# Atom Transfer Radical Polymerization of 3-Ethyl-3-(acryloyloxy)methyloxetane

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ABSTRACT: Ethyl-3-(acryloyloxy)methyloxetane (EAO), a monomer bearing an oxetane group in the side chain, was polymerized via ATRP using ethyl 2-bromoisobutyrate (EBIB) as initiator and CuBr as a catalyst complexed with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as ligand. The polymer was characterized by $^1$H NMR, FT-IR, GPC, and MALDI−TOF-MS. $^1$H NMR and FT-IR analyses revealed no ring opening of the oxetane group during polymerization.

Transition-metal-mediated controlled radical polymerization, also known as atom transfer radical polymerization (ATRP), is one of the most versatile controlled radical polymerization methods.[1,2] One of the advantages of ATRP is that it can be applied over a wide range of temperatures. It tolerates many functional groups present in the monomers and initiators and allows the preparation of end-functionalized polymers, star, comb, or grafted polymers, nanoparticle hybrids, and polymer monolayers.[3−5] It is assumed that ATRP proceeds via a reversible redox process between an alkyl halide as an initiator and transition metal (pseudo)halides based on Cu, Fe, Ni, and Ru with a suitable phosphine- or nitrogen-based ligand.[1,2,6−12] The transition metal catalyst abstracts the halogen atom from the initiator in order to generate a radical which in turn initiates and then propagates the polymerization. The polymerization process involves a reversible equilibrium between the propagating radical and the dormant species. ATRP has been utilized to polymerize monomers bearing different functionalities that could find potential applications in coatings and adhesives, such as monomers with an epoxide in the side.[12,13] Both epoxides and oxetanes are important monomers in cationic UV-curing technology.[14] The basicity of oxetane group toward cationic ring-opening reagent is much higher than that of the epoxide group.[15−18] Hence, oxetanes are more facile toward cationic polymerization.[19−23] Oxetane-based polymers reveal low shrinkage and high flexibility.[24] Because of these advantages, oxetanes are becoming increasingly important monomers in UV-curing applications.[20−24] Polymers containing oxetane moiety in the pendant group can act as macroinitiators for graft copolymerization or as monomeric species in cross-linking reaction in coating and adhesive applications. There are reports of free radical polymerization of (meth)acrylates bearing an oxetane group.[25,26] In some cases, it is difficult to polymerize these monomers due to excessive chain transfer during the course of polymerization.[27] ATRP is a very useful technique of controlled radical polymerization where chain transfer reactions diminish to a great extent. Here we report the successful ATRP of 3-ethyl-3-(acryloyloxy)methyloxetane (EAO) without affecting its ring structure.

## Experimental Section

**Materials**. Acryloyl chloride (96%), 3-ethyl-3-hydroxymethyloxetane (96%), hydroquinone, ethyl 2-bromoisobutyrate (EBIB) (98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), azobis(isobutyronitrile) (AIBN) (98%), CuBr (98%), and *p*-xylene were obtained from Aldrich and were used as received.

**Synthesis of 3-Ethyl-3-(acryloyloxy)methyloxetane (EAO).** EAO was prepared by the condensation of acryloyl chloride (3.0 g, 33.15 mmol) with 3-ethyl-3-hydroxymethyloxetane (3.60 g, 31.10 mmol) in the presence of triethylamine (5.20 mL), as previously reported by Sato et al. for the methacrylate analogue.[25] EAO was purified by two distillations (bp 80 °C at 2.6 mbar, yield 40%). Hydroquinone was used as the stabilizer to prevent EAO from polymerizing during the distillation. IR (cm$^{-1}$): 1728 (⟩C═O in the ester group), 1635 ($CH_2$═CH−) 978 (−$CH_2$−O−$CH_2$− in oxetane). $^1$H NMR ($CDCl_3$, $\delta$, ppm): 6.35 ($CH_2$═C***H***−COO−) 6.05, 5.75 (C***H***$_2$═CH−COO−), 4.40, 4.30 (−C***H***$_2$−O−C− in oxetane), 4.20 (−COO−C***H***$_2$−C−), 1.65 (−C−C***H***$_2$−$CH_3$), 0.80 (−C−$CH_2$−C***H***$_3$).

**Polymerization.** EAO (2.0 g, 11.75 mmol) in *p*-xylene (2.0 mL) was filled into a three-neck round-bottom flask. HMTETA (0.046 g, 0.20 mmol) and CuBr (0.029 g, 0.20 mmol) were added to the round-bottom flask. Butyl acetate (0.10 mL) was used as an internal standard for the gas chromatography (GC). The round-bottom flask was equipped with a condenser in one neck and a silicon septum in the other. The flask was degassed and refilled with argon by three freeze/pump/thaw cycles. EBIB (0.039 g, 0.20 mmol) was added before the polymerizations were carried out at 90 °C. At different time intervals the samples were taken out by a syringe and diluted with tetrahydrofuran (THF). Parts of these samples were analyzed with GC to determine the monomer conversion, and the other parts were purified by passing through an alumina column prior to gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis.

**Characterization.** Monomer conversion was determined from the concentration of residual monomer using a Hewlett-

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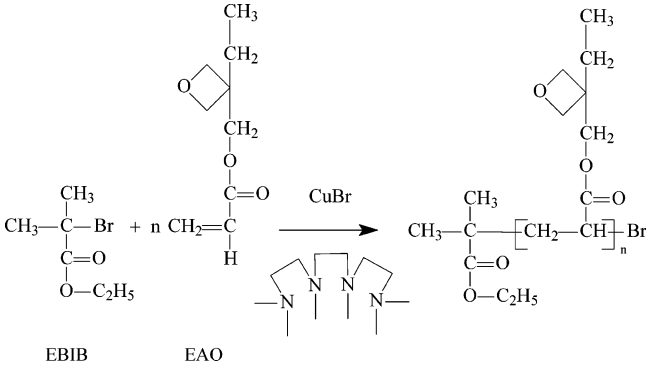
**Scheme 1. Atom Transfer Radical Polymerization (ATRP) of 3-Ethyl-3-(acryloyloxy)methyloxetane (EAO) Using Ethyl 2-Bromoisobutyrate (EBIB) as Initiator and CuBr as a Catalyst Complexed with HMTETA as Ligand**




Packard (HP 5890) gas chromatograph, equipped with an AT-Wax capillary column (30 m × 0.53 mm id 10 $\mu$m). The samples were run at a temperature profile of 40 °C (initial time was 5 min) to 150 °C at the heating rate of 10 °C/min. Injection and detector temperatures were 150 and 250 °C, respectively. Molar masses and molar mass distribution were measured at ambient temperature using a Waters GPC equipped with a Waters model 510 pump, a model 410 refractive index detector, and a model 486 UV detector. THF was used as eluent at a flow rate of 1.0 mL/min. A set of two linear columns (mixed-C, Polymer Laboratories) [a PLgel guard (5 $\mu$m particles) 50 × 7.5 mm guard column, followed by 2 PLgel mixed-C (5 $\mu$m particles) 300 × 7.5 mm columns in series] was used. Data acquisition and processing were performed using Waters Millennium 32 software (version 3.2). Low polydispersity linear polystyrene samples (Polymer Laboratories, $M = 580$ to $M = 7.1 \times 10^6$) were used as standards to construct the calibration curve. MALDI-TOF-MS analysis was carried out using a Voyager DE-PRO (PerSeptive BioSystem). The MALDI instrument was equipped with a 337 nm pulsed nitrogen laser (4 ns pulse width) and a 1.0 m linear time-of-flight mass spectrometer with a 30 kV source voltage. MALDI experiment was carried out using 2,5-dihydroxybenzoic acid (2,5-DHB) as the matrix. The matrix solution was prepared by dissolving 40 mg of 2,5-DHB in 1 mL of THF. The matrix solution was added to 0.10% PEAO solution in THF. Sufficient sample was applied to cover the sample position of 2.5 mm diameter. The spot was allowed to air-dry without any assistance. Mass spectra were acquired by accumulating spectra from 256 selected laser shots. The number-average molecular weight of the polymers was determined in the linear mode. TGA analysis was carried out in Perkin-Elmer Pyris TGA 6 instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. DSC analysis was carried out using a Perkin-Elmer Pyris 1 instrument, and indium was used as the standard for the calibration of the instrument. DSC was carried out from −100 to 150 °C at a heating rate of 10 °C under nitrogen. The sample was first heated to 150 °C, then quenched to −100 °C, and then finally heated to 150 °C at a rate of 10 °C/min. The glass transition temperature was determined as the inflection point in heat flow curve of the second scan. IR spectra were recorded on a Bio-Rad FTS 6000 FT-IR spectrometer. $^1$H NMR spectra were recorded on a Varian AM-400 NMR instrument (400 MHz) using $CDCl_3$ as solvent.

## Results and Discussion

3-Ethyl-3-(acryloyloxy)methyloxetane was polymerized in *p*-xylene using ethyl 2-bromoisobutyrate as initiator (Scheme 1). CuBr complexed with HMTETA as ligand was used as the catalyst. Figure 1 displays the curves of conversion vs time and logarithmic conversion vs polymerization time. The plot of the logarithmic conversion of EAO with polymerization time is close to linear, indicating the concentration of active species remains constant throughout the polymerization. Figure

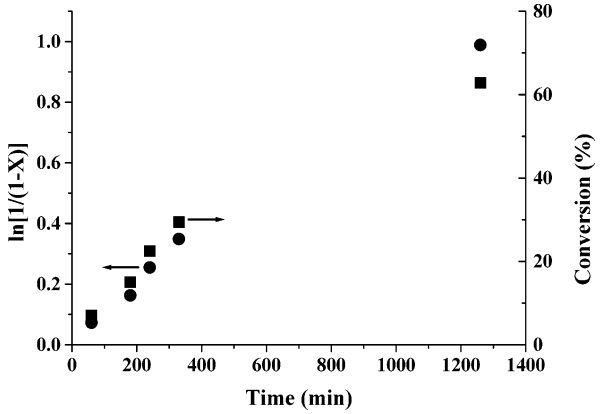



**Figure 1.** Plots of conversion vs time (square symbols) and semilogarithmic kinetic plot (circles) for the ATRP of EAO in *p*-xylene at 90 °C using ethyl 2-bromoisobutyrate (EBIB) as initiator and hexamethyltriethylenetetramine (HMTETA) as ligand. $[EAO]_0 = 2.93$ M, [HMTETA] = 0.05 M, [EBIB] = 0.05 M, [CuBr] = 0.05 M.

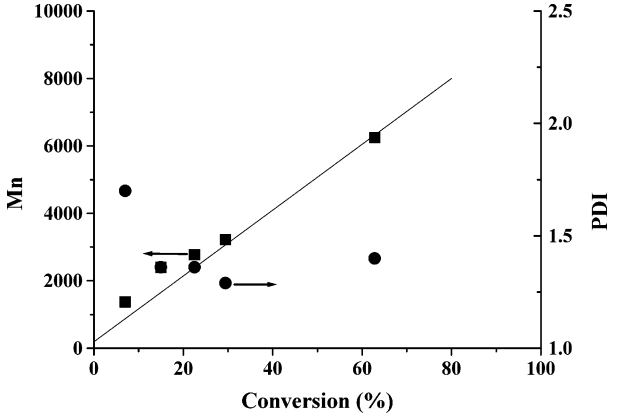



**Figure 2.** Dependence of molecular weights (square symbols) and polydispersity indices (circles) of PEAO on monomer conversion for the ATRP of MMA in *p*-xylene at 100 °C using ethyl 2-bromoisobutyrate (EBIB) as initiator and HMTETA as ligand. $[EAO]_0 = 2.93$ M, [HMTETA] = 0.05 M, [EBIB] = 0.05 M, [CuBr] = 0.05 M.

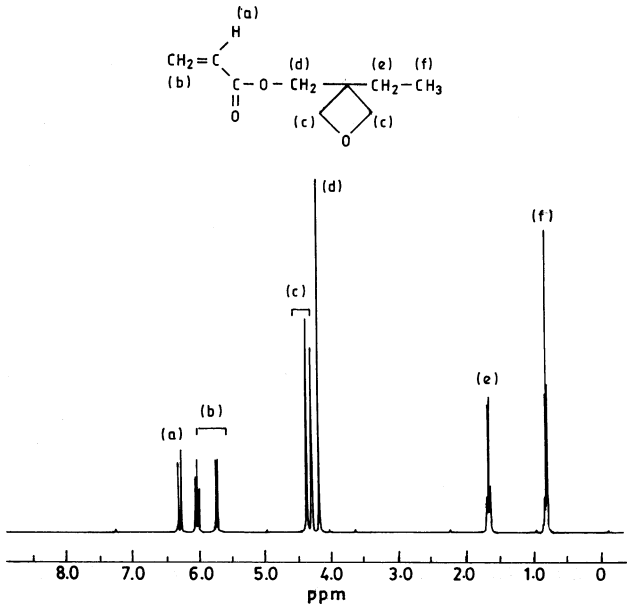



**Figure 3.** $^1$H NMR of the monomer 3-ethyl-3-(acryloyloxy)-methyloxetane (EAO).

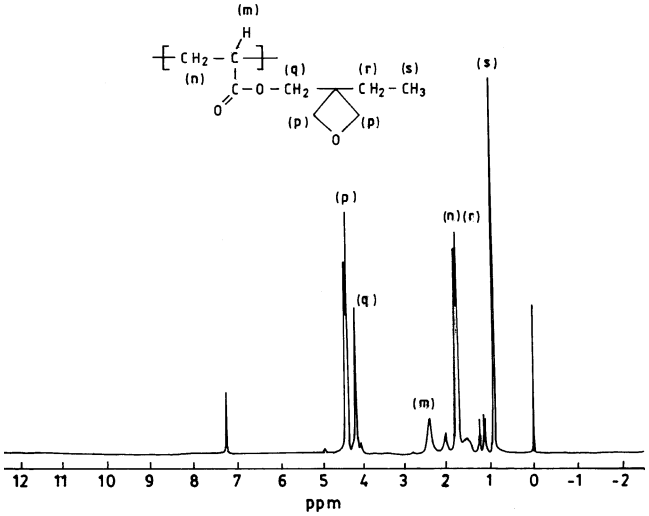



**Figure 4.** $^1$H NMR of poly(3-ethyl-3-(acryloyloxy)methyloxetane) (PEAO).

2 shows a gradual increase in $M_n$ with the conversion of the monomer. Initially, the observed molecular weight of the polymer was slightly greater than the theoretical molecular weight. It could be due to the addition of multiple monomer units per activation−deactivation cycle. At the start of the polymerization the polydispersity index was about 1.6 (Figure 2), and the GPC curve also showed a small tailing, indicating the low molecular weight species. However, with increasing reaction time the tail disappeared and polymers with relatively narrow polydispersity indices were obtained. Most importantly, the observed molecular weight also became almost equal to the theoretical $M_n$. Good correlation between $M_{n,GPC}$ and $M_{n,theo}$ indicates there is reasonably low amount of transfer during the polymerization. The conventional free radical polymerization of EAO was carried out at 70 °C in *p*-xylene for 6 h using AIBN (20 mM) as the initiator. There was 60% conversion, and the resultant polymer showed the molecular weight of 9000 and high polydispersity (PDI = 3.0). This is caused by excessive chain transfer reaction involving the labile protons in the pendant group of the monomer EAO as previously reported.[24,26,27]

The $^1$H NMR spectrum of EAO is shown in Figure 3. It showed peaks at $\delta$ = 5.75−6.35 ppm which are attributed to the different olefinic protons. The resonance at $\delta$ = 4.20 ppm is due to the protons of −O−$CH_2$− group (designated as "d" in Figure 3). The resonances at 4.30−4.40 ppm are due to oxetane protons and are designated as "c" in Figure 3. The ratio of the −O−$CH_2$− protons and oxetane protons is 1:2. The peaks at $\delta$ = 1.65 and 0.80 ppm are due to the saturated aliphatic protons in EAO. Figure 4 shows the $^1$H NMR spectra of poly(3-ethyl-3-(acryloyloxy)methyloxetane) (PEAO). Absence of any signals at 5.75−6.35 ppm indicates the resulting polymer is free from any unreacted monomer. The new peaks at 0.90−2.40 ppm emerged due to the saturated aliphatic protons of the desired polymer when the unsaturated protons became the part of the polymer backbone. The resonances at 4.20 and 4.40 ppm are due to −O−$CH_2$− (designated by "q" ) and oxetane protons (labeled by "p" ), respectively. The ratio of the integrated area of these two types of protons is 1:2, which is also observed in the monomer EAO. Sato et al.[25] reported the cationic ring-opening polymerization of 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO) which showed an intense peak at $\delta$ = 3.5 ppm due to −O−$CH_2$− protons which appear due to the opening of oxetane ring. Opening of the oxetane ring[25] in EAO would result in signals at 3.5 ppm in the $^1$H NMR of PEAO, and the integrated ratio of the −O−$CH_2$− protons to oxetane protons would have been more than 1:2. The absence of any resonance at 3.5 in Figure 4 and the ratio of 1:2 of the −$OCH_2$− protons to oxetane protons indicate the oxetane ring was not opened during ATRP of EAO. The IR spectra of EAO (Figure 5) show the characteristic peaks at 1635 $cm^{-1}$ which are due to C=C stretching vibration and at 978 $cm^{-1}$ which is due to C−O−C antisymmetric stretching in oxetane ring. The peak at 1728 $cm^{-1}$ is assigned due to the ⟩C=O stretching of the ester group in EAO. The IR spectrum

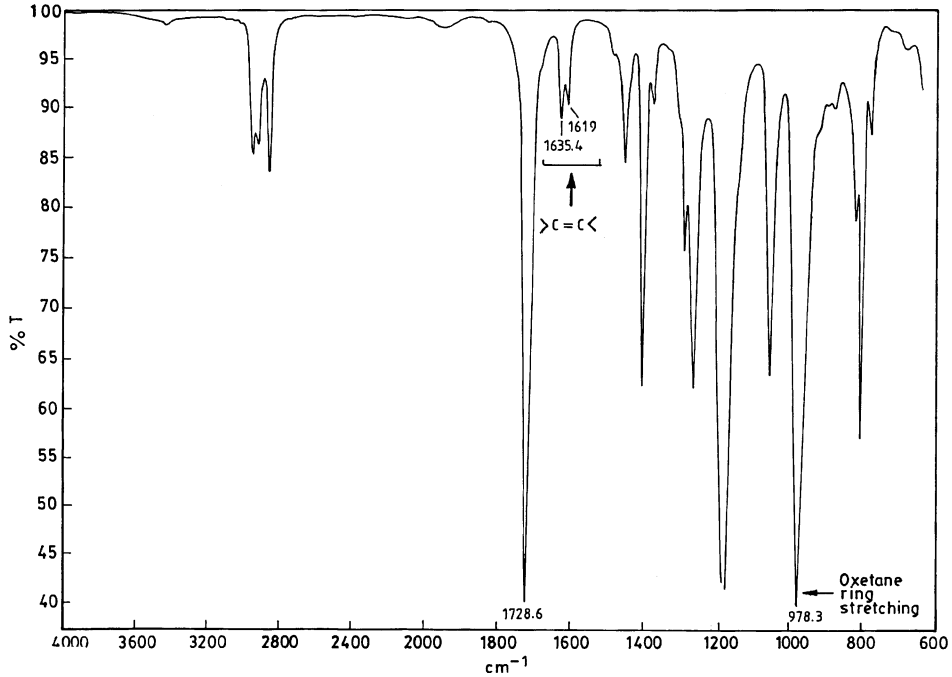



**Figure 5.** FT-IR of 3-ethyl-3-(acryloyloxy)methyloxetane (EAO).

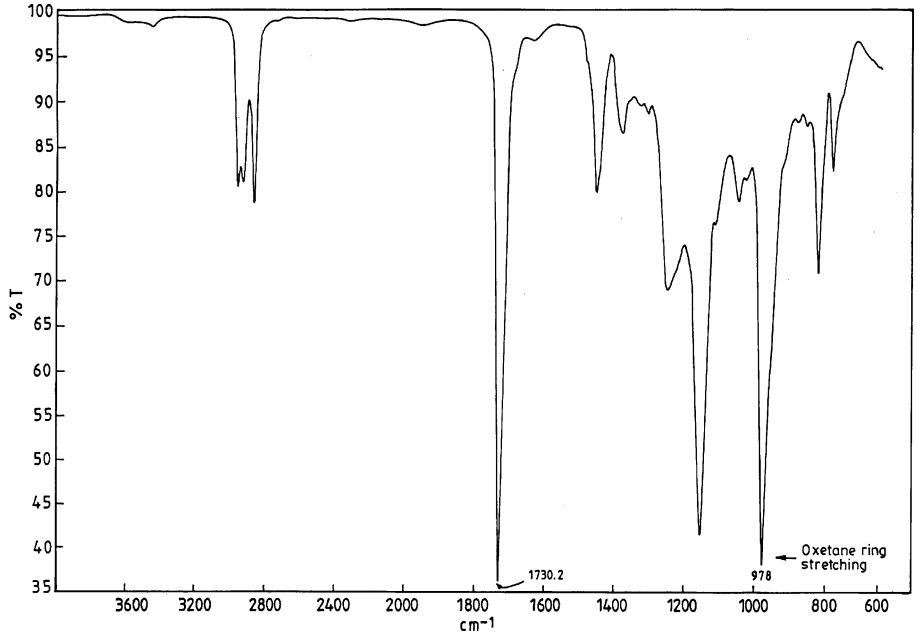



**Figure 6.** FT-IR of the poly(3-ethyl-3-(acryloyloxy)methyloxetane) (PEAO).

of PEAO (Figure 6) does not show any peak at 1635 $cm^{-1}$, which indicates it is free from any monomer, EAO. More importantly, Figure 6 shows that the peak at 978 $cm^{-1}$ characteristic of the oxetane ring remains unaffected. The intense peak at 1730 $cm^{-1}$ attributed to ester group is also not affected in PEAO. Corey and Raju[28] reported that oxetane esters on treatment with boron triflouride etherate at −15 °C was converted to isomeric bridged ortho esters by intramolecular rearrangement between the ester and the oxetane group. Recently, Kanoh et al.[29] reported the cationic isomerization of oxetane rings bearing an ester group in the presence of a Lewis acid and subsequent polymerization of the isomerization product to yield poly(ortho ester)s or polyethers. In our case, polymerization via the vinyl group and simultaneous opening of ring in EAO would have led to gelled polymer. However, the resultant polymer, PEAO, was highly soluble in $CHCl_3$, THF, etc. Interestingly, $^1H$ NMR spectra, FT-IR spectra, and solubility experiment of PEAO unambiguously prove that ATRP of EAO did not open the oxetane ring, which is usually opened by cationic mechanism.[30]

The MALDI-TOF-MS of PEAO shows a series of 170 mass unit, which is the mass of the repeating units, EAO (Figure 7a,b). The detailed analysis of the signals, e.g., at 3599 mass unit, reveals that the distribution can be assigned to EBIB−$(PEAO)_n$−Br species (in the case of $m/z$ = 3599, $n$ = 20). This proves that each PEAO macromolecular chain contains EBIB as the end group. The second distribution at 3621 can be attributed to $Na^+$ adducts (with abstraction of a proton). MALDI-TOF-MS reveals that this sample had the $M_n$ of 3900 and PDI of 1.19. This MALDI sample had a conversion of 30%, which corresponds to the theoretical $M_n$ of 3200. The little excess molecular weight may be due to the multiple monomer addition per activation−deactivation cycle because of the slower dynamics of the equilibrium, especially for the monomer having a long side chain. Interestingly, the MALDI experiment shows that the polymer has well-defined end groups and the polydispersity is relatively low. Sato et al.[25] have analyzed the polymer of 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO) obtained by cationic ring-opening polymerization

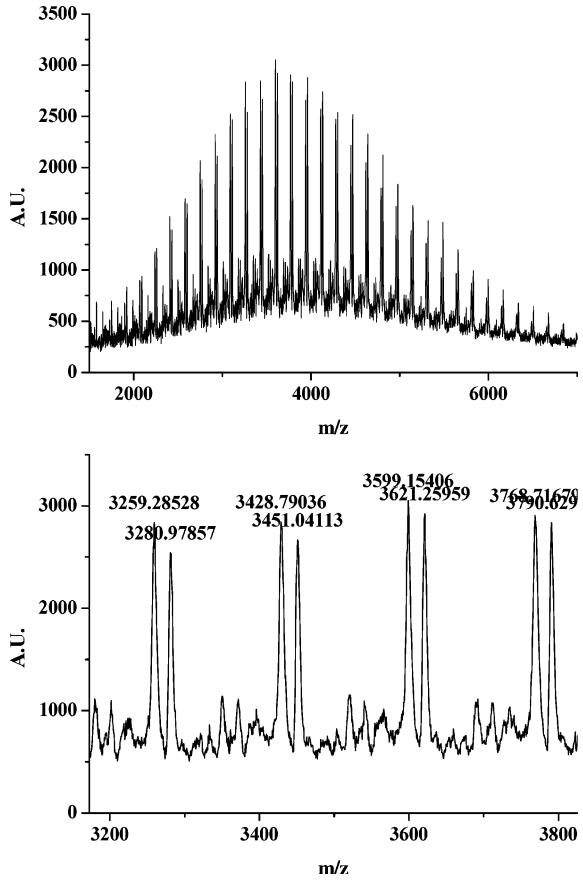



**Figure 7.** (a) MALDI-TOF-MS spectrum of the poly(3-ethyl-3-(acryloyloxy)methyloxetane) (PEAO). (b) Magnification of a region in the MALDI-TOF-MS spectrum.

by thermal gravimetric analysis (TGA) and reported two steps decomposition at 320 and 440 °C. This is due to two degradation mechanisms because of unsaturated part and the main chain scission in cationically polymerized EMO. The TGA curve of our PEAO shows mainly a single decomposition at around 400 °C (Figure 8). Controlled radical polymerization has an impact on the thermal properties of the (meth)acrylate polymers.[9]

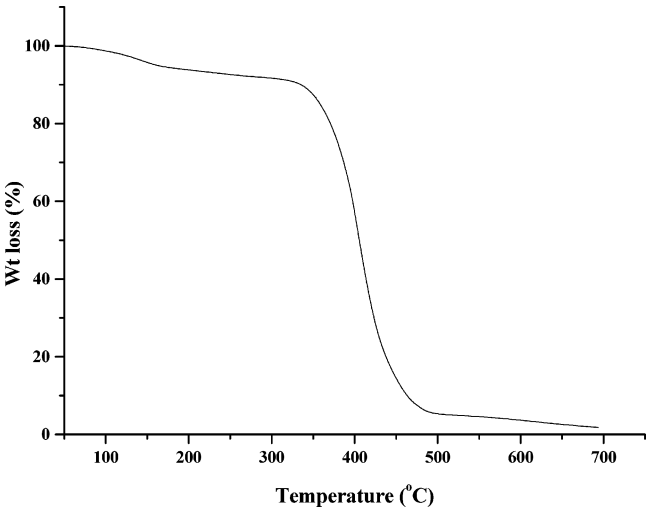



**Figure 8.** TGA of PEAO prepared by ATRP.

Granel et al.[9] reported that PMMA obtained by Ni complex catalyzed controlled radical polymerization had only a single decomposition, as it was free from head-to-head linkages and vinylidene end groups which are common in conventional free radical polymerization. PMMA obtained by Cu-catalyzed ATRP has only single decomposition temperature at about 400 °C, whereas PMMA obtained by free radical polymerization shows several stages of decomposition.[31,32] DSC analysis of PEAO shows a $T_g$ at −10 °C. This agrees well with the fact that the $T_g$ of acrylate polymers decreases when the side chain length increases.[33]

## Conclusion

An acrylate bearing an oxetane group was successfully polymerized by ATRP. The polymer was characterized by $^1$H NMR, IR, and MALDI-TOF analysis. $^1$H NMR and FT-IR demonstrate that the oxetane group was present in the polymer without being affected during polymerization. This finding opens new possibilities for the incorporation of an important cationically cross-linkable moiety into tailor-made macromolecules using controlled radical polymerization procedures such as ATRP.

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