**Thermo–Responsive Block Copolymers of Ethylene Glycol Derivatives and Methacrylic Acid**

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**Abstract** - The synthesis of polymers designed to imitate the chemistry behind naturally–occurring polymers is only a recently emerging field of research. Their most notable feature involves reversible transitions in response to external stimuli, like temperature and pH. In this study, thermo–responsive homopolymers of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and di(ethylene glycol) methyl ether methacrylate (DEGMA), and their corresponding block copolymers with methacrylic acid (MAA) were synthesized via the reversible addition–fragmentation chain transfer (RAFT) polymerization technique. Data from gel permeation chromatography showed increasing molecular weight and polydispersity index (PDI) with increasing monomer feed ratio. The low PDI justified the method’s great control over the polymerization process. Structural characterization with infrared spectroscopy and proton nuclear magnetic resonance then demonstrated the success of RAFT polymerization. This was supported by morphological changes before and after copolymerization, as observed using atomic force microscopy. Lastly, the lower critical solution temperature (LCST) was investigated through ultraviolet–visible light spectroscopy and dynamic light scattering. General observations suggested efficient LCST tailoring by varying the molar feed ratios. These results show the efficiency and versatility of RAFT polymerization in the synthesis of thermo–responsive polymers, with their promising applications in the fields of sensors and biotechnology.

Keywords: RAFT polymerization; Thermo–responsive polymers; Ethylene glycol derivatives; LCST; Biotechnology

I. INTRODUCTION

Natural polymers in biological systems (proteins, carbohydrates, and nucleic acids) exhibit remarkable versatility and adaptability to changing conditions. Their behavior and characteristics ignited the pursuit for similar synthetic polymers with the ability to respond to various environmental stimuli. Over the last two decades, these endeavors have been aimed at mimicking the smartness of these natural polymers at desired levels.

Since then, these synthetic polymers, so–called smart polymers, find promising applications on a wide array of biotechnological and biomedical issues, including bioseparation, drug delivery, biosensors, tissue engineering scaffolds, protein folding, and microfluidics [1], among others.

4th Annual International Conference on Chemistry, Chemical Engineering and Chemical Process (CCECP 2016)  
Copyright © GSTF 2016  
ISSN 2301-3761  
doi: 10.5176/2301-3761_CCECP16.9

In general, the term ‘smart polymers’ refers to synthetic and polymeric macromolecules able to undergo physical or chemical changes induced by external stimuli such as temperature, pH, light, magnetic or electric fields, ionic strength, and the presence of other compounds [2]. For instance, the pH sensitivity of copolymers of N–isopropylacrylamide (NIPAM) and acrylic acid allows for the pH–controlled binding and release of biotin [3]. The temperature–responsive behavior of copolymers of NIPAM and hydroxyethyl methacrylate was then utilized in the controlled release of zinc tetraphenylporphyrin for photo-induced antimicrobial action [4].

The temperature–induced behavior of thermo–responsive polymers may be categorized into two: the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST). A polymer below its LCST is completely soluble in the medium of interest, but insoluble above its LCST. In contrast, a polymer is insoluble in its medium below its UCST, but soluble above it.

Among a variety of thermo–responsive polymers, poly(N–isopropylacrylamide) (PNIPAM) is the most studied one, primarily because its LCST (~32°C) is close to the physioloigical temperature. It exhibits a coil to globule transition at its LCST as a result of its complex polarity. However, Vihola et al. [5] suggested that acrylamide–based polymers exhibit cytotoxicity and, thus, non–biocompatibility. It was then discovered that poly(ethylene glycol) analogues offered significant advantages [6]: versatile and ease of synthesis from commercially available monomers, plausible attachment to biological compounds, and properties like water–solubility, biocompatibility, thermostensitivity, and biodegradability [6]. Moreover, the LCST of these polymers can be tailored by changing the length of the ethylene glycol side chain [7]: a longer chain imparts greater hydrophilicity, thus increasing the LCST. As a result, the LCST can be tuned in the range of 26–90°C.

The synthesis of smart polymers can be performed via the conventional free radical polymerization technique. This method has dominated the field mainly due to its ability to polymerize monomers with the vinyl moiety. Moreover, the method can be performed in homogeneous or heterogeneous media, can tolerate trace amounts of impurities, and can be conducted at moderate temperatures and pressures [8, 9]. However, free radical polymerization fails to control polymer structure and functionality, particularly unable to control molecular mass distributions and produces polymers with high
polydispersity indices [8, 9]. The synthesis of complex architectures like block, star, and graft polymers, and those with defined end groups is limited, while the production of polymers with a specific stereochemistry is theoretically impossible. With these limitations, smart polymers produced by this method fail to suffice as models for complex applications.

In the search for a better polymerization method without the said difficulties, a novel process called reversible addition-fragmentation chain transfer (RAFT) polymerization was developed, a type of controlled radical polymerization. RAFT polymerization, unlike free radical polymerization, offers exceptional versatility in the synthesis of polymers with predetermined molecular weight, narrow polydispersity, and even complex architectures [10].

The aim of this study is to employ RAFT polymerization in the synthesis of thermosensitive homopolymers of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and di(ethylene glycol) methyl ether methacrylate (DEGMA), and their corresponding block copolymers with methacrylic acid (MAA). The synthesized polymers were then assessed and tested for their characteristics, properties, structure, and temperature sensitivity.

II. METHODOLOGY

A. General Analytical Procedure

The monomers poly(ethylene glycol) methyl ether methacrylate (PEGMA, Mn 300 g mol⁻¹) and methacrylic acid (MAA, 99%) were activated prior to use by passing through a column with alternating layers of basic aluminum oxide (activated, Sigma–Aldrich) and inhibitor remover (Sigma–Aldrich). Azobisisobutyronitrile (AIBN) was dissolved and recrystallized in methanol for purification. Acetonitrile (Lab–Scan), methanol (J. T. Baker), dichloromethane (J. T. Baker), n–hexane (95%, J. T. Baker), ethanol (absolute, APS Finechem), ethyl acetate (J. T. Baker), 4-cyano-4–(phenylcarbonothioylthio)pentanoic acid (CPAD, Sigma–Aldrich), deuterated dimethyl sulfoxide (DMSO-D₆, Cambridge Isotope Laboratories, Inc.), and tetrahydrofuran (THF, dry) were used as received.

B. Homopolymerization

The homopolymer of PEGMA was synthesized as follows: PEGMA (4.0 g), CPAD, AIBN (250:0.2 PEGMA:CPAD: AIBN mole ratio), and acetonitrile (7 mL) were added into a 100 mL septum–sealed round-bottom flask equipped with a magnetic bar. The solution was then degassed for one hour with nitrogen, and subsequently placed in a preheated oil bath at 70°C to carry out RAFT polymerization. The reaction was stopped after 6 hours by immersion of the flask in an ice bath and exposure of the contents to air. The solution was then concentrated through rotary evaporation, dissolved in dichloromethane, and precipitated thrice in large excess of cold n–hexane. The product was collected via centrifugation and finally dried under vacuum.

The homopolymer of DEGMA was then synthesized as follows: DEGMA (1.02 g), CPAD, AIBN (250:5:1 DEGMA: CPAD:AIBN mole ratio), and acetonitrile (5 mL) were added into a septum–sealed 100 mL septum–sealed round-bottom flask equipped with a magnetic bar. The same conditions and procedures as that of PEGMA homopolymerization were performed in the synthesis, collection, and purification of the product.

Likewise, the homopolymer of MAA was synthesized as follows: MAA (4.30 g), CPAD, AIBN (100:1:0.25 MAA:CPAD:AIBN mole ratio), and methanol (25.37 g) were added into a 100 mL septum–sealed round–bottom flask with a magnetic bar. The same procedures as that of PEGMA homopolymerization were performed, however, the reaction conditions were set at 60°C for 24 hours instead. The purifying solvents used were ethanol and ethyl acetate.

C. Block Copolymerization

The MAA–b–PEGMA copolymerization was performed utilizing the previously purified and dried MAA homopolymer. A 5:1 MAA homopolymer:AIBN mole ratio was used, with the PEGMA monomer added in three different proportions (100:1, 200:1, and 300:1 PEGMA:MAA homopolymer mole ratio). The reaction was set at 60°C for 24 hours. The product purification and treatment procedures used were also the same as that for the PEGMA homopolymer.

The same copolymerization scheme was performed in the synthesis of MAA–b–DEGMA.

D. Gel Permeation Chromatography

GPC was performed with Shimadzu LC–20AD Liquid Chromatograph equipped with an RI detector, using dry THF as the mobile phase. Samples were first dissolved in ample amounts of the mobile phase to render a concentration of approximately 10 mg/mL. The run was then conducted at 15 minutes per polymer sample solution, with a flow rate of 1 mL/min. Shimadzu LCSolution GPC Analysis software was used to process the data.

E. Fourier Transform–Infrared Spectroscopy

The transmission spectra were collected by employing a Shimadzu IR Prestige–21 spectrometer, equipped with an attenuated total reflectance (ATR) system. Scans were recorded from 4000 cm⁻¹ to 400 cm⁻¹.

F. Proton Nuclear Magnetic Resonance Spectroscopy

1H–NMR spectra were recorded on an Agilent Varian 500 MHz NMR instrument, using DMSO–D₆ as solvent. The residual solvent peak was used as an internal standard.

G. Atomic Force Microscopy

Surface morphologies and aggregation patterns were observed using Park Systems XE–70 at non-contact mode. Samples were prepared by drop casting aqueous polymer solutions onto mica plates, and drying them under vacuum. Two– and three–dimensional images were generated at 10x10 and 5x5 μm scan size resolutions. Further processing and analysis were made with an XEI software.
H. Ultraviolet–Visible Light Spectroscopy

Shimadzu UV–1606 Double Beam spectrophotometer was utilized in the absorbance measurements of the polymer samples in aqueous solutions. Photometric measurements of sample absorbance was performed at the wavelength of maximum absorption (320 nm), as a function of temperature. An independent thermal accessory was used to ramp the temperature from 18 to 45°C. At a changed temperature, the samples were allowed to equilibrate for 1 minute prior to the measurement.

I. Dynamic Light Scattering

The polymer solutions were analyzed with a Malvern Zetasizer Nano ZS90, using polymer concentrations of 1 mg/mL in distilled water. Sample equilibration for every 1°C rise in temperature was performed for 2 minutes. Parameters were set at 3 measurements for 10 runs each.

III. RESULTS AND DISCUSSION

A. RAFT Polymerization

In this study, the efficiency of the RAFT polymerization technique in the synthesis of smart, thermo-responsive polymers was assessed. The AIBN initiator used in the study has been commonly employed in both free-radical and living radical polymerizations, primarily due to its general availability and versatility [11].

The radical initiator used to drive RAFT polymerization gives rise to polymer defects that present as impurities in the polymer product. The prevalence of these defects is heavily influenced by the initiator concentration. While the use of a low initiator concentration reduces the incidence of these defects, a sufficiently high concentration is required to obtain acceptable rates of polymerization. This varies depending on the identity of the monomer, and hence, optimization of the relative molar ratios of the reaction components was necessary.

The choice of CPAD as the RAFT agent or chain transfer agent (CTA) is then justified by the fact that it is of the dithioester type (specifically a dithiobenzoate), particularly known for its higher activity than most other types of RAFT agent (e.g. trithiocarbonates, xanthates, dithiocarbamates). Moreover, dithioesters produce living polymers with low polydispersities and are the only RAFT agents with an R group generating a secondary radical that gives good control over methacrylic polymers [12]. However, these advantages come with a set of drawbacks, including retardation in the polymerization of some monomers, like styrene and acrylates, and its intense color and offensive smell making it less suitable for some biological and industrial applications [13].

Indeed, dithioesters offer generally good control over the polymerization process, but it is only compatible with a characteristic set of monomers. PEGMA, DEGMA, and MAA, in particular, are classified as more-activated monomers (MAMs), in contrast with less-activated monomers (LAMs). MAMs have the vinylic group conjugated to a neighboring functionality such as a carbonyl group (e.g. methacrylates, methacrylamides) or an aromatic ring (e.g. styrenes); LAMs, on the other hand, have the vinylic group adjacent to an electron rich atom, such as oxygen or nitrogen (e.g. vinyl esters, vinylamides) [14]. The polymerization of MAMs are generally well controlled through the use of active RAFT agents, such as dithioesters, as these provide a high rate of reversible chain transfer, consequently allowing for rapid equilibration of growing polymer chains [14]. This reinforces the compatibility of MAMs with dithioesters.

Upon consideration of the monomer–RAFT agent compatibility and optimization of the reaction conditions, success on homopolymerization has been achieved. An inert atmosphere for the reaction mixture was necessary, as oxygen can also be a source of radicals, thereby dampening the method’s control over the polymerization process.

Block copolymers with different monomer compositions were then prepared by aiming at different initial macro–CTA and monomer feeds. The order by which the two monomers were polymerized is very crucial as this dictates the success of block copolymerization via RAFT. For an AB diblock copolymer, the propagating chain A must have a better, or comparable, leaving group ability relative to monomer B. Otherwise, chain A may not fragment and propagate with monomer B to produce the desired product. In the study, block copolymerization was performed in two different routes: (1) using polyPEGMA or polyDEGMA, and; (2) using polyMAA as the macro–CTA. For the first case, it was observed that the MAA monomer failed to incorporate into the macro–CTA moiety. Assessment of the polymer’s structure, properties, and thermo-responsive behavior has proven so. Only for the second case was a successful block copolymerization attained. This suggests that MAA is a better leaving group than PEGMA or DEGMA, under the reaction conditions used. This was further justified by evaluation of the monomeric molecular structures and properties.

B. Gel Permeation Chromatography

The polymers’ number average molecular weights, \( M_n \), and polydispersity indices, PDI (weight average molecular weight \( M_w \) / number average molecular weight \( M_n \)), as determined by GPC are shown in table I.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Number Average Molecular Weight, ( M_n )</th>
<th>PDI, Weight Average MW/Number Average MW, ( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyPEGMA</td>
<td>104476</td>
<td>1.03589</td>
</tr>
<tr>
<td>polyDEGMA</td>
<td>36165</td>
<td>1.28276</td>
</tr>
<tr>
<td>polyMAA</td>
<td>9495</td>
<td>1.05795</td>
</tr>
<tr>
<td>MAA–PEGMA (1:100)</td>
<td>34598</td>
<td>1.08887</td>
</tr>
<tr>
<td>MAA–DEGMA (1:200)</td>
<td>156020</td>
<td>1.09961</td>
</tr>
<tr>
<td>MAA–PEGMA (1:300)</td>
<td>175984</td>
<td>1.17695</td>
</tr>
<tr>
<td>MAA–DEGMA (1:100)</td>
<td>12499</td>
<td>1.11903</td>
</tr>
<tr>
<td>MAA–DEGMA (1:200)</td>
<td>51621</td>
<td>1.07290</td>
</tr>
<tr>
<td>MAA–DEGMA (1:300)</td>
<td>52867</td>
<td>1.07775</td>
</tr>
</tbody>
</table>
As theoretically expected, the molecular weights of the block copolymers increase with increasing monomer feed ratio, with respect to the macro–CTA. This trend strongly suggests the success of block copolymerization, and that the activity of the CPAD RAFT agent was still intact after the first polymerization process, thereby allowing further chain propagation with the second monomer.

Likewise, a generally increasing trend for the PDI was also observed. This increase is attributed to the persistence of small amounts of polymer defects, formed inevitably during block copolymer synthesis. These defects include initiator–derived block copolymers, initiator–derived homopolymers, dead copolymers, and dead homopolymers. The influence of the dead chains formed during the RAFT process increases with the addition of successive blocks to such a degree that reports of block copolymers of low dispersity from more than three successive RAFT polymerizations are rare; the highest number of successive RAFT polymerizations resulting in block copolymers of relatively low dispersity appearing in the literature is currently five [14].

C. Fourier Transform–Infrared Spectroscopy

The FT–IR spectra for the homopolymers are in good agreement with their corresponding molecular structures and functional groups. The significant peaks include that for the ester and ether groups of polyPEGMA and polyDEGMA, and that for the carboxylic acid functionality of polyMAA. Also noted were the peaks for CPAD functionality in the polymers. This supports and confirms the inference made with the GPC data on the structural integrity of the RAFT agent.

The block copolymers then exhibit distinct peaks for both the ester and ether groups of the PEGMA or DEGMA unit, and the carboxylic acid group of MAA. The peaks for the CPAD RAFT agent, however, were hardly distinguishable most likely due to either masking by other more prominent peaks, or shielding of the involved functional moiety by the long polymeric chains.

For better comparative analysis, the superimposed spectra of the synthetic polymers under study are graphically represented in fig. 1 and 2.

D. Proton Nuclear Magnetic Resonance Spectroscopy

Fig. 1 and 2 demonstrate the varying degrees of monomer feed ratio, as suggested by the increasing intensity of the O–H peak attributed to the MAA unit. This is further proof that block copolymers of different compositions were successfully synthesized.

Figure 1. Superimposed FT–IR spectra of PEGMA–based polymers

Figure 2. Superimposed FT–IR spectra of DEGMA–based polymers

Figure 3. NMR spectrum for polyMAA

Figure 4. NMR spectrum for polyPEGMA
Like the FT–IR data, the obtained \(^1\)H–NMR data are in good agreement with the polymeric structures. The significant peaks to distinguish polyPEGMA and polyDEGMA from polyMAA were likewise observed: peaks for the ethylene glycol chain of both polyPEGMA and polyDEGMA (6.2–4.0 ppm), and peaks for the O–H functionality of polyMAA (13–11.5 ppm). Also, peaks for the CPAD moiety were noted for the homopolymers at around 0.7–4.2 ppm.

The NMR spectra of representative block copolymers with the peak designations are then shown in figures 6 and 7.

The block copolymers show peaks corresponding to both the ethylene glycol chain of PEGMA or DEGMA and the hydroxyl group of MAA, thereby suggesting the successful incorporation of both monomer units into the diblock copolymer product, in accordance with the GPC and FT–IR data. NMR data also exhibit the absence of peaks for the CPAD RAFT agent in the spectra of the block copolymers. Unlike that of the FT–IR peaks, however, NMR peaks are much less prone to masking by other more prominent signals, as the latter are considerably sharper than the former. As such, NMR data associates the absence of such CPAD peaks more closely to the possibility of the shielding effect the long polymeric chains has on the RAFT agent’s moiety. With the flexibility of single bonds, it is highly likely that in solution, the polymer chains bend and twist in a configuration that may hide the CTA backbone against the incoming magnetic field introduced by the NMR instrument.

With NMR integration data, the fractional conversion was then calculated, and subsequently, the theoretical \(M_n\), according to the equation below.

\[
M_n = \frac{[M_o] \times M_{mon} \times \rho}{[CTA]_o} + M_{CTA} \tag{1}
\]

Where \([M_o]\) is the initial monomer concentration, \(M_{mon}\) is the molecular weight of the monomer, \(\rho\) is the fractional conversion, \([CTA]_o\) is the initial CTA concentration, and \(M_{CTA}\) is the molecular weight of the CTA. The fractional conversion, the calculated theoretical \(M_n\), and the experimental \(M_n\) based on the GPC data are then shown in table II.

### TABLE II. COMPARISON OF THE EXPERIMENTAL AND THEORETICAL NUMBER AVERAGE MOLECULAR WEIGHTS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Experimental (M_n) (GPC)</th>
<th>Conversion</th>
<th>Theoretical (M_n)</th>
<th>%difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolyPEGMA</td>
<td>104476</td>
<td>0.9198</td>
<td>69271</td>
<td>50.82</td>
</tr>
<tr>
<td>PolyDEGMA</td>
<td>36165</td>
<td>0.6822</td>
<td>32101</td>
<td>12.66</td>
</tr>
<tr>
<td>PolyMAA</td>
<td>9495</td>
<td>0.8946</td>
<td>7981</td>
<td>18.97</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:100)</td>
<td>34598</td>
<td>0.8520</td>
<td>30109</td>
<td>14.91</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:200)</td>
<td>156020</td>
<td>0.8104</td>
<td>119836</td>
<td>30.19</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:300)</td>
<td>175984</td>
<td>0.7991</td>
<td>126579</td>
<td>39.03</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:100)</td>
<td>12499</td>
<td>0.7862</td>
<td>14796</td>
<td>15.52</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:200)</td>
<td>51621</td>
<td>0.9751</td>
<td>36706</td>
<td>40.63</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:300)</td>
<td>52867</td>
<td>0.8025</td>
<td>45314</td>
<td>16.67</td>
</tr>
</tbody>
</table>

It can be observed that the fractional conversion varies from as low as 0.6822 to as high as 0.9751. However, the theoretical molecular weights differ significantly with the experimental values, with about a 12–51 %difference range.
This may then be attributed to the use of polystyrene standards for GPC, polymer standards that vary greatly in size and character relative to the polymer samples synthesized in the study.

**E. Atomic Force Microscopy**

Figure 8. 2D and 3D AFM images of polyPEGMA

Figure 9. 2D and 3D AFM images of polyDEGMA

Figure 10. 2D and 3D AFM images of polyMAA

AFM images generated for polyPEGMA and polyDEGMA show considerable differences, relative to that of polyMAA, in terms of surface morphology and aggregation patterns. PolyPEGMA and polyDEGMA exhibit roughly spherical aggregation patterns, whereas polyMAA exhibits a more tuft-like or powdery texture. Macroscopically, the ethylene glycol-based homopolymers are soft gel-like while polyMAA is more powder-like, characteristics consistent with the generated AFM images.

Figure 11. 2D and 3D AFM images of MAA–b–PEGMA (1:100 macro CTA:PEGMA)

Figure 12. 2D and 3D AFM images of MAA–b–DEGMA (1:100 macro CTA:DEGMA)

Significant changes in the AFM images were then observed upon copolymerization. The process produced even more rigid gel products that were difficult to dissolve in water and even hard to physically tear apart into bits. This explains the capability of the polymer to assemble into a film across the mica plate, with microscopic protrusions on the surface.

These changes show how different polymer compositions and physical properties can elicit different surface morphologies and aggregation patterns.

**F. Ultraviolet–Visible Light Spectroscopy**

In the assessment of the thermo–responsive behavior of the polymers in aqueous solution, absorbance measurements as a function of temperature were performed.

![Absorbance vs Temperature](image)

Figure 13. Absorbance as a function of temperature for the PEGMA–based polymers

![Absorbance vs Temperature](image)

Figure 14. Absorbance as a function of temperature for the DEGMA–based polymers

Fig. 13 and 14 show how the absorbance of an aqueous solution of polyMAA is invariant with temperature. The homopolymer of MAA is soluble in water because of the hydrophilicity of the carboxylic acid groups capable of hydrogen bonding. This hydrophilicity is the reason why no LCST behavior was observed for the polymer, even at
temperatures up to 105°C as reported by Becer et al. [7] With this character, a high temperature is not enough a force to disrupt the polymer–water interactions and cause aggregation.

On the other hand, an abrupt increase in absorbance of both the polyPEGMA and polyDEGMA solutions was observed, as expected of a polymer with reported temperature sensitivity. This increase is linked to how the polymer behaves before and after the LCST. Below its LCST, the homopolymers’ ester and ether functionalities form hydrogen bonds with water molecules and is, thus, water soluble. Its ethylene glycol side chains are sufficiently long enough to shield the methacrylate backbone from water, making the polymer fully soluble in aqueous solution. An increase in temperature then causes the disruption of these hydrogen bonds. The more favorable polymer–polymer interactions result in a structural collapse and subsequently, a more hydrophobic polymer chain. The collapsed chains finally start to aggregate and precipitate in solution.

Precipitation manifests macroscopically as solution turbidity. This justifies the sharp increase in absorbance of the aqueous polyPEGMA and polyDEGMA solutions at elevated temperatures, confirming its thermo–responsive property.

Similar sharp responses were likewise noted for the block copolymers. A general shift to lower absorbance measurements, however, was observed for these polymers upon aggregation; decreasing light absorption with increasing PEGMA or DEGMA content or increasing molecular weight. While a greater molecular weight should theoretically elicit greater absorbance upon aggregation, such was not the case in the study. This may be attributed to more complex molecular interactions of the polymer and its dissolving medium. It is possible that with higher PEGMA or DEGMA content, there is better polymer hydration, owing to the presence of more hydrophilic groups. Better solvation then causes better dispersion and less light absorption.

### TABLE III. LCST VALUES VIA UV–VIS DATA

<table>
<thead>
<tr>
<th>Polymer</th>
<th>LCST (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyPEGMA</td>
<td>25</td>
</tr>
<tr>
<td>polyDEGMA</td>
<td>32</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:100 macro CTA:PEGMA)</td>
<td>26</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:200 macro CTA:PEGMA)</td>
<td>33</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:300 macro CTA:PEGMA)</td>
<td>38</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:100 macro CTA:DEGMA)</td>
<td>35</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:200 macro CTA:DEGMA)</td>
<td>37</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:300 macro CTA:DEGMA)</td>
<td>38</td>
</tr>
<tr>
<td>polyMAA</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Apart from the shift in absorbance readings, a significant shift in the LCST among the block copolymers was also observed. The trend suggests direct proportionality between the LCST and the %mol PEGMA or DEGMA content of the copolymers, or alternatively, an inverse proportionality between the LCST and the %mol MAA content. However, the incorporation of hydrophilic comonomers, in this case MAA, should theoretically increase the LCST. Fortunately, Jones et al. [11] also observed an opposition to such a theoretical inference, using similar monomers as those employed in the study. Furthermore, Becer et al. [7] also obtained the same trend with copolymers of MAA and oligo(ethylene glycol) methacrylate. The rationale behind this is the apparent intramolecular interactions between PEGMA or DEGMA’s ether group and MAA’s carboxylic acid group, thereby negating the hydrophilicity introduced by the MAA unit and ultimately, its effects on the LCST of the polymer.

The copolymerization molar ratios utilized in the study led to experimental LCSTs that considerably differ from each other. This suggests that an even wider molar ratio range can produce copolymers with more varied LCSTs. Consequently, this proves how efficient LCST tailoring can be by varying molar feed ratios.

#### G. Dynamic Light Scattering

![](image1.png)

**Figure 15. Z–average particle diameter as a function of temperature for the PEGMA–based polymers**

![](image2.png)

**Figure 16. Z–average particle diameter as a function of temperature for the DEGMA–based polymers**

DLS was performed to gather data in support of the observations of the polymers’ thermo–responsive behavior via UV–Vis spectroscopy. As can be noted in fig. 15 and 16, the DLS data show striking resemblance and are in excellent agreement with the UV–Vis data. The sharp LCST transitions were still observed, and so was the shift in measurements of the Z–average particle diameter among the synthetic block copolymers.
The LCST values of the polymers via UV–Vis and DLS data are presented in Table IV.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>LCST from UV–Vis data (°C)</th>
<th>LCST from DLS data (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyPEGMA</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>polyDEGMA</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:100 macro CTA:PEGMA)</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>MAA–b–PEGMA (1:200 macro CTA:PEGMA)</td>
<td>33</td>
<td>35</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:300 macro CTA:DEGMA)</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:100 macro CTA:DEGMA)</td>
<td>35</td>
<td>32</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:200 macro CTA:DEGMA)</td>
<td>37</td>
<td>35</td>
</tr>
<tr>
<td>MAA–b–DEGMA (1:300 macro CTA:DEGMA)</td>
<td>38</td>
<td>36</td>
</tr>
<tr>
<td>polyMAA</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The LCST values of the polymers via UV–Vis spectroscopy and DLS are all significantly near the physiological temperature. Previously reported literatures have been aiming at producing thermo-responsive polymers with such LCSTs, a feat commonly achieved with PNIPAM. However, as already pointed out, PNIPAM has high cytotoxicity making it less suitable for biological applications. PEG–based polymers, on the other hand, are more biocompatible while also exhibiting temperature sensitivity. Both biocompatibility and LCST near the physiological temperature, the synthetic polymers under study may then be considered for applications such as surgical sutures, or drug delivery systems. For the latter, however, further biocompatibility studies are necessary.

Comparison of the LCST values obtained via UV–Vis and DLS reveal offsets of up to 3°C, which is not that significant considering how these two instruments, or these two methods of assessing the LCST, have different mechanisms and/or limits of sensitivity. Overall, these results still suggest a great correlation between the responses of light absorption and the Z–average particle diameter in aqueous solution to increasing temperatures. Moreover, the sharp LCST transitions observed for both methods show how well–defined the synthesized polymers are, and this is exactly what the GPC data shows with the low PDI values.

IV. CONCLUSION

In this study, the efficiency of the RAFT method in the synthesis of thermo–responsive block copolymers was assessed. The GPC data showed increasing molecular weights and increasing PDI with a corresponding increase in monomer feed ratio, with the latter attributed to the inevitable persistence of small amounts of polymer defects. Low PDI values (1.03–1.28) were obtained, indicative of the great control the RAFT technique has over the polymerization process. FT–IR data then demonstrated the varying degrees of monomer feed ratio, as suggested by the increasing intensity of the MAA unit’s hydroxyl group peak, whereas the NMR data opened the possibility of the shielding effect the long polymeric chains has on CPAD’s moiety. In conjunction, both FT–IR and NMR data showed good agreement with the molecular structures and functional groups of the polymers, and also with reported literatures. These characterization techniques also revealed the structural integrity of the RAFT agent, thereby allowing further block copolymerization. Fractional conversion values from NMR integration data range from 0.68–0.98, whereas the difference between the calculated theoretical $M_n$ and the experimental values range from 12–21%.

The generated AFM images then exhibited changes in surface morphologies and aggregation patterns with varying polymer compositions. In the order of increasing cohesive property: polyMAA showed a powdery texture, polyPEGMA with roughly spherical assemblies, and the block copolymers as films with surface protrusions.

Lastly, the thermo–responsive behavior of the synthetic polymers was analyzed via both UV–Vis spectroscopy and DLS. The two methods exhibited sharp LCST transitions, a proof of how well–defined the polymers are. A general shift in both the absorbance and the particle diameter among the block copolymers was also observed due to the effect of increasing the PEGMA or DEGMA content of the copolymers. Increasing LCST was duly noted with increasing %mol PEGMA or DEGMA, primarily due to intramolecular interactions. Generally, UV–Vis and DLS results suggest the efficient LCST tailoring by variation of the macro CTA:PEGMA or DEGMA molar ratio.

All the structural and polymer behavior studies conducted in this work indicate how powerful and versatile RAFT polymerization is. With its exceptional control over the whole polymerization process, it is able to produce smart polymers with fine–tuned properties, for very particular applications.

ACKNOWLEDGMENT

This study was done with funding from the Natural Sciences Research Institute, with instrumental and intellectual support from Dr. Portia Mahal Sabido laboratory and associates, and from Dr. Florentino Sumera laboratory and associates, both part of the Institute of Chemistry, University of the Philippines Diliman. Further support on instrumental use was provided by the Analytical Services Laboratory (ASL) in the Institute of Chemistry.

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