ARGET ATRP of Ethylene Glycol Dicyclopentenyl Ether Methacrylate with Vegetable Oil and Terpene-derived Methacrylic Monomers

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Abstract: Homo and statistical copolymerization reactions of ethylene glycol dicyclopentenyl ether methacrylate (EGDEMA) and a vegetable-oil based methacrylic ester C13MA (average alkyl chain length = 13) are studied via activator regenerated electron transfer polymerization (ARGET ATRP) using only trace amounts of copper catalyst. Poly(EGDEMA) and poly(C13MA) homopolymers and statistical poly(EGDEMA-*stat*-C13MA) copolymers are cleanly synthesized with monomodal molecular weight distribution and dispersities Đ = M_w/M_n= 1.39-1.76 and $M_n \sim$ 12 kg mol^{-1}. Chain end fidelity is confirmed by chain extension from poly(C13MA) macroinitiator with EGDEMA to make poly(C13MA-b-EGDEMA) diblock copolymers, which exhibit two distinct glass transition temperatures (T_gs), one for the poly(C13MA) block (~-39°C) and the other for the poly(EGDEMA) block (23.9°C), suggesting microphase separation. Due to the relatively low T_g of poly(EGDEMA-*stat*-C13MA), terpene-derived isobornyl methacrylate (IBOMA) is copolymerized with EGDEMA forming poly(EGDEMA-*stat*-IBOMA) statistical copolymers with T_gs ranging from 22.9°C-113°C. Additionally, crosslinking of the poly(EGDEMA) homopolymer and poly(EGDEMA/C13MA) and poly(EGDEMA/IBOMA) copolymers is achieved by UV thiol-ene clicking of the pendent double bonds of EGDEMA units with suitable dithiols at 365 nm. For

poly(EGDEMA), conversion of the thiol-ene click reaction reaches 70% while conversion is higher in the copolymers poly(EGDEMA-*stat*-C13MA) with a conversion up to 92% and poly(EGDEMA-*stat*-IBOMA)) reaching 97%.

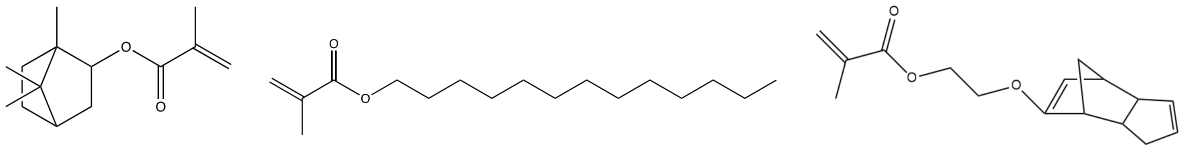
1.Introduction

The synthesis of tailor-made polymers with specific structures and functionality has long been a goal of polymer scientists to enhance performance for advanced applications in diverse areas such as thermoplastic elastomers, coatings, adhesives, surfactants, and biomedical materials.[1] Particularly, polymers in these applications possessing pendent double bonds are desirable for post-polymerization modifications by Diels-Alder, thiol-ene click chemistry, and photochemical cross-linking chemistries.[2] Polymers possessing such pendant side groups are challenging to polymerize in a controlled fashion as the reactive functional group may participate in unwanted side reactions or compete with the main chain vinyl groups, yielding broad molecular weight distributions, poorly controlled microstructures, and possibly gel formation. [2] Control of the active radical concentration is one way to reduce the frequency of such side reactions and advanced reversible deactivation radical polymerization methods can achieve this goal.

Atom transfer radical polymerization (ATRP) has emerged as a very powerful and versatile controlled polymerization method (known more properly as reversible deactivation radical polymerization (RDRP)). ATRP allows the synthesis of polymers with narrow molecular weight distribution (characterized by dispersity Đ), predictable molecular weights, complex architectures, and high chain-end fidelity.[3,4] ATRP is tolerant to low impurity concentrations and recently has been reported to be tolerant of oxygen.[5] Efforts in green or sustainable ATRP have been directed towards using green solvents, lowering catalyst concentrations, and synthesizing degradable polymers.[6] Such improvements are in line with principles of green chemicals and processes, which are defined as being environmentally friendly (eg. less hazardous, and safer chemicals), and have lower material and energy requirements, respectively, amongst others.[7] ATRP traditionally utilizes a metal complex as a catalyst to mediate its dynamic equilibrium between active and dormant chains. Using metallic catalysts is often viewed as the main weakness of ATRP as it causes discoloration of the final polymer product and requires extensive treatment to be removed.[8,9] The metal catalyst, typically copper-based, can be toxic and environmentally problematic once discarded.[10]

Many methods have aimed to reduce the catalyst concentration in ATRP. [11,12] For example, altering the initiation method to allow the regeneration of the lower oxidation state to push the reaction forward was proposed. The different initiation methods all follow the same ATRP reaction mechanism but vary in terms of the concentration of the metal complex used, the oxidation state of the added transition metal, and the procedure of activating the metal complex.[13,14] Activator regenerated by electron transfer (ARGET) is an electron transfer technique in which the activator species is continuously regenerated from the deactivator species. It is favorably considered because it uses only ppm amounts of catalyst in the presence of a reducing agent.[15] For example, ARGET was successfully employed in the synthesis of poly(butyl acrylate) with 50 ppm of $CuBr_2$ with a target number average degree of polymerization (DP_n) of 500, whereas a higher concentration of 500 ppm was required to achieve the same Đ with a DP_n of 50.[16] In another work, the concentration of copper was successfully reduced to only 10 ppm of copper in the polymerization of styrene using ARGET ATRP yielding polymers with low Đ = 1.17 at 110°C and Đ = 1.35 at 90°C.[17] New advances with lower ligand requirements and trace amounts of copper catalyst used show potential to be adopted on an industrial scale. [16,17] ARGET ATRP demonstrated good control and was used to synthesize well-defined, essentially colorless polymers using only trace amounts of the copper catalyst.[18–20]

Increasingly in the polymer industry, petroleum-derived monomers are being substituted with monomers made from renewable resources like carbohydrates and vegetable oils.[21, 22] The latter is an excellent choice due to its abundance, competitive price, and their non-toxic and biodegradable nature.[23, 24] Triglycerides in vegetable oils can be chemically modified and reacted to enhance cross-linking, adhesion, and other properties.[25] Many examples exist of bio-based monomers;[26] one interesting example of a bio-based monomer, derived from pine sap, is isobornyl methacrylate (IBOMA). IBOMA is often copolymerized in tandem with other unsaturated monomers. Poly(IBOMA) has a high glass transition temperature which varies with its molecular weight in the range of 110-200 ºC. [27–29] This makes IBOMA suitable for use as it forms high T_g polymers when copolymerized with other monomers.[30] Another example of a partially sustainably sourced monomer is the vegetable-oil-based methacrylic ester, similar to lauryl methacrylate (C13MA, average alkyl side chain length = 13 carbons). It is a hydrophobic methacrylate whose polymer has a very low glass transition temperature of around -46°C;[31] the structures of the monomers are presented in **Figure 1**.



IBOMA C13MA EGDEMA

Figure 1. The chemical structures of the monomers IBOMA, C13MA, and EGDEMA.

Moreover, functional monomers with a pendent bicyclic moiety containing a reactive double bond, such as that in ethylene glycol dicyclopentenyl ether methacrylate (EGDEMA), allow modification by the reaction of the double bond by various chemistries such as thiol-ene click chemistry.[32]

EGDEMA, also known as dicyclopentenyloxyethyl methacrylate (DCPMA), is a methacrylate bearing pendent reactive cyclo-alkenyl functionality.[32] There are several applications for EGDEMA-based polymers, including dental fillings,[33] polymer-based bone grafts, [34] wood coatings,[35] and anti-bacterial films.[36] The norbornene group in EGDEMA allows thiol-ene click reactions with a suitable thiol. The thiol-ene reaction can also be applied in UV curing, in which EGDEMA acts as the crosslinking agent.[37] EGDEMA polymerization by RDRP processes has only recently been explored. EGDEMA was successfully polymerized by nitroxide mediated polymerization (NMP) using Dispolreg 007 initiator;[37] it was also copolymerized with a low fraction of styrene (~ 10 mol% in the initial monomer mixture) via NMP by Maupu et al·[38] Additionally, EGDEMA was successfully homopolymerized via ambient temperature ATRP (AT-ATRP) both in bulk and in solution by Mandal and Singha, where polymers exhibiting low Đ were obtained (Đ = 1.39) with solution polymerizations reaching 42% conversion after 60 min at room temperature.[32] The synthesis of a triblock copolymer of EGDEMA and poly(2-ethylhexyl acrylate) PEHA by ATRP and post-modification with thiol-ene click chemistry was also reported·[32] Lastly, Mandal et al. reported the synthesis of EDGEMA and 2-ethylhexylacrylate (EHA) copolymer and modification using thiol-ene click chemistry and subsequent UV crosslinking. [32]

This work reports the homopolymerization of EGDEMA by the reduced catalyst RDRP method, ARGET ATRP, which has not been reported yet to the best of our knowledge. This study also reports the synthesis of photocurable resins of copolymers of EGDEMA and the bio-based monomers C13MA and IBOMA via ARGET ATRP. IBOMA and C13MA can be used to impart specific mechanical properties into the photocurable resins: IBOMA provides hardness and strength whereas C13MA provides flexibility. EGDEMA adds functionality through its cyclic pendent group which allows post-polymerization modification for crosslinking. Copolymers with different ratios of EGDEMA and bio-based monomers were synthesized and studied. The polymers were used to prepare UV curable formulations. Photo-curing of the colorless polymers containing the functional EGDEMA groups was done through a post-polymerization reaction of the pendent double bond via thiol-ene click chemistry.

2. Experimental Methods

2.1. Materials

Ethylene glycol dicyclopentenyl ether methacrylate (EGDEMA ≥ 90%) was purchased from Millipore Sigma. Isobornyl methacrylate (IBOMA, >99%) and a mixture of alkyl methacrylates with an average chain length of 13 carbons (C13MA, >99%) were obtained from Evonik. The monomers were purified to remove the inhibitor by passing through a column of basic alumina (Brockmann, Type 1, 150 mesh, Sigma-Aldrich) mixed with 5 wt % calcium hydride (90–95% reagent, Sigma-Aldrich) and then stored in a sealed round bottom flask under a head of nitrogen in a refrigerator until needed. Ethyl α-bromoisobutyrate (EBiB 98%), copper (I) bromide (CuBr 99%), copper (II) bromide ($CuBr_2$ 99%), tin(II) 2-ethyl hexanoate (Sn(II)EH 92.5-100%), silica gel (Davisil grade 633, pore size 60 Å, 200-425 mesh particle size), and N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA≥99%) were all obtained from Sigma-Aldrich and used as received. Ethylene bis(3-mercaptopropionate), Thiocure®320, was obtained from Bruno Bock Chemische Fabrik GmbH & Co, and used as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA ≥99%) was obtained from Aldrich and used as received. Toluene (≥99%), tetrahydrofuran (THF, 99.9% HPLC grade), methanol (MeOH, ≥99%), and dimethylformamide (DMF, 99.8%) were obtained from Fisher Scientific and used as received. The deuterated chloroform ($CDCl_3$,

≥99%) used as a solvent for proton nuclear magnetic resonance (^{1}H NMR) was purchased from Cambridge Isotopes Laboratory.

2.2. Synthesis of poly(EGDEMA), poly (C13MA), or poly(EGDEMA-*stat*-C13MA) via traditional ATRP

Homopolymers and copolymers with EGDEMA and C13MA were initially synthesized using traditional ATRP as a benchmark. For the typical synthesis of poly(EGDEMA), in a 100 mL round bottom three-necked reactor flask, 14.86 g (75 mmol) of the monomer EGDEMA and 14.86 g (0.16 mol) of toluene are added to produce a 50 wt% monomer solution. For the statistical EGDEMA/C13MA copolymers, the concentrations of each monomer used were varied to obtain different copolymer ratios. 0.13 g (0.7 mmol) of the initiator EBiB is added to the reactor flask along with 0.11 g (0.6 mmol) of the ligand PMDETA, and 0.044 g CuBr (0.3 mmol). The target number average degree of polymerization at complete conversion (DP_n) which indicates the number of repeating units in the polymeric chain, was set to DP_n=100 for this set of reactions.

2.3. Synthesis of poly(EGDEMA), poly (C13MA), or poly(EGDEMA-*stat*-C13MA), poly(EGDEMA-*stat*-IBOMA) via ARGET ATRP

ARGET ATRP was used for the synthesis of homopolymers and copolymers of EGDEMA and C13MA. For the typical synthesis of poly(EGDEMA), in a 100 mL round bottom three-necked reactor flask was added 14.76 g (74.5 mmol) of the monomer EGDEMA in a 50wt% toluene solution (14.77 g (0.16 mol) of toluene). For the statistical EGDEMA/C13MA copolymers, the concentrations of each monomer used initially were varied to obtain different copolymer ratios. 0.24 g (1.23 mmol) of initiator EBiB are added to the reactor flask along with 0.0798 g (0.5 mmol) of the ligand PMDETA, 0.0069 g $CuBr_2$ (0.03 mmol), and 0.12 g (0.3mmol) of $Sn(EH)_2$. The target DP_n for this set of reactions was 50, corresponding to a molecular weight $M_{n,\ target}$ = 13 kg/mol at complete conversion for homo poly(EGDEMA); a relatively low DP_n was targeted to obtain low viscosity polymers that can be easily applied onto substrates for application. The reactor was attached to a condenser to prevent the evaporation of monomer or solvent; the condenser set to 5°C was fixed into the middle neck of the flask. A magnetic stir bar was added to the reactor which is placed on a heating mantle on top of a stirrer. The mixture in the reactor was purged with nitrogen for 20 minutes while stirring and the purging remained for the rest of the polymerization. The mixture was then heated at a rate of 3°C/min. The nitrogen purge was vented through the condenser via a needle poked into a septum. The polymerization was considered to begin when the temperature reached 80°C. A thermocouple in the left neck of the flask monitored the temperature of the solution. The reactions were stopped when very high viscosity was reached, and the reaction times varied between 40-80 minutes. After the reaction was deemed completed (when samples could not be taken any further due to the high viscosity), the heating was switched off and the reactor was left to cool down. The resulting polymers were precipitated in methanol, decanted, and then left to dry in the fume hood.

2.4. Thiol-ene clicking of the polymers with the bi-functional thiol ethylene bis(3-mercaptopropionate)

Ethylene bis(3-mercaptopropionate), commercially available as Thiocure®320, was used for thiol-ene clicking. It is a bifunctional thiol with low viscosity and with less odor compared to other thiols like ethane dithiol. For the crosslinking of the poly(EGDEMA) homopolymer (2.0 g), the functional polymer was dissolved in a 50wt% solution of the bio-sourced solvent 2-MeTHF (2.0

g). To the solution was added the dithiol in the ratio of 0.8:1 of EGDEMA: thiol groups (Thiocure®320, 0.7 g) and a photo-initiator (DPMA, 0.04g) to prepare a photo-curable formulation. As for the copolymers, the polymers were dissolved in 50wt% toluene to ensure complete dissolution and mixed with the dithiol ethylene bis(3-mercaptopropionate) and DMPA. The mixtures were stirred vigorously, and after ensuring sufficient mixing, they were applied onto the samples and left to dry in a fume hood overnight under ambient conditions to evaporate the solvent. The UV chamber (Spectroline-XL1000) with a UV wavelength of λ=365 nm was used for curing the samples. The samples were placed in the reactor for 6 minutes to crosslink and then left in the fume hood overnight to completely cure.

2.5. Polymer characterization

During each polymerization, two samples were withdrawn using a syringe at each of the following times: 10 minutes, 20 minutes, 40 minutes, and 60 minutes. The first sample taken at each time was 0.3 mL in volume, which was then mixed with methanol to precipitate the polymer for gravimetric conversion measurement. The second sample taken at each time was 0.1 mL in volume, which was dissolved in tetrahydrofuran (THF) for the determination of the molecular weight via gel permeation chromatography (GPC).

The M_n and Đ were evaluated using GPC (Waters Breeze) with HPLC grade THF as a mobile phase and a differential refractive index detector (RI 2414). The GPC was equipped with three Waters Styragel HR columns (HR1 with a molecular weight measurement range of $1\times10^2 - 5\times10^3$ g/mol, HR2 with a molecular weight measurement range of $5\times10^2 - 2\times10^4$ g/mol, and HR4 with a molecular weight measurement range of $5\times10^3 - 6\times10^5$ g/mol), and a guard column was used. A mobile phase flow rate of 0.3 mL/min was applied, and the columns were heated to 40°C during the characterization. The molecular weights we determined by calibration with linear narrow molecular weight distribution PMMA standards at 40°C without applying the Mark–Houwink–Sakurada equation.

The conversion was determined gravimetrically for C13MA/EGDEMA copolymers, and using ^{1}H NMR (Varian NMR Mercury spectrometer, 300 MHz, 32 scans, using $CDCl_3$ deuterated solvent) for EGDEMA homopolymers. For gravimetric conversion, samples removed during the reaction were precipitated and decanted to remove unreacted monomers and the remaining solvent. The samples were then left to dry in the fume hood for 2 days before being placed in the vacuum oven to ensure complete removal of solvent before being weighed again. The formula used to calculate the conversion is shown below in equation 2.1.

$$Conversion\,X = \frac{m_{polymer\ obtained}}{m_{monomer\ added}} = \frac{m_{dry\ sample} - m_{tare\ vial}}{m_{wet\ sample} - m_{wet\ vial}} \qquad \text{Equation 2.1}$$

As for the conversion obtained from ^{1}H NMR the following equation was used for calculation (equation 2.2):

$$X = X_{IBOMA} f_{IBOMA,0} + X_{EGDEMA} f_{EGDEMA,0} \qquad \text{Equation 2.2}$$

where X_{IBOMA} and X_{EGDEMA} are the individual conversion for each monomer obtained from the peaks obtained from ^{1}H NMR and $f_{IBOMA,0}$ and $f_{EGDEMA,0}$ are the initial molar compositions of each monomer.

2.6. Thermogravimetric analysis and differential scanning calorimetry

DSC Discovery 2500 from TA Instruments was used to estimate the glass transition temperatures (T_g) of the polymers. The T_g was measured using DSC under a nitrogen atmosphere at a heating/cooling rate of 15 °C/min using three scans per cycle (heat/cool/heat). The values of T_g were obtained by the inflection point method [39] on DSC traces obtained from the first heat run. Thermogravimetric analysis (TGA) was also performed using a Discovery 5500 TGA (TA

Instruments). TGA analysis was done on the polymers to test their thermal stability. The analysis was performed at a temperature ramp rate of 15°C/min from 25°C to 550°C under nitrogen.

2.7. Fourier-transform infrared spectroscopy (FTIR)

Thermo Scientific Nicolet IS50-ATR FTIR spectrophotometer equipped with an attenuated total reflectance (ATR) diamond attachment was used. Series scans were recorded with a total of 32 scans per spectra. The dried samples were placed on the diamond for the analysis of the functional groups to monitor the thiol-ene click reaction. The norbornene functional groups were monitored with the absorption peak of the double bond at 1638 cm^{-1}. The thiol group was observed with the absorption peak of the S-H bond at 2570 cm^{-1}. The signal was normalized to a constant peak to account for the differences in concentrations of different samples. The conversion in FTIR was calculated by integrating the peak corresponding to the pendant double bond and comparing it to that of the polymer before curing.

3. Results and Discussion

3.1. Synthesis of poly(EGDEMA), poly (C13MA), or poly(EGDEMA-*stat*-C13MA) via traditional ATRP

Homopolymers and copolymers of EGDEMA and C13MA were first prepared using traditional ATRP with the ATRP initiator ethyl 2-bromoisobutyrate (EBiB). In all reactions, the toluene solvent concentration was 50 wt% and the polymerization temperature was 80°C. The experimental results for poly(EGDEMA), poly(C13MA), and poly(EGDEMA-*stat*-C13MA) syntheses by normal ATRP are summarized in Table 1. Throughout the reaction, samples were taken periodically for kinetic analysis and the conversion at different reaction times was measured gravimetrically. The start of the reaction was considered when the reaction mixture reached the set temperature. Starting at time zero, samples were taken every 20 minutes until the solution became very viscous and the reaction is stopped; for reactions with a shorter time frame, a sample after the first 10 minutes was also taken. Reaction time for the various polymerizations was in the range of 60-80 minutes except for the homopolymerization of EGDEMA which was only 40 minutes due to its fast polymerization rate. Kinetic plots of monomer conversion (X) in the form of ln[1/(1 – X)] versus time show good linear fits over the periods studied for the different EGDEMA/C13MA compositions; Figure 2 shows the kinetic plots for the traditional ATRP experiments. The plot confirms linear dependency of ln(1-X) with polymerization time is a characteristic of ATRP and controlled radical polymerization.[40]

Table 1. Summary of molecular properties of the homopolymers and copolymers with different ratios of EGDEMA and C13MA by traditional ATRP at 80°C with EBiB initiator in toluene with [EBiB]:[CuBr]:[PMDETA]=1:0.35:0.73 with 4136 ppm of CuBr.

Experiment	*T* (°C)	Time (min)	$f_{0,\ \mathrm{EGDEMA}}$[a]	F_{EGDEMA}[b]	Mn[c] (kg/mol)	Đ[c]	Conversion [d](%)
EG_C13MA_1	80	40	1.00	1	11.6	1.38	96.9
EG_C13MA_2	80	40	0.90	0.88	17.1	1.32	89.8
EG_C13MA_3	80	80	0.64	0.66	19.7	1.47	89.6
EG_C13MA_4	80	80	0.43	0.44	16.1	1.31	78.0
EG_C13MA_5	80	60	0.24	0.28	20.5	1.29	79.6
EG_C13MA_6	80	80	0.08	0.12	11.9	1.25	66.5
EG_C13MA_7	80	80	0.00	0	11.6	1.21	77.5

a. The initial molar fraction of EGDEMA in the initial feed.

b. The final molar fraction of EGDEMA in the copolymer (F_{EGDEMA}) as determined by ^{1}H NMR in CDCl3.

c. The final product's number average molecular weight (M_n) and dispersity (Đ) as estimated by GPC relative to PMMA standards at 40°C in THF.

d. The conversion was determined gravimetrically.

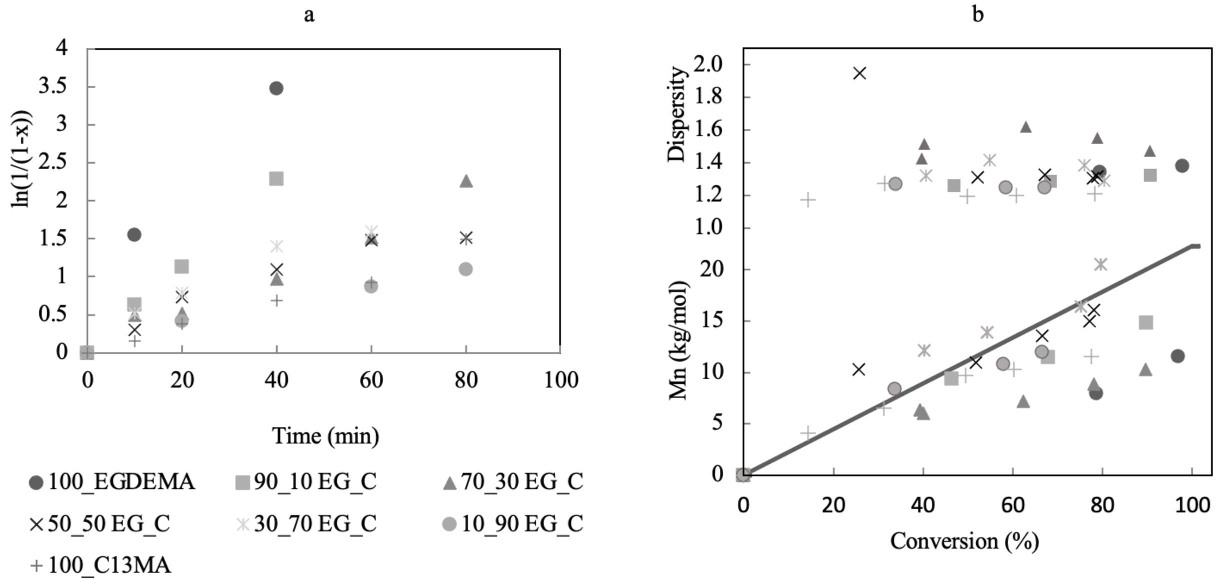


Figure 2: a- Kinetic plot for homopolymers and copolymers with different ratios of EGDEMA and C13MA by standard ATRP at 80°C with EBiB initiator in toluene solvent. b- Plot of number average molecular weight with Đ and conversion for homopolymers and copolymers with different ratios of EGDEMA and C13MA by standard ATRP at 80°C with EBiB initiator in toluene solvent.

Samples obtained throughout the EGDEMA homopolymerization and EGDEMA/C13MA copolymerization were analyzed by GPC (relative to PMMA standards at 40°C in THF) to estimate the number average molecular weight (M_n) and dispersity (Đ) of the polymer chains. The conversion was calculated gravimetrically; the samples were precipitated in a non-solvent, methanol, and then dried and weighed for conversion determination. The M_n versus conversion plots for all the different copolymers were constructed, and the plots are displayed in Figure 2b. A steady increase in the molecular weight as the reactions progressed indicated well-controlled ATRP reactions; a well-controlled ATRP process is defined as exhibiting a linear increase of molecular weight with the monomer conversion with retention of narrow molecular weight distribution (Đ) (and presumably an active chain end capable of reinitiating a second batch of monomer). The data obtained from the EGDEMA/C13MA copolymerization reactions is linear with high conversions of up to 97% and narrow molecular weight distributions (Đ = 1.21-1.47). Although the samples were dissolved and reprecipitated to ensure complete removal of the solvent, nevertheless some trace solvent may have remained in the dry polymer samples and affected the conversion results. The trapped solvent was observed in the TGA analysis as a decrease in the heating curve with an onset at around 110 ºC was observed indicating the evaporation of the trapped solvent (toluene) as shown in Figure 3 below.

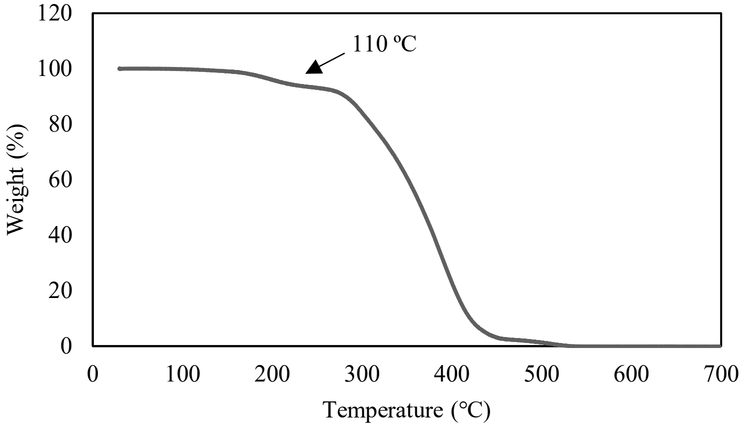


Figure 3. TGA heating curve of the EGDEMA-C13MA copolymer (EG_C13MA_4)

TGA analysis was done for poly(EGDEMA) and poly(C13MA) to test thermal stability (Table 2) and the graphs are presented in Supporting Information Figure S1. For example, poly(EGDEMA) homopolymer started to decompose (onset temperature, $T_{dec,1}$) at 337°C and it decomposed completely at 451.7°C ($T_{dec,2}$) with only 4% ash content remaining. The derivative of weight percent (wt%/°C) shows the temperature $T_{dec,max}$, which corresponds to the peak at which there is the most apparent weight loss (in this case 381.8°C). An apparent decrease in the decomposition temperatures of the copolymers is observed as the mole fraction of C13MA increases in the polymer composition. Therefore, EGDEMA-rich compositions were more thermally stable.

Table 2. TGA analysis results for the decomposition temperatures.

Experiment ID	F $_{\text{EGDEMA}}$[a]	*Tdec,1*[b] (°C)	*Tdec,2*[b] (°C)	*Tdec,3*[b] (°C)	Residue (%)
EG_C13MA_1	1	337.4	381.8	451.8	4.0
EG_C13MA_2	0.85	342.9	386.9	454.9	2.7
EG_C13MA_3	0.65	340.7	395.6	444.3	1.9
EG_C13MA_4	0.46	309.0	391.0	422.6	1.4
EG_C13MA_5	0.30	281.2	384.1	417.2	3.8
EG_C13MA_6	0.16	297.2	386.4	402.0	-

a. The final molar fraction of EGDEMA in the copolymer (F $_{\text{EGDEMA}}$) as determined by ^{1}H NMR in $CDCl_3$.

b. Tdec,1 (onset of decomposition), Tdec,2 (the temperature at which weight loss is most apparent), and Tdec,3 (end of decomposition) measured by TGA under nitrogen flow at a ramp rate of 15°C/min

In typical ATRP reactions, Đ is expected to decrease with monomer conversion;[41] this trend was evident in most of the copolymerization reactions that Đ decreased as higher conversions were approached, except for the EGDEMA homopolymer and the EGDEMA-rich copolymer (EG_90_C13MA_10) which displayed higher Đ at very high conversions. The high Đ may be partially attributed to side reactions that may occur between the active radicals and the double bond in the pendent norbornenyl group thus leading to an increase in the Đ. This was evident in the ^{1}H NMR data as the concentration of the olefin groups decreased towards the end of the reaction relative to the concentration at the beginning, indicating the partial reaction of the double bonds in the norbornenyl groups. The dispersity depends on the concentration of the activator and deactivator species, and the fraction of terminated chains.[41] The increase in the Đ at high conversion is due to the unavoidable termination reactions that are more significant at higher conversion. [41]

The use of traditional ATRP proved to be a successful method for the homopolymerization and copolymerization reactions of C13MA and EGDEMA, yielding polymers with Đ =1.21-1.47; however, the high concentration of copper catalyst resulted in blue-colored polymers that require rigorous purification and post-polymerization treatment. A route for polymerization was thus pursued to avoid these issues.

3.2 Synthesis of poly(EGDEMA) via ARGET ATRP

After establishing the feasibility of the conventional ATRP to polymerize the desired monomers with acceptable DP_n and Đ, ARGET ATRP was used to synthesize homopolymers of the functional methacrylate EGDEMA. The reactions performed are very similar to the traditional ATRP reactions, however, a much lower concentration of the higher oxidation state copper catalyst ($CuBr_2$) is used in conjunction with a reducing agent which continuously regenerates the lower oxidation state of the copper catalyst to maintain the equilibrium. The homopolymerization reactions via ARGET ATRP with the catalytic system ([Monomer]:[EBiB]: [$CuBr_2$]:[PMDETA]= DP/1/0.025/0.375, [$CuBr_2$]: [$Sn(EH)_2$]=1:10) were very fast; high conversion (~99%) was achieved in only 40 minutes. PMDETA was used in 15 times molar excess to 250 ppm ($CuBr_2$) to ensure complexation of the ligand with copper. A high molar excess is required to stabilize the copper complex because of the relatively low activity of the PMDETA/Cu(II) complex. The resultant homopolymer had a M_n = 13.5 kg/mol and Đ = 1.65, which is higher than that obtained via traditional ATRP (M_n = 11.6 kg/mol, Đ = 1.38). The higher obtained Đ is due to the lower rate of deactivation in the ARGET ATRP system. The same reaction was carried out with a higher target DP_n, and a slightly lower Đ was obtained (M_n= 19 kg/mol, Đ = 1.61) which is consistent with literature as lower Đ is expected for a higher degree of polymerization.[41]

3.2.1 Varying the ligand used in ARGET ATRP

The choice of ligand in ARGET ATRP directly impacts the stability and activity of the metal catalyst, thus affecting the control over the polymerization reaction. Nitrogen-based ligands, such as branched aliphatic tetramines, have been applied broadly and successfully in ATRP as they form some of the most stable catalyst complexes.[42] Ligands such as tris((N,N-dimethyl-amino)-ethylamine (Me_6-TREN) and tris(2-pyridylmethyl)amine (TPMA),[43] are commonly used in ARGET ATRP due to their high activity and ability to form stable metal complexes.[16, 44] These ligands form complexes that have equilibrium constants several orders of magnitude higher than other lower activity ligands.[41] The main disadvantages of tetradentate nitrogen ligands are their comparatively higher cost and low solubility in non-polar solvents.[42] Consequently, cheaper ligands with lower activity and better solubility in non-polar media have been sought for ARGET ATRP. These include PMDETA, tris(2-aminoethyl)amine (TREN), diethylenetriamine (DETA), and 2,2'bipyridine (bpy).[45] The main drawback associated with using these ligands is excess concentration is needed to maintain polymerization control, typically requiring at least three to ten times molar excess to stabilize the metal complex and avoid side reactions. Possible destabilizing side reactions include monomer complexation with catalyst and complexation of the catalyst with Lewis acids formed from the reduction mechanism. [10,43] Moreover, the excess ligand not only complexes and stabilizes the metal complex, but also acts as a reducing agent that aids in the success of ARGET ATRP.[46]

For the same ARGET ATRP catalytic system, Me_6TREN was also investigated as a ligand for the homopolymerization of EGDEMA; the results are summarized in Table 3. The catalytic system [EGDEMA]:[EBiB]:[$CuBr_2$]: [Me_6TREN]= DP/1/0.025/0.05 and [$CuBr_2$]: [$Sn(EH)_2$]=1:10. The ligand Me_6TREN was used in only 2 times molar excess to 250 ppm of $CuBr_2$. Due to the higher activity of the Me_6TREN ligand compared to PMDETA, higher control over the polymerization was achieved, yielding polymers with M_n = 16.3 kg/mol and Đ = 1.44. The homopolymerization reaction of EGDEMA was fast with a conversion of ~ 70% in only 35 minutes. However, PMDETA was selected for the copolymerization reactions that will follow because it is a more industrially viable option due to its significantly lower price compared to Me_6TREN,[16,43] and the higher conversions reached using this ligand as shown in the results of the homopolymerization of EGDEMA in table 3. Some parameters were varied in attempt to gain higher control over the polymerization reaction. For example, the reducing agent was fed semi-continuously to maintain a low concentration of the lower oxidation state catalyst species throughout the reaction. The reducing agent was fed drop-wise in three steps at the beginning of the reaction (t=0 min) and every 5 minutes. However, the resulting homopolymer had M_n = 15.3 kg/mol, Đ = 1.54, which is nearly identical to when the reducing agent was all fed initially before the start of the reaction. The same reaction was also carried out at ambient temperature (AT-ARGET-ATRP). The reaction mixture was purged with nitrogen initially, and the temperature was maintained at 25 °C. After 6 hours the polymerization yielded a polymer with 12% conversion with M_n = 11.5 kg/mol and Đ = 1.66 with virtually no improvement in control (based on the molecular weight characterization). The relatively high molecular weight of the polymer at very low conversion may be the result of fractionation.

Table 3. Experimental results for the synthesis of homopolymers of EGDEMA by ARGET ATRP at 80°C with EBiB initiator in toluene solvent.

Experiment	*T* (°C)	Time (min)	Ligand	DP_{target}[a]	Mn_{exp}[b](kg/mol)	Đ[b]	Conversion[c](%)
PM1	80	40	PMDETA	100	13.5	1.65	99
PM2	80	35	PMDETA	200	19.0	1.61	98
MT2	80	40	Me$_6$TREN	100	16.3	1.44	68
MT3	80	35	Me$_6$TREN	100	15.3	1.54	70
MT4	25	360	Me$_6$TREN	100	11.5	1.66	12

a. The target degree of polymerization at complete conversion ([monomer]:[initiator] ratio).

b. The final product's number average molecular weight (Mn_{exp}) and dispersity (Đ) as determined by GPC relative to PMMA standards at 40°C in THF.

c. The conversion was determined gravimetrically.

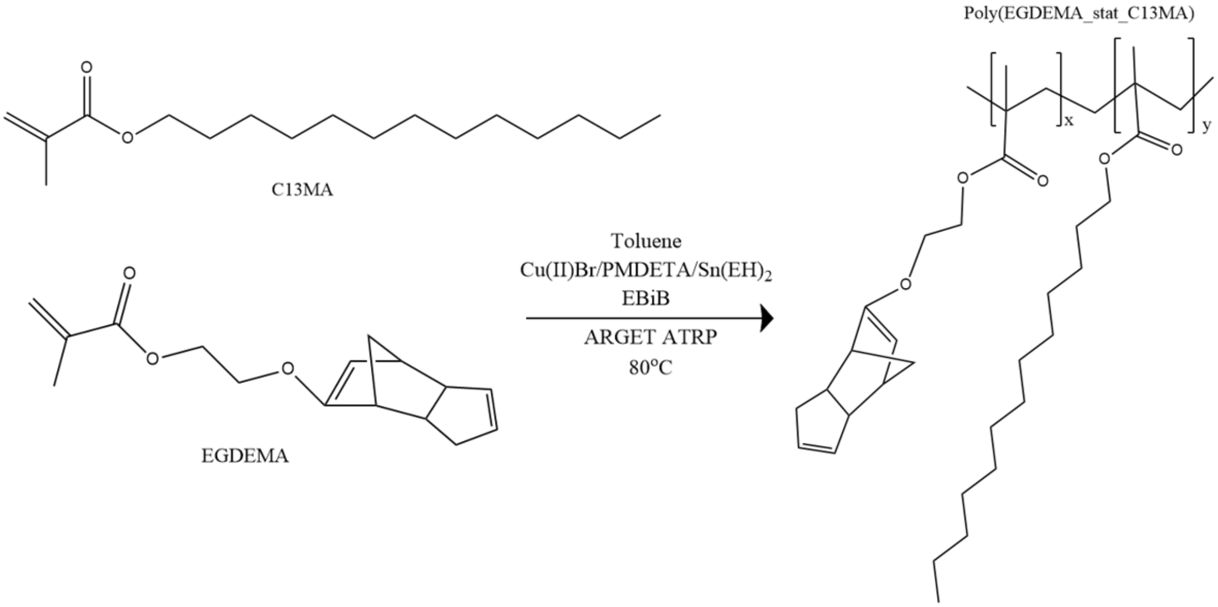


Figure 4. Copolymerization of EGDEMA and C13MA using ARGET ATRP.

3.3 Synthesis of poly(EGDEMA-*stat*-C13MA) via ARGET ATRP

The catalytic system [Monomer]:[EBiB]: [$CuBr_2$]: [PMDETA]= 50/1/0.025/0.375, [$CuBr_2$]: [$Sn(EH)_2$]=1:10 in 50wt% toluene solution was used to synthesize EGDEMA/C13MA copolymers with a target molecular weight of M_n=12 kg/mol; the experimental results are summarized in Table

4. The lower target molecular weight however implies a slight loss of control as lower DP_n typically yields slightly higher Đ.[41] Moreover, the use of a reduced catalyst method like ARGET will also result in a broader molecular weight distribution due to a lower deactivation rate. [41,43] Therefore, we expect Đ to be higher compared to that obtained in traditional ATRP. Reactions were all run to as high conversion as possible until the solution became very viscous to maximize polymer yield. A visual representation of the copolymerization reaction using ARGET ATRP is shown in Figure 4.

The linear increase in the kinetic plots, Figure 5a, indicates well-controlled ATRP reactions.[47] The M_n versus conversion plot for EGDEMA/C13MA copolymerization reactions is linear up to 99% conversions with dispersity Đ =1.39-1.76. Like the conventional ATRP system, EGDEMA-rich copolymers had broader molecular weight distributions compared to C13MA-rich ones. The bulky bicyclic moiety in EGDEMA contains a double bond that can participate in side reactions (such as chain transfer and chain coupling) and hence affects the control over the polymerization reaction yielding higher Đ. This is also confirmed by the tailing observed in the GPC traces and the widening of the distribution for the EGDEMA-rich copolymers shown in Figure S5 in the supporting information. This result is consistent with that reported for EGDEMA via NMP where Đ = 1.5-1.64.[37] Notably, only 250 ppm of $CuBr_2$ was used, and the polymers produced had a very faint blue color and did not require any further purification or post-polymerization treatment for the removal of copper.

Table 4. Experimental results for the homopolymers and copolymers with different ratios of EGDEMA and C13MA by ARGET ATRP at 80°C with EBiB initiator in toluene solvent.

Experiment ID	*T* (°C)	Time (min)	f_0(EG)[a]	F(EG)[b]	Mn[c] (kg/mol)	Đ[c]	Conversion [d](%)
AR_EG/C13MA_1	80	60	1.00	1	7.5	1.76	79
AR_EG/C13MA_2	80	60	0.87	0.85	8.51	1.40	99
AR_EG/C13MA_3	80	60	0.64	0.65	7.95	1.59	88
AR_EG/C13MA_4	80	60	0.43	0.46	10.99	1.45	96
AR_EG/C13MA_5	80	60	0.25	0.30	8.53	1.49	77
AR_EG/C13MA_6	80	60	0.08	0.16	9	1.49	67
AR_EG/C13MA_7	80	60	0.00	0.00	8.05	1.39	70

a. The initial molar fraction of EGDEMA in the initial feed.
b. The final molar fraction of EGDEMA in the copolymer (F_{EGDEMA}) as determined by ^{1}H NMR in $CDCl_3$.
c. The final product's number average molecular weight (Mn) and dispersity (Đ) as determined by GPC with PMMA standards at 40°C in THF.
d. The conversion was determined gravimetrically.

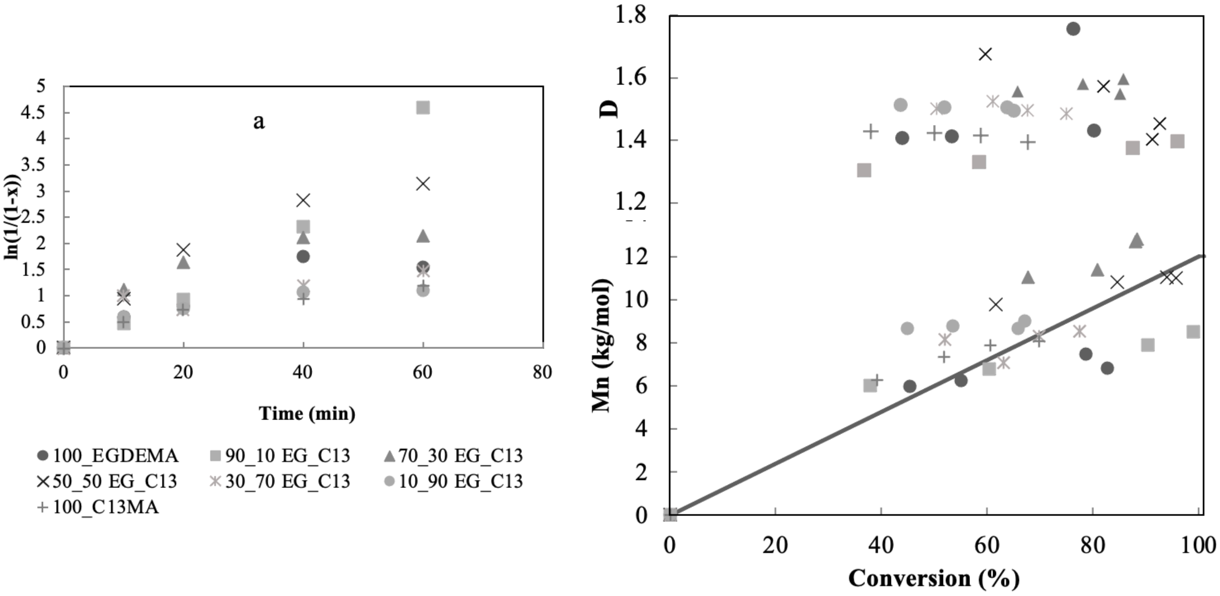


Figure 5. a- Semi-logarithmic kinetic plot for homopolymerization and copolymerization with different ratios of EGDEMA and C13MA. b- Plot of number average molecular weight M_n with dispersity Đ and conversion for different ratios of EGDEMA and C13MA. All polymerization reactions were done by ARGET ATRP at 80°C with an EBiB initiator in 50wt% toluene solvent.

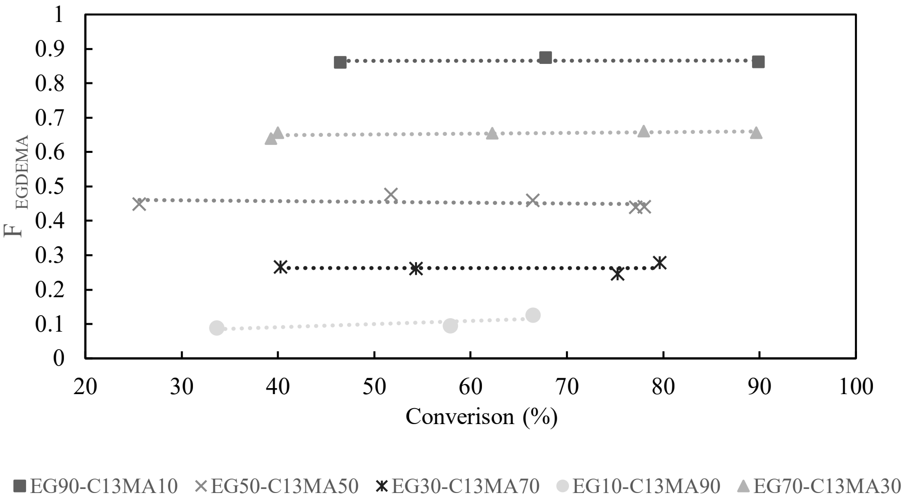


Figure 6. The drift in the molar composition of EGDEMA at different overall conversion values throughout the ARGET ATRP copolymerization of different ratios of EGDEMA and C13MA.

The composition was monitored throughout the reaction and a plot of the composition (F_{EGDEMA}) at different conversions throughout the reaction was constructed (Figure 6). It was observed that the composition does not vary significantly from the initial polymer composition throughout the reaction, as indicated by the linear dotted trendlines, suggesting that the copolymer microstructure is essentially random.

3.4 Synthesis of Poly(C13MA-b-EGDEMA) via ARGET ATRP

The chain-end fidelity of the polymers was tested by performing chain extension of poly(C13MA) homopolymer with EGDEMA to form a block copolymer. Poly(C13MA) homopolymer (M_n = 26.0 kg/mol, Đ =1.38) was synthesized via ARGET ATRP with the catalytic system [Monomer]:[EBiB]:[$CuBr_2$]: [Me_6TREN] = 100/1/0.025/0.05. Poly(C13MA) was then used as the macro-initiator to carry out the chain extension reaction to form poly(C13MA-b-EGDEMA). The reaction yielded a poly(C13MA-b-EGDEMA) with 54 mol% EGDEMA in the final copolymer. The molecular characterization is summarized in Table 5. The reaction was stopped when the high viscosity of the reaction mixture was reached. Initially, after 10 minutes of the reaction, the dispersity was relatively low (Đ = 1.37) and then increased significantly by the end of the reaction (45 mins, Đ = 2.07) but the distribution remained monomodal and shifted to higher molecular weights (Figure 7). An estimation of the dispersity of the second block showed a rather polydisperse block with Đ = 3.1; the calculation was done using the equations provided by Fukuda et. al. [48] The notable increase in the dispersity towards the end of the reaction may be due to the inefficient deactivation as well as the side reactions that the growing radicals have with the pendant double bond. ^{1}H NMR analysis of the samples (Figure S8) shows a decrease in the peaks of the olefin groups from the pendant double group; it was estimated that 8% of the pendant double bonds have reacted in undesirable side reactions yielding an increase in the dispersity value. Successful chain extension indicates the activity of the macroinitiator and the growth of all chains.

Table 5. Experimental results of the chain extension of P(C13MA) with EGDEMA.

A. Macroinitiator					
P(C13MA-Br)	Conversion ^{a} (%)	Mn, exp (kg/mol)	Đ^b		
	90	18.4	1.52		
B. Chain Extended Copolymer					
P(C13MA-b-EGDEMA)	Conversion ^{a} (%)	F^c_{EGDEMA}	Mn,$_{target}$ (kg/mol)	Mn^b,$_{exp}$ (kg/mol)	Đ^b
	91	0.54	55	60	2.07

a. The conversion was determined using ^{1}H NMR in $CDCl_3$.

b. The final product's number average molecular weight (Mn) and dispersity (Đ) as determined by GPC with PMMA standards at 40°C in THF.

c. The final molar fraction of EGDEMA in the copolymer (F_{EGDEMA}) as determined by ^{1}H NMR in $CDCl_3$.

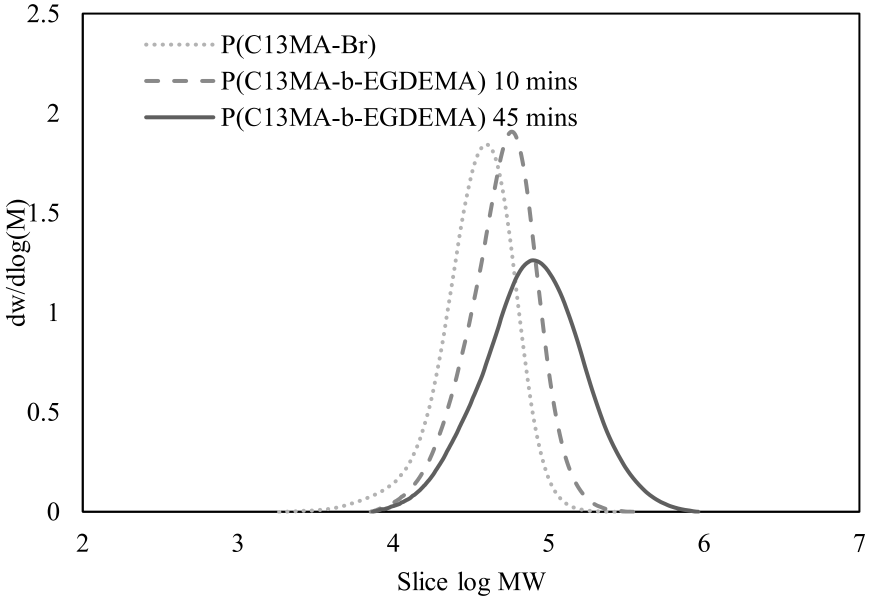


Figure 7. GPC traces of C13MA macroinitiator and the chain extended C13MA/EGDEMA block copolymer poly(C13MA-b-EGDEMA) at 10 mins and 45 mins.

DSC analysis was performed on the obtained block copolymer and the results of the second heating curve are presented in Figure 8. Close examination indicated the presence of two distinct glass transition temperatures, corresponding to the homopolymer T_gs. At -39°C, there is a clear change in the heat flow indicating the T_g of the poly(C13MA), which is in agreement with the literature T_g = -45°C.[31] Another change in heat flow is observed at around 23.9°C corresponding to the T_g of the poly(EGDEMA) block which is consistent with the value obtained earlier for poly(EGDEMA) (T_g = 23°C). The two T_gs observed suggest microphase separation of the block copolymer. The relatively low T_gs suggested the addition of a third monomer, like IBOMA, whose homopolymer has a relatively high T_g, ~ 150 ºC, would improve the hardness of the material and make the resulting material more suitable for applications requiring the formation of a hard film.

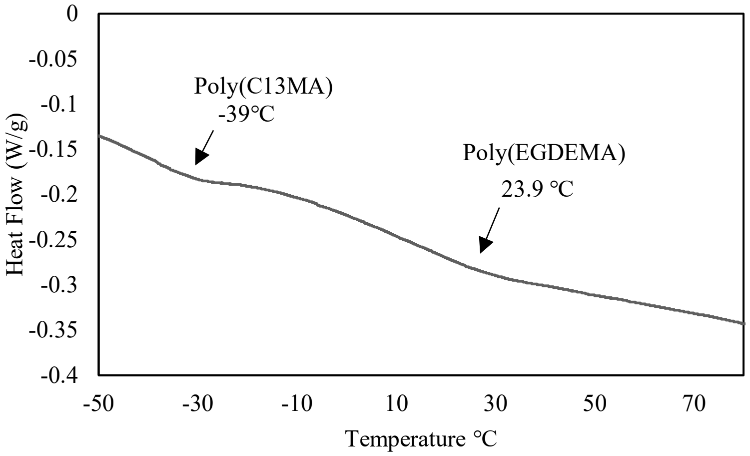


Figure 8. DSC shows the glass transition temperatures of the block copolymer Poly(C13MA-b-EGDEMA).

3.5 Synthesis of Poly(EGDEMA-*stat*-IBOMA) via ARGET ATRP

A set of IBOMA/EGDEMA copolymerization reactions were also performed to form copolymers with relatively higher T_g than those obtained by C13MA/EGDEMA copolymerization reactions, as the incorporation of the bulky IBOMA group imparts hardness whereas the EGDEMA functionality allows for post-polymerization curing. The same catalytic system was employed as that used for the C13MA and EGDEMA copolymers and different ratios were targeted; the experimental results are presented in Table 6 below.

Table 6. Summary of EGDEMA/IBOMA copolymerization reactions by ARGET ATRP at 80°C with EBiB initiator in toluene solvent

Experiment ID	*T* (°C)	Time (min)	$f_{0,\ EGDEMA}$[a]	F_{EGDEMA}[b]	Mn[c] (kg/mol)	Đ[c]	Conversion [d](%)
AR_EG/IBOMA_1	80	40	1.00	1	7.0	1.78	80
AR_EG/ IBOMA _2	80	10	0.87	0.91	6.3	1.49	64
AR_EG/ IBOMA _3	80	40	0.64	0.69	5.4	1.47	81
AR_EG/ IBOMA _4	80	50	0.43	0.50	6.5	1.52	86
AR_EG/ IBOMA _5	80	20	0.25	0.33	5.4	1.45	86
AR_EG/ IBOMA _6	80	60	0.08	0.11	5.6	1.42	88
AR_EG/ IBOMA _7	80	60	0.00	0.00	5.5	1.34	85

a. The initial molar fraction of EGDEMA in the initial feed.
b. The final molar fraction of EGDEMA in the copolymer (F_{EGDEMA}) as determined by ^{1}H NMR in CDCl3.
c. The final product's number average molecular weight (Mn) and dispersity (Đ) as determined by GPC with PMMA standards at 40°C in THF.
d. The conversion was determined gravimetrically.

3.5.1 Thermogravimetric analysis

The thermal properties of the poly(EGDEMA) homopolymer and the poly(C13MA-*stat*-EGDEMA) and poly(IBOMA-*stat*-EGDEMA) homopolymers and copolymers were characterized using differential scanning calorimetry (DSC). DSC was applied to study the T_gs for the block copolymer in the section above but also the homo and statistical copolymers.

The poly(EGDEMA) homopolymer had a T_g of 23°C, whereas the poly(C13MA) homopolymer had a T_g of -39°C, which agrees with previously reported data.[31] The T_g varied between this range for the different EGDEMA/C13MA copolymer compositions. For the copolymerization of IBOMA with EGDEMA, the poly(EGDEMA) homopolymer had a T_g of 23°C, whereas the poly(IBOMA) homopolymer had a T_g of 113°C, which agrees with previous studies.[31] The T_g was then found to vary from 22.9°C to 113°C for different EGDEMA/C13MA copolymer compositions. The DSC results for various compositions of EGDEMA-IBOMA copolymers and EGDEMA-C13MA copolymers are summarized in Figure 9 below. The data is presented in Table S1 and S2 and Figures S2 and S3 in the Supporting Information.

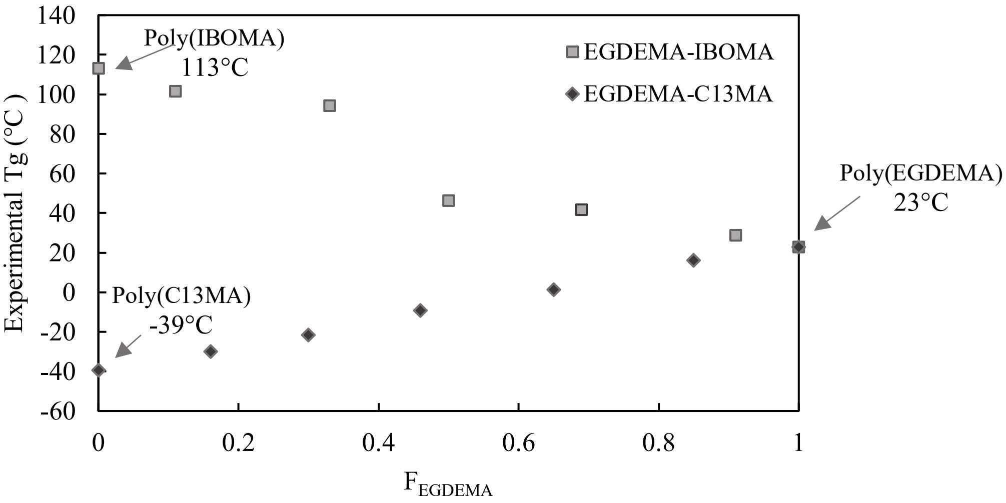


Figure 9. Glass transition temperatures (T_g) of EGDEMA/IBOMA/C13MA copolymers as a function of copolymer composition F_{EGDEMA}.

3.6 Thiol-ene click reactions

3.6.1 Poly(EGDEMA)

Samples of poly(EGDEMA) prepared via ARGET ATRP were used for the thiol-ene click reaction as shown in Figure 10. The dried polymer was dissolved in 2Me-THF and mixed with the dithiol ethylene bis(3-mercaptopropionate) and the photoinitiator DMPA for UV crosslinking via thiol-ene clicking of the pendant double bonds on the EGDEMA unit with the thiols. Samples were prepared and applied as a thin layer on a glass petri dish with a dropper. The sample was dried in the fume hood overnight and then cured in the UV chamber to avoid shrinkage associated with curing before drying. Upon irradiation, the sample formed a crosslinked polymer network with a flat matte appearance. Analysis of the T_gs of the poly(EGDEMA) homopolymer (MT2) synthesized by ARGET ATRP using Me_6TREN ligand by DSC showed a T_g of 30ºC. This result is slightly higher than that obtained earlier due to the higher Mn (16.3 kg/mol) compared to the poly(EGDEMA) reported earlier for the homopolymer with a Mn of 7.5 kg/mol. The crosslinked polymer of poly(EGDEMA) by thiol-ene clicking showed a rise in the glass transition temperature of the crosslinked polymer (60.9ºC) confirming the success of the crosslinking reaction[49]. To study the efficiency of the thiol-ene click reaction, FTIR analysis was performed to track the disappearance of the double bond in the norbornene functionality. The band corresponding to the methacrylate double bond at 1638cm^{-1} (C=C stretching)[50] decreased after curing. This indicates the pendent double bond was reacting with the thiol groups and a new peak emerged at ~670 cm^{-1} corresponding to the C-S bond formed in the thiol-ene click. The thiol-ene conversion was estimated to be 70% with some excess unreacted thiol observed at ~2570 cm^{-1}. We did not observe complete conversion possibly due to steric effects; this observation prompted us to test further in the following section, where we effectively had more spacers in between the click sites.

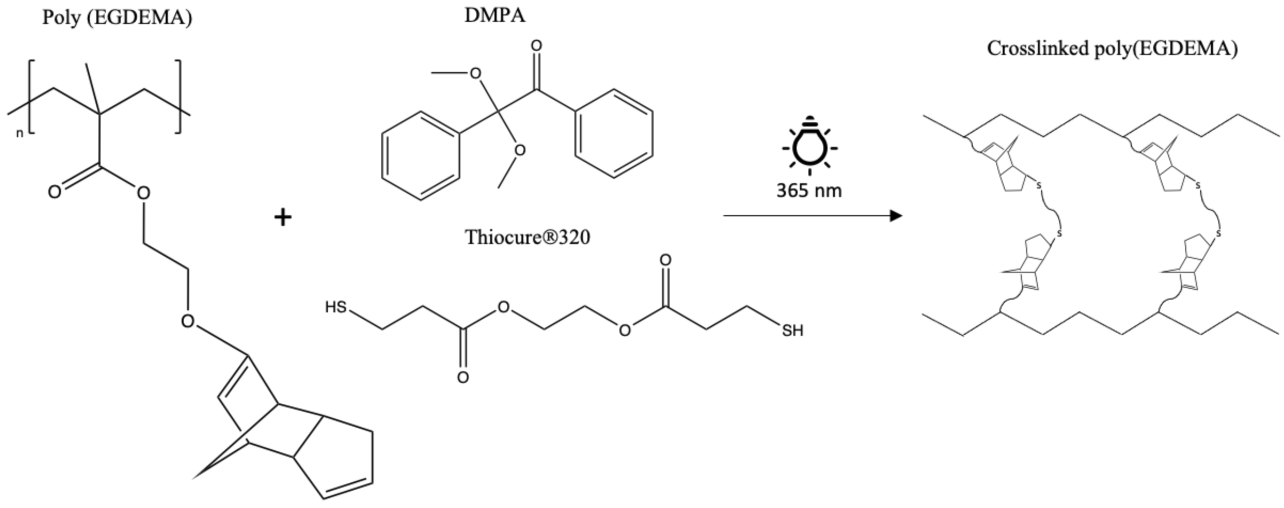


Figure 10. Thiol-ene click reaction for the crosslinking of poly(EGDEMA).

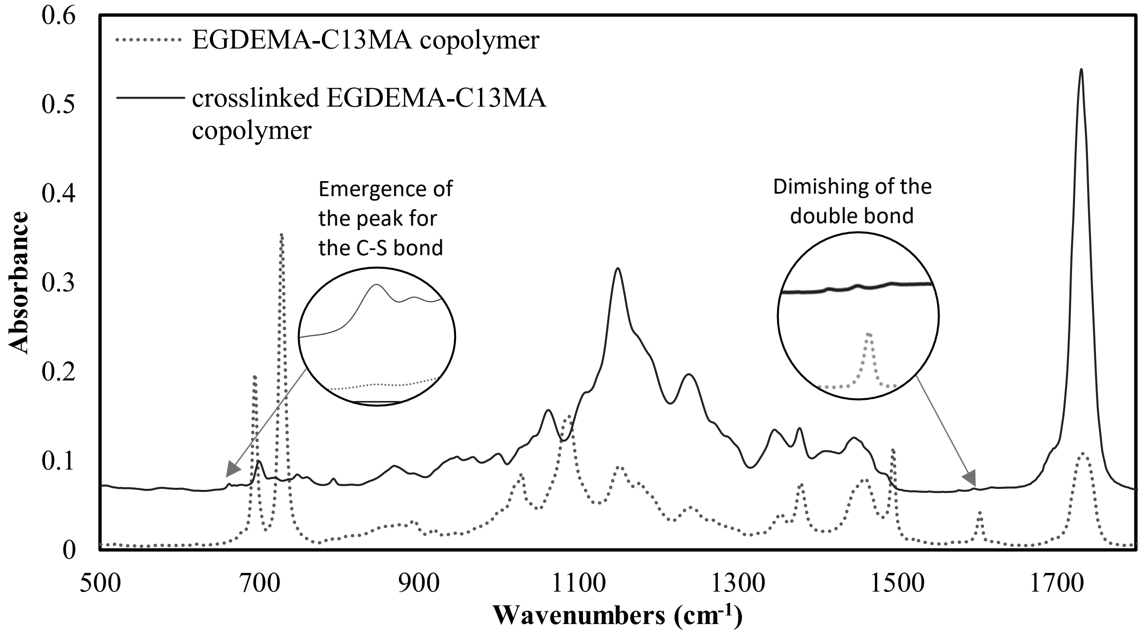


Figure 11. FTIR absorbance peaks for ETC2 (poly(EGDEMA-*stat*-C13MA)) before and after crosslinking. Conversion of the pendent double bond is observed at ~1638 cm^{-1}.

3.6.2 Poly(EGDEMA-stat-C13MA)and Poly(EGDEMA-stat-IBOMA)

Similarly, copolymers of EGDEMA with C13MA and copolymers of EGDEMA with IBOMA were investigated with thiol-ene clicking. The results of the thiol-ene curing are presented in Table 7 below. The thiol-ene conversion was estimated by analysis of the area of the corrected peaks at 1638 cm^{-1}estimated as an average of 3 readings due to spatial variations in photo-curing. All prepared samples exhibited relatively high conversion of the double bond (86-97%) whereas the formulations with IBOMA had slightly higher conversion than those with C13MA; FTIR data for ETC2 as an example is shown in Figure 11. The crosslinked polymers obtained have variable T_gs. Unlike the poly(EGDEMA) homopolymer, the cured copolymers exhibited lower T_g compared to their respective polymers upon the addition of thiol and subsequent curing. The decrease in the T_g obtained is due to the flexible thiol-ether linkages and the spacers between the crosslinks in the copolymers which produce soft materials with T_gs at curing temperature or below.[51]–[53] The

C13MA containing cured polymers were flexible and had a glue-like consistency, whereas the IBOMA containing polymers were hard and brittle. Shrinkage was observed in formulations with higher EGDEMA content (above 50%).

Table 7. Results for the thiol-ene crosslinking of EGDEMA/C13MA and EGDEMA/IBOMA copolymers irradiated at 365 nm for 6 minutes.

Exp	Polymer	F_{EGDEMA}[a]	Thiol-ene click conversion[b]	Tg_1(°C)[c]	Tg_2(°C)[d]
ETC1	AR_EG/C13MA_2	0.85	86%	16.1	-4
ETC2	AR_EG/C13MA_4	0.46	92%	-9.3	-15
ETC3	AR_EG/ IBOMA _2	0.91	97%	28.8	5.8
ETC4	AR_EG/ IBOMA _4	0.69	96%	46.4	38

a. The final molar fraction of EGDEMA in the copolymer (F_{EGDEMA}) as determined by ^{1}H NMR in CDCl3.

b. The conversion was determined by estimating the corrected average area of three readings of the peak for the normalized signal at ~1638 cm^{-1}; conversion was calculated 4 days after the samples' irradiation.

c. Tg1: glass transition temperature of the copolymer.

d. Tg2: glass transition temperature of the resultant cured copolymer after thiol-ene clicking.

4. Conclusion

The polymerization of EGDEMA was done using ARGET ATRP for the first time. Homopolymers and copolymers of EGDEMA and the vegetable oil-derived monomer C13MA were prepared via ARGET ATRP in order to reduce the concentration of the catalyst. Due to the pendent double bond in the norbornene group, controlled polymerization of EGDEMA was challenging. To first establish the feasibility of synthesis of homopolymers and copolymers of EGDEMA and C13MA, well-controlled traditional ATRP reactions were performed. The reactions yielded statistical copolymers with a relatively narrow molecular weight distribution (Đ =1.21-1.47, M_n=11.6-20.5 kg/mol). ARGET ATRP was first optimized for EGDEMA homopolymerization. Poly(EGDEMA) was prepared using Me_6TREN ligand and 250 ppm of copper(II) bromide yielded polymers with M_n = 16.3 kg/mol and Đ = 1.44, whereas the homopolymers synthesized via the less expensive ligand PMDETA yielded polymers with M_n= 13.5 kg/mol and Đ = 1.65. Various statistical poly(EGDEMA-*stat*-C13MA) copolymers were synthesized via ARGET ATRP having T_gs varying between -39°C and 23°C. Moreover, the obtained copolymers had variable molecular weight distribution (Đ=1.39-1.76); with broader distributions occurring with higher EGDEMA content, suggesting the pendent double bond in EGDEMA participates in side reactions. The functional polymers obtained via ARGET ATRP had active chain ends which was confirmed by the chain extensions to obtain poly(C13MA-b-EGDEMA) block copolymers. DSC analysis of the block copolymer synthesized showed two distinct glass transition temperature values, -39°C and 23°C, corresponding to poly(C13MA) and poly(EGDEMA) respectively. Finally, IBOMA was incorporated to add rigidity to the photocurable polymers; copolymers with different ratios of EGDEMA with IBOMA were synthesized with T_gs varying between 23°C and 113°C. Thiol-ene clicking was first analyzed with the poly(EGDEMA) homopolymer; a crosslinked polymer network was observed with a conversion of 70% of the pendant double bond. Higher conversions (86%-97%) and lower T_gs compared to the respective polymers were observed in the thiol-ene crosslinked copolymers, suggesting that molecular characteristics (composition, T_g, steric hindrance) play a role in the kinetics.

Acknowledgments

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