**ABSTRACT**

Atom transfer radical copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) with PVAc-CCl₃ telomer as macroinitiator and CuCl/N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA) catalyst system in bulk at 80°C was investigated. The molecular structure of the poly(vinyl acetate-b-MA-co-MMA) block terpolymers were characterized by ¹H NMR and FTIR spectroscopies and gel permeation chromatography (GPC). The composition and end chain functionality of MA units in terpolymer increased with mole fraction of MA in the feed. The chain configuration of terpolymer indicated that the syndiotacticity of MMA repeating unit in terpolymer increased from 31.9 to 52.5 with MMA mole fraction in the feed. The experimental and theoretical number average molecular weights of terpolymer were studied. The molecular weight distributions of the synthesized block terpolymers were narrowed from 1.77 in macroinitiator to about 1.27-1.44. The theoretical number average molecular weight of terpolymer increased with overall molar conversion and composition of MMA unit in terpolymer. The overall propagation rate constants in ATRP of MA and MMA were calculated and increased with mole fraction of MA in the feed.

**Key Words:**
atom transfer radical polymerization; molecular structure; block terpolymer; copolymerization.

**INTRODUCTION**

Atom transfer radical polymerization (ATRP) is a valuable tool for the design and synthesis of novel materials. Many new functional polymers with novel and controlled compositions and topologies have been prepared by ATRP, and a complete structure property relationship has to be developed to allow a correlation of molecular structure with macroscopic properties. These materials can be employed to meet the requirement of numerous applications. The polymers can be prepared under facile reaction conditions, using a multitude of available...
polymerizable monomers with accessible chain functionalities [1-2].

The recent development of ATRP has opened a new route to produce several block copolymers from macroinitiators synthesized by ring opening polymerization (ROP) [3-4], conventional free radical polymerization (CFRP) [5-9] and atom transfer radical polymerization (ATRP) [10-13] 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 and functionalities [1-2]. A wide variety of block copolymers can be derived from the same family of vinyl monomers [14-15] or different families of vinyl monomers via ATRP [16-17] and $^1$H NMR analysis was used to confirm the formation of the block copolymers and compositional analysis of the blocks.

The molecular structure determination of copolymers synthesized by ATRP is of interest because of the control over the polymer architecture and design. Madruga et al. [18] have studied the sequence distribution and stereoregularity of methyl methacrylate and butyl acrylate copolymers with $^1$H and $^{13}$C NMR spectroscopies. Interestingly enough, once tested with nuclear magnetic resonance, they have found that copolymer composition and microstructure are independent of controllability of the ATRP process. The microstructure determination of the methyl acrylate and $\alpha$-butyl acrylate copolymer has been extensively studied and the results from heteronuclear single quantum coherence (HSQC) have been compared with total correlated spectroscopy and the Bernoullian statistics was confirmed for $\alpha$-methyl $^1$H NMR of MMA [19]. The effect of monomer in feed ratio on the composition of this copolymer and the resulting microstructures has also been extensively studied with $^{13}$C($^1$H) NMR and the cross correlations between non-equivalent protons of CH$_3$, CH$_2$ and CH of the copolymer were confirmed [19]. In spite of this elaborate study, there has been no report on the chemical selectivity of the copolymer.

A conventional radical telomerization has been used in synthesis of block copolymers with monomer that were inactive in ATRP [5-7]. In this respect, we have used telomerization in synthesis of PVAc-CCl$_3$. The effect of molecular weight of PVAc-CCl$_3$ as a macroinitiator was investigated in ATRP of MA [20].

The main objective of the present work was to study the molecular structure of poly(vinyl acetate-b-MA-co-MMA) terpolymer such as copolymer composition, end chain functionality, tacticity of MMA in terpolymer and theoretical values of molecular weight with $^1$H NMR method, which according to our literature survey they have not been reported elsewhere. In addition, the molecular weight and PDI of block terpolymers were obtained from GPC method and the overall propagation rate constants ($<K_p>$) of MA and MMA copolymerization were also investigated.

**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 (CaH$_2$). CuCl (Merck, 97%) as a catalyst was purified by washing with glacial acetic acid (three times), ethanol and diethyl ether, successively. The dried catalysts under nitrogen were used in reactions. PMDETA (Merck, 99.8%) and tetrahydrofuran (THF) were used as received. PVAc-CCl$_3$ as monofunctional macroinitiator was prepared via conventional free radical polymerization (CFRP) of vinylacetate monomer with chloroform as a solvent or telogen and AIBN as initiator at 60°C. In this study only one kind of PVAc-CCl$_3$ as macroinitiator was used in atom transfer radical copolymerization of MA and MMA. From the results of $^1$H NMR spectroscopy and GPC of macroinitiator, average number molecular weight, polydispersity and telomer percent of telomer were 2432 g/mol, 1.77, and 81% [20].

**Characterization**

$^1$H NMR Spectra of block terpolymers were recorded in CDCl$_3$ with a Bruker DRX400 spectrometer operated at 400 MHz. Infrared spectra were obtained on a Bruker IFS 48 FTIR spectrometer. Molecular weight and its distribution (MWD) were measured by a Waters 150C PS-calibrated GPC in THF at 35°C and 1 mL/min equipped with a refractive index detector and a 10$^4$, 10$^3$ and 500A set of ultrastyrogel 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, MMA, PVAc-CCl₃ telomer as macroinitiator 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 preheated oil bath at a desired temperature. The tube was then removed from oil bath and reaction mixture was dissolved in THF, filtered and passed through a neutral alumina column to remove the remaining copper catalyst and dried under vacuum to a constant weight and overall weight conversion (W=W₁/W₂) was determined gravimetrically with the weight of dried copolymer (W₁) and weight of MA and MMA monomers in the feed (W₂). The dried sample was then used in ¹H NMR and FTIR spectroscopies and GPC.

RESULTS AND DISCUSSION

Study of Molecular Structures

In atom transfer radical copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) with various feed ratios of MA to MMA in bulk at 80°C, several terpolymers with different copolymer compositions were synthesized. The mole fraction of MA (f₁) and MMA (f₂) in the feed and experimental condition of the reactions are shown in Table 1. Figure 1 shows ¹H NMR spectra of the PVAc-ₐ(PMA-co-PMMA) block terpolymer for sample 1 [20]. The signals at 0.7-1.2 ppm are assigned to methyl protons (-CH₃) of MMA [13,20]. The methine (C-H) protons of repeating units and chain end (with chlorine atom) of MA have broad signals at 2.4 and 4.2 ppm, respectively [7,20]. The copolymer composition of MA (F₁) and MMA (F₂ = 1-F₁) were calculated from the intensity of MA and MMA signals in ¹H NMR spectra (Figure 2) and using eqn (1). In eqn (1), I₃CH₃(0.7-1.2), I₃CH(2.4) and I₃CH(4.2) are intensity of the signals assigned to MA and MMA units in block terpolymer which were described.

\[
F_1 = \frac{I_{CH(2.4)} + I_{CH(4.2)}}{\left(\frac{I_{CH(0.7-1.2)} + I_{CH(2.4)} + I_{CH(4.2)}}{3}\right)}
\]

The intensity of signals at 0.7-1.2 ppm for MMA unit in terpolymer was higher when the mole fraction of MA (f₁) used in the feed (Figure 2) is low. The intensity of broad signals at chemical shift of 2.4 and
4.2 ppm for MA unit in terpolymer increased with mole fraction of MA in the feed. However, intensity of signals corresponded to MA and MMA units in terpolymer proved that compositions of MA and MMA changed with MA mole fraction in the feed and composition of MMA unit in copolymer decreased with the higher mole fraction of MA in the feed (Figure 3). The mole fraction of MMA unit in copolymer decreased with increasing of mole fraction of MA in the feed. This can be attributed to the different reactivities of MA or MMA radicals in the propagating chain end [21] and mole fraction of MA and MMA in the feed [18,22,23].

In atom transfer radical copolymerization of MA and MMA, structure-reactivity correlation [21] has an important role in activation rate constant when MA

<table>
<thead>
<tr>
<th>Sample</th>
<th>M₁ (mole)</th>
<th>M₂ (mole)</th>
<th>f₁</th>
<th>f₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.011</td>
<td>0.01408</td>
<td>0.438</td>
<td>0.562</td>
</tr>
<tr>
<td>2</td>
<td>0.0143</td>
<td>0.01126</td>
<td>0.56</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>0.0187</td>
<td>0.00751</td>
<td>0.714</td>
<td>0.286</td>
</tr>
<tr>
<td>4</td>
<td>0.0221</td>
<td>0.00469</td>
<td>0.825</td>
<td>0.175</td>
</tr>
<tr>
<td>5</td>
<td>0.0243</td>
<td>0.00284</td>
<td>0.895</td>
<td>0.105</td>
</tr>
</tbody>
</table>

- M₁ and M₂ are moles of MA and MMA in the feed.
- f₁ = M₁ / (M₁ + M₂) and f₂ = (1 - f₁). f₁ and f₂ are mole fractions of MA and MMA in the feed.
- Reactions carried out in bulk at 80°C and [MA + MMA][ligand]₀/[CuCl]₀/[PVAc-CCl₃]₀ = 100/2/1/1.

Figure 2. ¹H NMR Spectra of the PVAc-b-poly(MA-co-MMA) block terpolymers prepared by ATRP.
and MMA are considered and assigned in the chain end. The end chain functionality or composition of MA or MMA units in terpolymer chain end is dependent not only on the structure of the monomer units in the propagating chain end [21] but also on the mole fraction of the monomers in the feed. This can be attributed to different kinetic constants \( K_{eq} = k_a/k_{da} \) of MA and MMA during atom transfer radical copolymerization reactions.

The signal at 3.9 ppm corresponds to the methoxy protons (-O-CH\(_3\)) of MMA in terpolymer chain end and the methine proton (C-H) of MA with chlorine atom in terpolymer chain end appeared at 4.2 ppm [7,20] (Figure 1). The chain end functionality of MA \((f_{MA,end})\) and MMA \((f_{MMA,end})\) units in terpolymers were calculated with the intensity of signals corresponded to MA \((I_{MA,end})\) and MMA \((I_{MMA,end})\) units in terpolymer chain end [7,20] and with eqn (2).

\[
\begin{align*}
    f_{MA,end} &= \frac{I_{MA,end}}{I_{MA,end} + \left(\frac{I_{MMA,end}}{3}\right)} \\
    f_{MMA,end} &= 1 - f_{MA,end}
\end{align*}
\]  

The composition of MA unit in terpolymer chain end increased from 0.84 to 1 with mole fraction of MA in the feed. However, MMA unit was smaller under this condition and it decreased from 0.16 to zero (Figure 4). This is probably attributed to the higher dormant behaviour of MA unit and higher activation rate of MMA unit during the copolymerization reaction [21]. Furthermore, it was found that the influence of such a low conversion on the chain end functionality is negligible.

In this study, the chain tacticity of MMA repeating unit in block terpolymer was investigated by \(^1\)H NMR analysis (Figure 1). Three peaks are seen between 0.7-1.1 ppm corresponding to triad units, syndiotactic (rr) at 0.81 ppm, atactic (mr and rm) at 0.98 ppm and isotactic (mm) at 1.07 ppm, [18,19,24,25]. A broad peak at 1.1-1.3 ppm was assigned to some tetrads (rmr, mmr and mmm) units [25]. Figure 2 shows that the intensity of triads decreased with mole fraction of MA in the feed [18]. The triad tacticities of MMA repeating unit in terpolymer were calculated with eqn (3).

\[
\%\text{Isotactic}(mm) = \left(\frac{I_{mm}}{I_{mm} + I_{mr} + I_{rr}}\right) \times 100 \%
\]

\[
\%\text{Atactic}(mr,rm) + \%\text{Syndiotactic}(rr) = 100
\]

where \(I_{mm}\), \(I_{mr}\) and \(I_{rr}\) are intensity of isotactic (mm), atactic (mr and rm) and syndiotactic (rr) peaks in \(^1\)H NMR spectra, respectively (Figure 2). Table 2 shows almost the same isotacticity, but syndiotacticity and atacticity are different. The block terpolymer chain is more syndiotactic at higher MMA in the copolymer [18]. The higher feed of this monomer \(f_2\) is expected to decrease the atacticity and in this respect, when the feed of MMA is lowered, the atactic arrangement of the chain proportionally increased.

Figure 5 shows FTIR spectrum of PVAc-\(b-\...
poly(MA-co-MMA) terpolymer. The band at 1240 cm\(^{-1}\) is assigned to -O-COCH\(_3\) bond of PVAc block.

\[ \text{Table 2. The triad configuration of MMA repeating unit in terpolymer in atom transfer radical copolymerization of MA and MMA in bulk at 80°C.} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>(f_2)</th>
<th>(F_2^1)</th>
<th>% Isotactic (mm) (^2)</th>
<th>% Atactic (mr and rm) (^2)</th>
<th>% Syndiotactic (rr) (^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.562</td>
<td>0.733</td>
<td>3.9</td>
<td>43.6</td>
<td>52.5</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
<td>0.619</td>
<td>4.2</td>
<td>44</td>
<td>51.8</td>
</tr>
<tr>
<td>3</td>
<td>0.286</td>
<td>0.447</td>
<td>4.2</td>
<td>51.4</td>
<td>44.4</td>
</tr>
<tr>
<td>4</td>
<td>0.175</td>
<td>0.358</td>
<td>6.4</td>
<td>51.5</td>
<td>42.1</td>
</tr>
<tr>
<td>5</td>
<td>0.105</td>
<td>0.204</td>
<td>5.8</td>
<td>62.3</td>
<td>31.9</td>
</tr>
</tbody>
</table>

- \(f_2\) and \(F_2\) are mole fractions of MMA in the feed and copolymer.
- 1: Calculated from \(^1\)H NMR spectra and eqn (1) (\(F_2 = 1 - F_1\)).
- 2: \% Isotactic = \(\frac{l_{\text{imm}}}{l_{\text{imm}} + l_{\text{imr}} + l_{\text{irr}}} \times 100\). \(l_{\text{imm}}\), \(l_{\text{imr}}\) and \(l_{\text{irr}}\) are intensity of isotactic (mm), atactic (mr and rm) and syndiotactic (rr) peaks in \(^1\)H NMR spectra, and \% isotactic (mm) + \% atactic (mr and rm) + \% syndiotactic (rr) = 100.

\[ \text{Table 3. Calculation of overall molar conversion (X) in atom transfer radical copolymerization of MA and MMA in bulk at 80°C.} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>(f_1)</th>
<th>(f_2)</th>
<th>(f = f_1 / f_2)</th>
<th>(F_1^1)</th>
<th>(F = F_1 / F_2)</th>
<th>(W) (%)</th>
<th>(X_{\text{MA}}) (%)</th>
<th>(X_{\text{MMA}}) (%)</th>
<th>(X) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.438</td>
<td>0.562</td>
<td>0.779</td>
<td>0.267</td>
<td>0.733</td>
<td>0.3638</td>
<td>19</td>
<td>24.21</td>
<td>11.25</td>
</tr>
<tr>
<td>2</td>
<td>0.56</td>
<td>0.44</td>
<td>1.2727</td>
<td>0.381</td>
<td>0.619</td>
<td>0.6155</td>
<td>16</td>
<td>21.92</td>
<td>10.60</td>
</tr>
<tr>
<td>3</td>
<td>0.714</td>
<td>0.286</td>
<td>2.4965</td>
<td>0.553</td>
<td>0.447</td>
<td>1.2371</td>
<td>12.4</td>
<td>18.91</td>
<td>9.37</td>
</tr>
<tr>
<td>4</td>
<td>0.825</td>
<td>0.175</td>
<td>4.7143</td>
<td>0.642</td>
<td>0.358</td>
<td>1.7933</td>
<td>11.6</td>
<td>23.06</td>
<td>8.77</td>
</tr>
<tr>
<td>5</td>
<td>0.895</td>
<td>0.105</td>
<td>8.5238</td>
<td>0.796</td>
<td>0.204</td>
<td>3.9020</td>
<td>10.15</td>
<td>19.41</td>
<td>8.88</td>
</tr>
</tbody>
</table>

- \(f_1\) and \(f_2\) are mole fractions of MA and MMA in the feed. \(F_1\) and \(F_2\) are mole fractions of MA and MMA units in copolymer.
- \(W\) and \(X\) are overall weight and molar conversions.
- Reaction condition: \([\text{MA + MMA}]_0/[\text{ligand}]_0/[\text{CuCl}]_0/[\text{PVAc-CCl}_3]_0 = 100/2/1/1.\)
- For macroinitiator: \(M_n = 2432\) g/mol and PDI = 1.77.
- 1: Calculated from \(^1\)H NMR spectra and eqn (1) (\(F_2 = 1 - F_1\)).

The strong band at 1737 cm\(^{-1}\) is a stretching vibration of carbonyl group (C=O) of MA, MMA and VAc repeating units in block terpolymer. The peak at 2952 cm\(^{-1}\) corresponds to the asymmetric stretching vibration of -C-H (CH\(_3\)) bond of PVAc, PMA and PMMA in terpolymer [7,20].

**Study of Molecular Weights**

In this paper, at low overall molar conversions, the theoretical number average molecular weights of PVAc-\(b\)-(PMA-co-PMMA) block terpolymers are calculated with \(^1\)H NMR spectrum (Figure 2) and using eqn (4).

\[
M_{n, \text{theory}} = M_{n, \text{macroinitiator}} + \% X \times F_1 \times M_{MA} + \% X \times (1 - F_1) \times M_{MMA}
\]  \(\text{(4)}\)
where $\%X$, $F_1$, $M_{n,macroinitiater}$, $M_{MA}$ and $M_{MMA}$ are overall molar conversion, mole fraction of MA in the copolymers which were calculated by $^1$H NMR method, molecular weights of macroinitiator (2432 g/mol), MA (86.09 g/mol) and MMA (100.12 g/mol) monomers, respectively. Overall molar conversion ($X$) can be calculated by given values of overall weight conversion ($W$), mole ratio of MA ($f_1$) to MMA ($f_2$) mole fractions in the feed ($f = f_1/f_2$), mole ratio of MA ($F_1$) to MMA ($F_2$) mole fractions in the copolymer ($F = F_1/F_2$) and the molecular weight ratio of MMA to MA ($\mu = 1.1629$) via the following equations [26].

$$x_{MMA} = \frac{W(\mu + f)}{(\mu + F)}$$

$$x_{MA} = x_{MMA}(F/f)$$

$$X = f_1 \times x_{MA} + f_2 \times x_{MMA}$$

Results of calculations are given in Table 3 and then, the theoretical average number molecular weight of block terpolymers were calculated by eqn (4).

The theoretical and experimental (obtained from GPC method) number average molecular weights of block terpolymers are shown in Table 4. The molecular weight of macroinitiator was developed during ATRP of MA and MMA. The theoretical number average molecular weights of terpolymers were increased with overall molar conversion and composition of MMA ($F_2$) in terpolymers. The molecular weights of the resulting block terpolymers obtained from GPC were near to the theoretical values and the molecular weight distributions of the synthesized block terpolymers were narrowed from 1.77 in macroinitiator to about 1.27-1.44 in terpolymers (Table 4). A continuous exchange reaction in ATRP has been suggested for this observation [1]. GPC Trace of the resulting block terpolymers (samples 1-5 in Table 4) is shown in Figure 6.

### Table 4. Theoretical and experimental average number molecular weight ($M_n$) and PDI of PVAc-$b$-poly(MA-co-MMA) block terpolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F_1$</th>
<th>$F_2$</th>
<th>$X$ (%)</th>
<th>$M_{n, theory}$ (g/mol)</th>
<th>$M_{n, GPC}$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.267</td>
<td>0.733</td>
<td>18.53</td>
<td>4220</td>
<td>4390</td>
<td>1.27</td>
</tr>
<tr>
<td>2</td>
<td>0.381</td>
<td>0.619</td>
<td>15.58</td>
<td>3910</td>
<td>4060</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>0.553</td>
<td>0.447</td>
<td>12.10</td>
<td>3550</td>
<td>3470</td>
<td>1.44</td>
</tr>
<tr>
<td>4</td>
<td>0.642</td>
<td>0.358</td>
<td>11.27</td>
<td>3460</td>
<td>3240</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>0.796</td>
<td>0.204</td>
<td>9.99</td>
<td>3320</td>
<td>3310</td>
<td>1.43</td>
</tr>
</tbody>
</table>

- $F_1$ is mole fraction of MA in copolymer. $X$ is overall molar conversion.
- Polymerization carried out in the bulk at 80ºC and $[MA + MMA]/[ligand]/[CuCl]/[PVAc-CCl3] = 100/2/1/1$.
- For macroinitiator, $M_n = 2432$ g/mol and PDI = 1.77.
- 1: Calculated from $^1$H NMR spectra and eqn (1) ($F_2 = 1-F_1$).
- 2: From eqn (3), $M_{n, theo} = 2432 + 18.53 \times 0.267 \times 86.09 + 18.53 \times 0.733 \times 100.12 = 4220$ g/mol.
- 3: Obtained from PS-calibrated GPC.

$\mu = \frac{k_a}{k_{da}}$ (where $k_a$ and $k_{da}$ are rate of activation and deactivation), on the concentration of initiator and catalyst and inversely on the concentration of deactivator (eqn (7)) [27]. In this study, at the same reaction conditions, the overall propagation rate constant ($<k_p>$) and equilibrium constant ($<K_{eq}>$) were changed with the mole fraction of deactivator (eqn (7)) [27]. In this study, at

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**Figure 6.** Gel permeation chromatograph (GPC) traces of the PVAc-$b$-(PMA-co-PMMA) block terpolymers for samples 1-5 in Table 4.
Figure 7. Calculated overall propagation rate constants (<kp>) in ATRP of MA and MMA in bulk at 80°C. Reaction condition: [MA + MMA]₀/[ligand]₀/[CuCl]₀/[PVAc-CCl₃]₀ = 100/2/1/1.

In the same reaction conditions, the overall propagation rate constant (<kp>) and equilibrium constant (<Keq>) were changed with the mole fraction of MA and MMA in the feed [23]. Thus, knowing the values of the overall propagation rate constant (<kp>) of the reactions helps in calculating other kinetic parameters [23].

\[ k_{p}^{\text{app}} = \langle k_p \rangle \times \langle K_{eq} \rangle \frac{[RX]_0 \times [Cu(I)]_0}{[Cu(II)]_0} \]  

Eqn (8) was obtained from the terminal model [28]. In this study, this equation is used for calculation of the overall propagation rate constants (<kp>) in atom transfer radical copolymerization of MA and MMA. The overall propagation rate constant (<kp>) is affected by mole fractions, reactivity ratios and propagation rate constants of MA and MMA.

\[ \langle k_p \rangle = \frac{r_1 f_1^2 + f_1 f_2 + r_2 f_2^2}{r_1 f_1 + r_2 f_2} \]  

In eqn (8), f₁ and f₂ are mole fractions of MA and MMA in the feed, respectively (Table 1). The propagation rate constants of MA (kₚ₁ = 36400 M⁻¹s⁻¹) and MMA (kₚ₂ = 1127 M⁻¹s⁻¹) were calculated at 80°C from literature [29]. The reactivity ratios of MA (r₁ = 0.39) and MMA (r₂ = 2.01) in atom transfer radical copolymerization were determined with linear method of Kelen-Tüdős [20] and showed the same chemical reactivity in both ATRP and CFRP processes. Figure 7 shows the calculated overall propagation rate constant in atom transfer radical copolymerization of MA and MMA. The overall propagation rate constant increased with MA mole fraction in the feed. This may probably be attributed to increase participation of propagation rate constant of MA in eqn (7) with MA mole fraction in the feed (f₁) [23].

CONCLUSION

In this paper, molecular structure of PVAc-b-poly(MA-co-MMA) block terpolymer are discussed with ¹H NMR and GPC methods. Based on chain functionality, the chain composition is selective to MMA feed and at higher mole fraction of MA in the feed, chain composition and end chain functionality are low in MMA units and terpolymer is more atactic than syndiotactic.

The copolymer composition and overall molar conversion had a direct effect on the theoretical number average molecular weight of terpolymer. The theoretical number average molecular weights of synthesized block terpolymers were near to experimental values obtained from GPC. In this polymerization system, polydispersity of the block terpolymers is narrowed.

The calculated overall propagation rate constants (<kp>) in atom transfer radical copolymerization of MA and MMA increased with MA mole fraction in the feed.

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