increase slightly with temperature [25]. At lower conversions and temperature the theoretical molecular weight of the block copolymer is closer to measured molecular weight by GPC. But at higher conversions the difference is significant. This can be attributed to a difference in hydrodynamic volume between polystyrene used as a standard in calibration of the columns and block copolymers [10].

The extend of chemical selectivity of PVAc-CCl₃ macroinitiator in this copolymerization is evident in GPC results of PVAc-CCl₃ (PDI = 1.77) as compared to PVAc-*b*-PMA (PDI = 1.16) in Figure 4.

Effect of the Molecular Weight of the PVAc-CCl₃ as Macroinitiator

To confirm these results, the ATRP of MA was conducted using three different molecular weights of macroini-

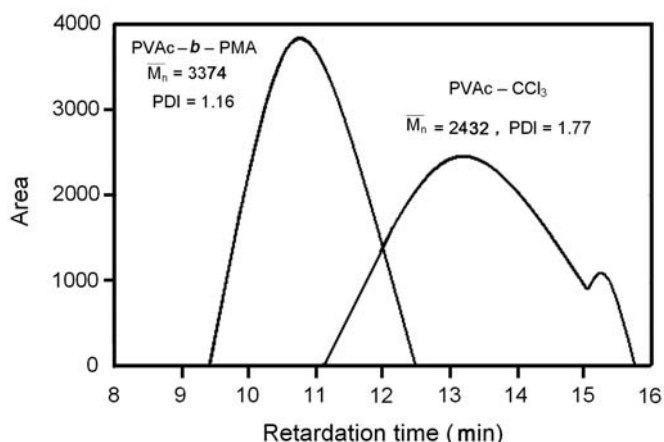


Figure 4. GPC Chromatograms of synthesized PVAc-CCl₃ macroinitiator and PVAc-*b*-PMA block copolymer.

tiators. The copolymerization was carried out at 80°C in bulk. The number average molecular weight of three macroinitiator of No. 1, 2, and 3 were 1656, 2432, and 3292. In Figure 5 the copolymerization shows a first order kinetics with respect to monomer concentration. It is suggested that the radical concentration remains constant during the reaction and termination reaction is negligible. Therefore, the apparent propagation rate constants (K_p^{app}) of the early reactions are independent of the molecular weight of macroinitiator [8]. But at moderate conversion the effect of macroinitiator is more apparent.

The theoretical and experimental molecular weight and PDI of MA block copolymers and polymerization reaction conditions are shown in Table 3. This Table shows that the polydispersities of the block copolymers are lower than macroinitiators. At moderately low conversion, the macroinitiator with lower average number molecular weight, is apparently more selective than the

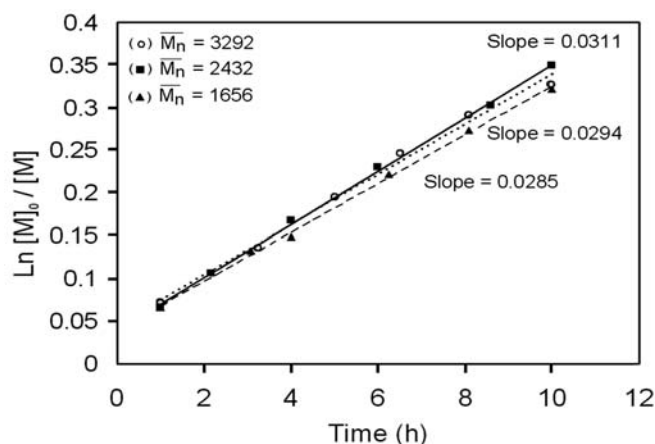


Figure 5. Effect of molecular weight of PVAc-CCl₃ macroinitiators on kinetic plots of ATRP of MA in bulk at 80°C. ([MA]₀ / [Ligand]₀ / [CuCl]₀ / [PVAc-CCl₃]₀ = 100 / 2 / 1 / 1, Molecular weights and PDIs of macroinitiators are 2432, 1656, and 3292 g/mol and 1.77, 1.7, and 1.72, respectively.)

Table 3. Effects of molecular weight of macroinitiator on ATRP of MA in bulk at 80°C.

Macroinitiator	Molecular weight (g/mol) and (PDI ²)	Time (h)	Conversion (%)	$M_{n, \text{theory}}^1$	$M_{n, \text{GPC}}^2$	PDI ²
1	3292 (1.72)	8	25.3	5470	3740	1.31
2	2432 (1.77)	10	29.1	4937	3350	1.16
3	1656 (1.70)	8	23.9	3713	3120	1.12

[MA]₀ / [Ligand]₀ / [CuCl]₀ / [PVAc-CCl₃]₀ = 100 / 2 / 1 / 1. ⁽¹⁾ Calculated with this equation: $M_{n, \text{theory}} = M_{n, \text{macroinitiator}} + \text{Conversion} \times M_0$ ($M_0 = 86.09$ g/mol). ⁽²⁾ From PS-calibrated GPC.

macroinitiator of larger average number molecular weight in the block copolymerization of MA at 80°C in bulk. Furthermore, the Table 3 shows that the larger PDI of macroinitiator from free radical polymerization is considerably broader than that in the polymerization reaction of block copolymers ATRP.

The GPC chromatograms of the synthesized block copolymers of the three average molecular weights of macroinitiators in Table 3 are shown in Figure 6.

The synthesized PVAc-*b*-PMA block copolymers were characterized by ¹HNMR spectroscopy and FTIR spectrometry techniques. The ¹HNMR spectra of synthesized PVAc-*b*-PMA is shown in Figure 7. The methylene hydrogens of the chain end (a) for vinylacetate monomer are assigned at 4.0 - 4.1 ppm. The peak about 4.7 - 5.1 ppm is characteristic of the methine proton (c) of the VAc repeating units. The methyl group of acetate (d) is at 1.9 - 2.1 ppm. The methylene protons of repeating units and chain end (b) of VAc have signals at 1.6 - 1.9 ppm. The peaks at 2.3 and 3.6 ppm are the characteristic of methine proton (f) in the MA repeating units and methoxy group hydrogens (h), respectively. The

methine hydrogen (g) of MA with chlorine atom at the chain end appeared at 4.3 ppm. The methylene hydrogens (e) of main backbone for MA monomer appeared in 1.6 - 1.9 ppm overlapped with hydrogen (b) peaks of PVAc block.

The FTIR spectra of synthesized PVAc-*b*-PMA block copolymer is also shown in Figure 8. The strong bands at 1738 cm⁻¹ are stretch vibration of carbonyl group (C=O) of PMA and PVAc blocks and the 2954 cm⁻¹ peak is due to the asymmetric stretch vibration of -C-H (CH₃) bond of PVAc.

Chemical Selectivity of MA and MMA Monomers

The electronic nature of substituents on vinyl monomer in polymerization reactions has been discussed extensively [26]. To study the overall effect of substituents, methyl acrylate (MA) and methyl methacrylate (MMA) monomers were copolymerized. It has been suggested that different reactivities of vinyl monomers of MA and MMA monomer in copolymerization [22] may have different equilibrium constants between dormant species and their corresponding radical species in ATRP [27].

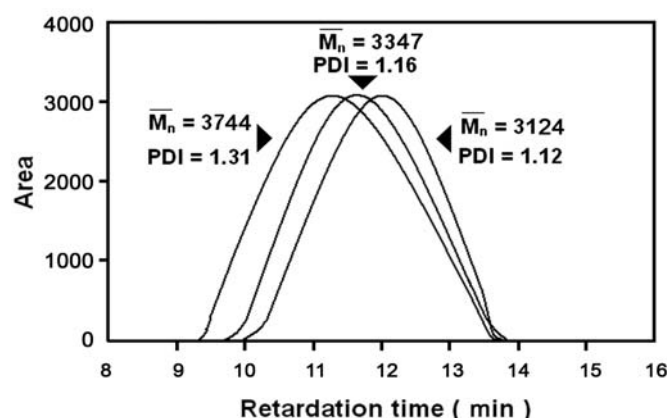


Figure 6. GPC Chromatograms of synthesized PVAc-*b*-PMA block copolymers.

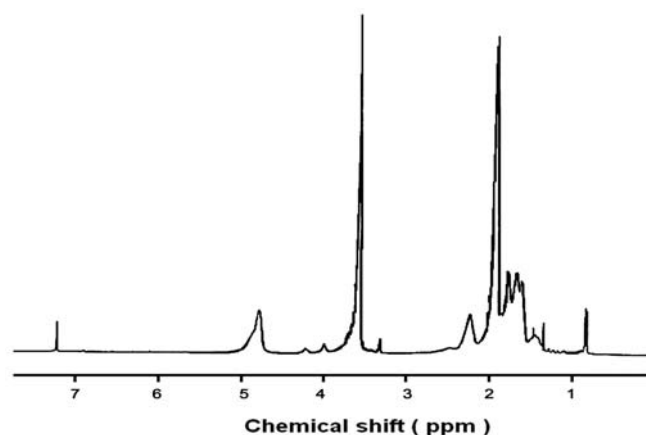


Figure 7. ¹HNMR Spectra of synthesized PVAc-*b*-PMA copolymer.

Table 4. Feed and copolymer composition of MA-MMA copolymers with molecular weight and PDI, polymerized in bulk at 80°C.

Sample No.	M ₁	m ₁	Conversion (%)	M _n , GPC (g/mol)	M _w , GPC (g/mol)	PDI
1	0.438	0.267	19	4390	5570	1.27
2	0.56	0.381	16	4060	5200	1.28
4	0.825	0.642	11.6	3240	4540	1.40
5	0.895	0.796	10.15	3310	4730	1.43

M₁ and m₁ are mole fraction of MA in feed and copolymer. [MA]₀ / [Ligand]₀ / [CuCl]₀ / [PVAc-CCl₃]₀ = 100 / 2 / 1 / 1.

We have studied two linear methods of Kelen-Tüdös, eqn (6) [28] and Fineman-Ross, eqn (7) [29] to estimate the reactivity ratios of MA (r₁) and MMA (r₂) in this copolymerization reaction [30,31].

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \quad (6)$$

$$\left(\frac{M_1(2m_1 - 1)}{m_1(1 - M_1)} \right) = r_1 \left(\frac{M_1^2(1 - m_1)}{m_1(1 - M_1)^2} \right) - r_2 \rightarrow \Psi = r_1 \times X - r_2 \quad (7)$$

In these equations η, ξ, α, Ψ, and X are constant with are described in Table 4 and M₁ and m₁ are mole fraction of MA monomer in feed and copolymer, respectively.

In copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) with various ratios of MA to MMA and [CuCl]/[PMDETA]/[PVAc-CCl₃] catalyst system in bulk at 80°C, several terpolymer were synthesized with different copolymer composition, molecular

weight, and molecular weight distribution. The reaction conditions and results are shown in Table 4. The number average molecular weight and molecular weight distribution of macroinitiator is 2432 and 1.77, respectively. In copolymerization reaction of MA and MMA with this macroinitiator, at moderately low conversion the polydispersity of synthesized terpolymers have stayed within a narrow range of 1.2-1.43.

Terpolymers of PVAc-*b*-poly(MA-*co*-MMA) were then characterized by ¹HNMR spectroscopy technique. Figure 9 shows ¹HNMR spectra of the PVAc-*b*-(PMA-*co*-PMMA) terpolymer prepared by ATRP. The signals at 0.7-1.2 ppm (l) [32] are assigned to methylene protons (-CH₂) in the MMA monomer unit and the broad signals at 2.4 ppm (f) and 4.3 ppm (g) are assigned to methin (C-H) proton for MA monomer unit in terpolymer. The methine hydrogen (g) of MA and methylene protons (q) of MMA with chlorine atom at the chain end appeared at 4.3 and 3.9 ppm, respectively. The mole

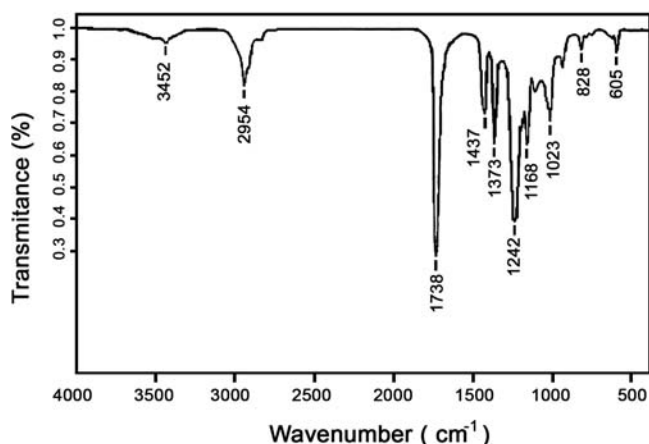


Figure 8. FTIR Spectra of synthesized PVAc-*b*-PMA copolymer.

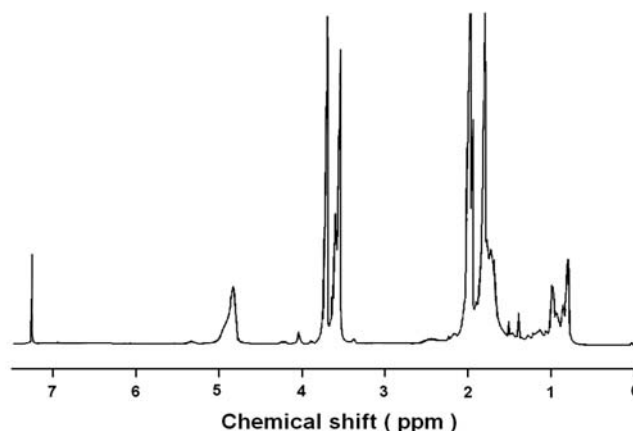


Figure 9. ¹H NMR Spectra of the PVAc-*b*-Poly(MA-*co*-MMA) terpolymers prepared by ATRP.

Table 5. Kelen-Tüdös parameters of the copolymerization of MA and MMA.

Sample No.	F = M ₁ /M ₂	f = m ₁ /m ₂	G = F(f-1) / f	H = F ² / f	η = G/(α + H)	ξ = H/(α + H)
1	0.78	0.364	-1.363	1.671	-0.1877	0.23
2	1.27	0.615	-0.795	2.623	-0.0968	0.32
3	2.5	1.03	0.073	6.068	0.006	0.52
4	4.71	1.8	2.093	12.324	0.117	0.688
5	8.53	3.891	6.338	18.7	0.261	0.77

M₁ and M₂ are mole fractions of MA and MMA in feed; m₁ and m₂ are mole fractions of MA and MMA in copolymer. α = (H_{min} · H_{max})^{0.5} = 5.59, H_{min} and H_{max} are the lowest and highest values of H.

fractions of MA and MMA units in the copolymer were determined from the signal intensities of (C-H) proton of MA units at 2.4 and 4.2 ppm, methylene protons for MMA units at 0.7-1.2 ppm, and eqn (7):

$$f = \frac{m_1}{m_2} = \frac{I_{CH(2.4)} + I_{CH(4.2)}}{\frac{I_{CH_3(0.7-1.2)}}{3}} \quad (7)$$

In this equation m₁ and m₂ are the mole fractions of MA and MMA units in the copolymers, respectively. The various ratios of copolymer composition (f = m₁/m₂) and copolymer composition (m₁ and m₂) which were calculated from ¹HNMR spectra, notation descriptions, and calculation results of Kelen-Tüdös and Fineman-Ross methods are summarized in Tables 5 and 6.

Figure 10 shows the plots of η versus ξ for Kelen-Tüdös method and Ψ versus X for Fineman-Ross method. From the slopes and intercepts of the straight lines, monomer reactivity ratios of MA and MMA were determined which the results are shown in Table 7. The values of r₁ and r₂ which were estimated for MA and

MMA monomer pair indicates that the growing radicals with MA ends add to the monomers with lower polymerization rate.

Table 7 shows that monomer reactivity ratios of MA and MMA monomer pairs in ATRP and CFRP [23] are very close. This indicates that in addition to radical reactivity that broadens the molecular weight distribution in CFRP, terpolymerization reaction via ATRP may play an important role in selectivity of monomers and narrowing the PDI of the terpolymers [33,34].

CONCLUSION

Atom transfer radical polymerization of MA and PVAc-CCl₃ macroinitiator with CuCl/PMDETA catalyst in bulk showed that apparent propagation rate constants (K_p^{app}) and the propagation radicals ([P[•]]) increased with reaction temperature. The apparent activation enthalpy (ΔH^{app} = 83.68 kJ/mol) and enthalpy of the equilibrium (ΔH_{eq}⁰ = 65.98 kJ/mol) are different in comparison with other systems which is attributed to the

Table 6. Fineman-Ross parameters of copolymerization of MA and MMA.

Sample No.	M ₁	m ₁	$\left(\frac{M_1(2m_1-1)}{m_1(1-M_1)}\right)$	$\left(\frac{M_1^2(1-m_1)}{m_1(1-M_1)^2}\right)$
1	0.438	0.267	-1.36	1.668
2	0.56	0.381	-0.795	2.632
3	0.714	0.553	0.478	5.038
4	0.825	0.642	2.085	12.393
5	0.895	0.796	6.34	18.62

M₁ and m₁ are mole fractions of MA monomer in feed and copolymer.

Table 7. Monomer reactivity ratios of MA-MMA monomer pair in ATRP and CFRP.

Reactivity Ratios	ATRP Kelen-Tüdös	ATRP Fineman-Ross	CFRP Kelen-Tüdös
r_1	0.39	0.42	0.4
r_2	2.01	2.02	2.1

kind of monomer, initiator, catalyst, and solvent. The block copolymerization with MA indicates a narrow polydispersity as expected from ATRP polymerization. The polydispersity broadens with polymerization temperature during the conversion. The PDI of several block copolymers become increase with higher polydispersity of macroinitiators.

The reactivity ratios of MA and MMA monomers were determined with two linear methods of Kelen-Tüdös and Fineman-Ross and shows the same chemical reactivity in both ATRP and CFRP processes. This work shows that it is possible to use PVAc- CCl_3 macroinitiator in ATRP and synthesis novel block terpolymers of

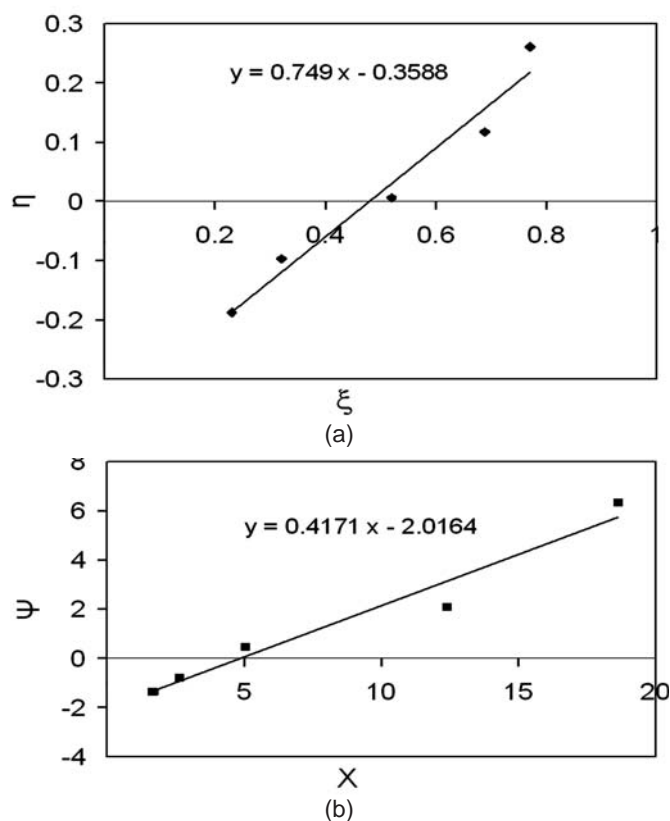
PVAc-*b*-poly(MA-*co*-MMA) with a far more specific PDI. The precise control of composition in the block terpolymers with further narrowing of terpolymer molecular weight distribution from 1.77 in macroinitiator to about 1.2-1.43 in terpolymers shows that there is a chemical selectivity within the ATRP or CS-ATRP that directs free radicals in this process. Furthermore, the chlorine functionalities on these novel block copolymers are useful in the new synthesis of the star block copolymers and dendrimers of specific functionality and size in molecular design of macromolecules.

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**Figure 10.** The plots of (a) Kelen-Tüdös and (b) Fineman-Ross plots for MA-MMA copolymers prepared via ATRP.

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