

Electronic Supplementary Information (ESI)

Aziridine in Polymers: A Strategy to Functionalize Polymers by Ring-Opening Reaction of Aziridine

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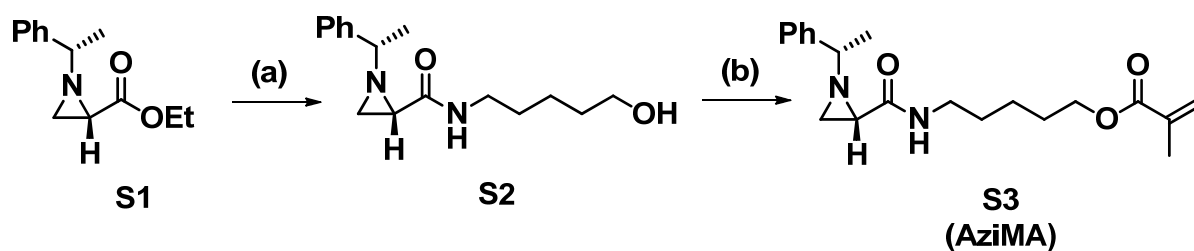
Materials.

All reagents were used as supplied unless otherwise specified. All organic solvents were purchased from Sigma-Aldrich or SAMCHUN (toluene, 99.8%) while water was purified using an Aqua MAX-Basic System (deionized water, electrical resistivity of which is $\sim 18.2 \text{ M}\Omega \cdot \text{cm}$). Methyl methacrylate ($>99.8\%$) was obtained from TCI and used as supplied. 2,2-Azobisisobutyronitrile ($>99.0\%$) was obtained from DAEJUNG and recrystallized from cold methanol and dried at room temperature and dried under vacuum prior to use. Polymethyl methacrylate for control experiments was purchased from Acros Organics (molecular weight = $\sim 350,000 \text{ Da}$; LOT: A010113001). Aziridine-terminated methacrylate (AziMA) was stored under N_2 atmosphere and $<4^\circ \text{C}$.

Methods.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Gemini 300 and Varian Mercury 400 using CDCl_3 or acetone- d_6 as solvents and residual solvents as an internal standard. Measurements of FT-IR were carried out using a Thermo Electron Corporation NICOLET 380. UV-vis spectra were measured using Agilent technologies - Agilent 8453 UV-Vis spectrometer. Gel-permeation chromatography (GPC) analysis was performed in Korea Polymer Testing & Research Institute (Koptri; [www. polymer.co.kr](http://www.polymer.co.kr)). The molecular weights of polymers were measured relative to polystyrene standards on a Tosoh HLC-8320 gel-permeation chromatography (GPC) equipped with EcoSEC software, $2 \times \text{TSKgel Supremultipore HZ-M}$ ($4.6 \times 150 \text{ mm}$) columns and RI detector. THF was used as an eluent at a flow rate of 0.35 mL/min , and the instrument was calibrated using polystyrene standards. GPC samples were prepared by passing a THF solution of sample through $0.45 \mu\text{m}$ PTFE filter. $10 \mu\text{L}$ of 3 mg/mL sample

dissolved in THF was injected, and GPC analysis was done at 40°C. The contact angle measurements were performed at room temperature (20 – 25 °C) with ~20% relative humidity. The droplet volume for the measurement was ~1 µL. A solution of polymer was spin-coated on a glass substrate using ISP-200FL (Jaesung ITS Co.).



Scheme S1. Synthesis of methyl methacrylate terminated with aziridine (AziMA)

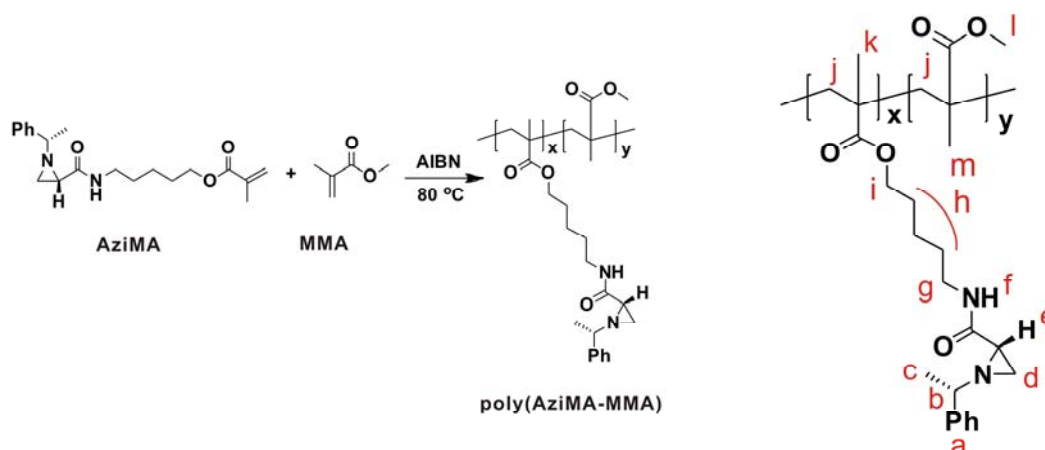
Synthetic Procedures

Synthesis of (S)-N-(5-hydroxypentyl)-1-((S)-1-phenylethyl)aziridine-2-carboxamide (**S2**). To a flask charged with anhydrous LaCl_3 (0.062 mmol) was added dry toluene (6.2 mL), 5-aminopentanol (1.55 mmol). Then *n*-BuLi (1.37 mmol) was added at 0 °C. After 15 minutes, the solution was heated to reflux (100 °C). (S)-Ethyl 1-((S)-1-phenylethyl)aziridine-2-carboxylate¹ (0.62 mmol) was added and refluxed for additional 12 h. The reaction mixture was cooled to r.t., and quenched with aqueous NaHCO_3 solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL $\times$ 3). The combined organic extracts were washed with 20 mL of brine, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo.

Purification by silica gel flash chromatography (with EtOAc 100%) gave 149 mg (87 %) of the product **S2** as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.36 (m, 4H), 7.28 (m, 1H), 6.73 (t, 1H), 3.63(t, $J=6.8$ Hz, 2H), 3.24 (q, $J=6.8$ Hz, 2H), 2.61 (q, $J=6.4$ Hz, 1H), 2.30 (s, 1H), 2.22

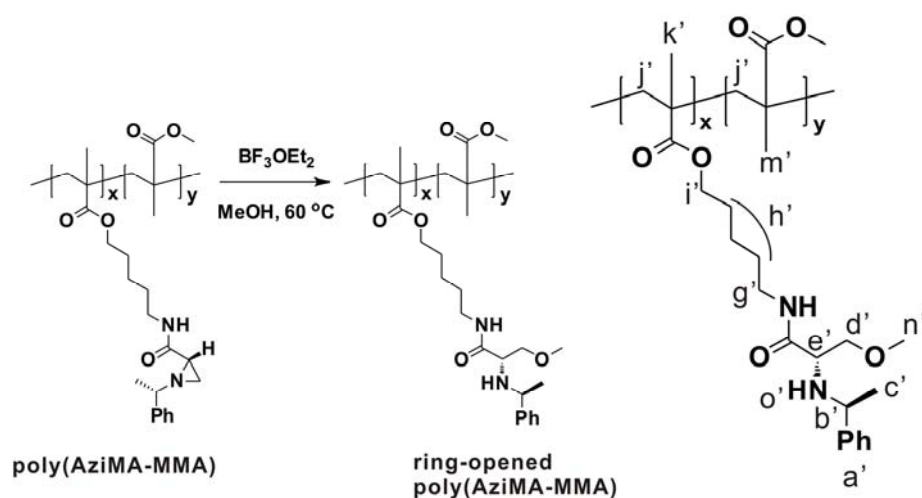
(dd, $J=6.8, 3.2$ Hz, 1H), 1.82 (d, $J=3.2$ Hz, 1H), 1.66 (d, $J=6.8$ Hz, 1H), 1.52-1.59 (m, 4H), 1.43 (d, $J=6.4$ Hz, 3H), 1.39-1.41 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 143.5, 128.5, 127.4, 126.6, 68.4, 62.4, 39.5, 38.7, 34.9, 32.2, 29.4, 23.1, 23.0. HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$, 299.1729; found, 299.1730.

Synthesis of 5-((*S*)-1-((*S*)-1-phenylethyl)aziridine-2-carboxamido)pentyl methacrylate (**S3**, **AziMA**). To a solution of (*S*)-*N*-(5-hydroxypentyl)-1-((*S*)-1-phenylethyl)aziridine-2-carboxamide (**S2**; 1.22 mmol) in 10 mL of methylene chloride under nitrogen at 0 °C was added sodium hydride (2.43 mmol). The mixture was stirred for 20 min at 0 °C, and was added distilled methacryloyl chloride (1.46 mmol) and triethylamine (3.65 mmol). Then the reaction mixture was warmed to room temperature, and quenched with aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with methylene chloride (6 mL $\times$ 3). The combined organic extracts were washed with 12 mL of brine, dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. Purification by silica gel flash chromatography (with 50:50 of EtOAc:Hex; v.v.) gave 378 mg (90 %) of the product **S3** as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 4H), 7.29-7.30 (m, 1H), 6.68 (t, 1H), 6.09 (s, 1H), 5.54 (s, 1H), 4.15 (t, $J=6.8$ Hz, 2H), 3.25 (q, $J=7.2$ Hz, 2H), 2.61 (q, $J=6.4$ Hz, 1H), 2.22 (dd, $J=7.2, 2.8$ Hz, 1H), 1.94 (s, 3H), 1.82 (d, $J=2.8$ Hz, 1H), 1.71 (m, 2H), 1.66 (d, $J=7.2$ Hz, 1H), 1.56 (m, 2H), 1.43 (d, $J=6.4$ Hz, 3H), 1.39 – 1.41 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 167.4, 143.5, 136.3, 128.4, 127.4, 126.6, 125.3, 68.4, 64.4, 39.5, 38.6, 34.9, 29.3, 28.3, 23.3, 23.1, 18.3. HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_3$, 367.1993; found, 367.1992.



Scheme S2. Copolymerization of AziMA and MMA to yield poly(AziMA-MMA)

Synthesis of Poly(AziMA-MMA). A typical polymerization procedure is as follows: to an oven-dried round-bottom flask equipped with a magnetic stir bar was added a toluene-solution (0.25 M) of monomers and initiator with stoichiometry, [MMA]:[AziMA]:[AIBN]=60:10:1 (mole ratio). The resulting solution was deoxygenated by bubbling N₂ for 20 min, and heated at 80 °C for 20 h. The final polymer was purified by precipitation into *n*-hexane. ¹H NMR (300 MHz, CDCl₃): δ = 7.49 – 7.12 (phenyl group; a in Scheme S2), 6.74 (proton of nitrogen in amide; f in Scheme S2), 3.93 (α-proton of amide; g in Scheme S2), 3.58 (methoxy group; l in Scheme S2), 3.25 (α-proton of ester; i in Scheme S2), 2.61 (benzyl proton of *N*-substituent; b in Scheme S2), 2.22 (proton in aziridine; e in Scheme S2), 2.06 – 1.16 (aliphatic regions; c, d, h and j in Scheme S2), 1.01 – 0.82 (methyl group in the polymer backbone; k and m in Scheme S2)



Scheme S3. Ring-opening reaction of the aziridine in poly(AziMA-MMA) with methanol in the presence of Lewis acid, $\text{BF}_3 \cdot \text{OEt}_2$.

Ring-opening Reaction of Poly(AziMA-MMA) with MeOH. A methanol solution of poly(AziMA-MMA) copolymer (10 M) was heated at 60°C in air for 2 h in the presence of activator for aziridine (33 wt% relative to poly(AziMA-MMA) copolymer), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$). The solution was then cooled to room temperature, and concentrated in vacuo. ^1H NMR (300 MHz, Acetone- d_6) δ 8.38(proton of nitrogen in amide; f in Scheme S3) 7.83-7.52(phenyl group a' in Scheme S3), 4.77 (proton of secondary nitrogen in ring-opened aziridine; o' in Scheme S3), 3.98(proton of nitrogen in amide; i' in Scheme S3), 3.77(benzyl proton of *N*-substituent; b' in Scheme S3), 3.60(methoxy group; l' in Scheme S3), 3.43(α -proton of amide; g' in Scheme S3), 3.38-3.17(methoxy group in ring-opened aziridine ring and α -proton of secondary amine; n' and e' in Scheme S3), 1.85-1.28(aliphatic regions; c', d', h' and j' in Scheme S3), 1.03 – 0.86 (methyl group in backbone; k' and m' in Scheme S3).

Typical Procedure for Ring-Opening Reactions with other alcohols. A THF solution containing poly(AziMA-MMA) copolymer (0.031 mmol), alcohol derivative (0.031 mmol) and boron trifluoride diethyl etherate (0.046 mmol) was heated at 60°C in air for 2 h. The solution was then cooled to room temperature, and concentrated in vacuo. Products were not soluble in conventional organic solvents, and thus characterized with FT-IR spectroscopy. Ring-opening reaction was confirmed by observing absorbance IR peak at 1083 cm⁻¹ indicating the presence of alkyl ether and therefore the formation of ring-opened aziridine.

Preparation of Thin Films of Polymer on Glass. A typical procedure for preparing a thin film of polymer is as follows: a solution of acetone containing polymer (15.5 mM; poly(AziMA-MMA), ring-opened poly(AziMA-MMA) or polymethyl methacrylate) was prepared, and 0.6 mL of the solution was placed to surface of bare glass (25mm × 25mm × 1.2-1.5 mm) and spin-coated at 2500 rpm for 30s under ambient conditions. The resulting film was dried in air for at least 3 h.

Figure S1. ^1H NMR spectra for aziridine-terminated methacrylate (AziMA) in different solvents (CDCl_3 and $\text{acetone-}d_6$).

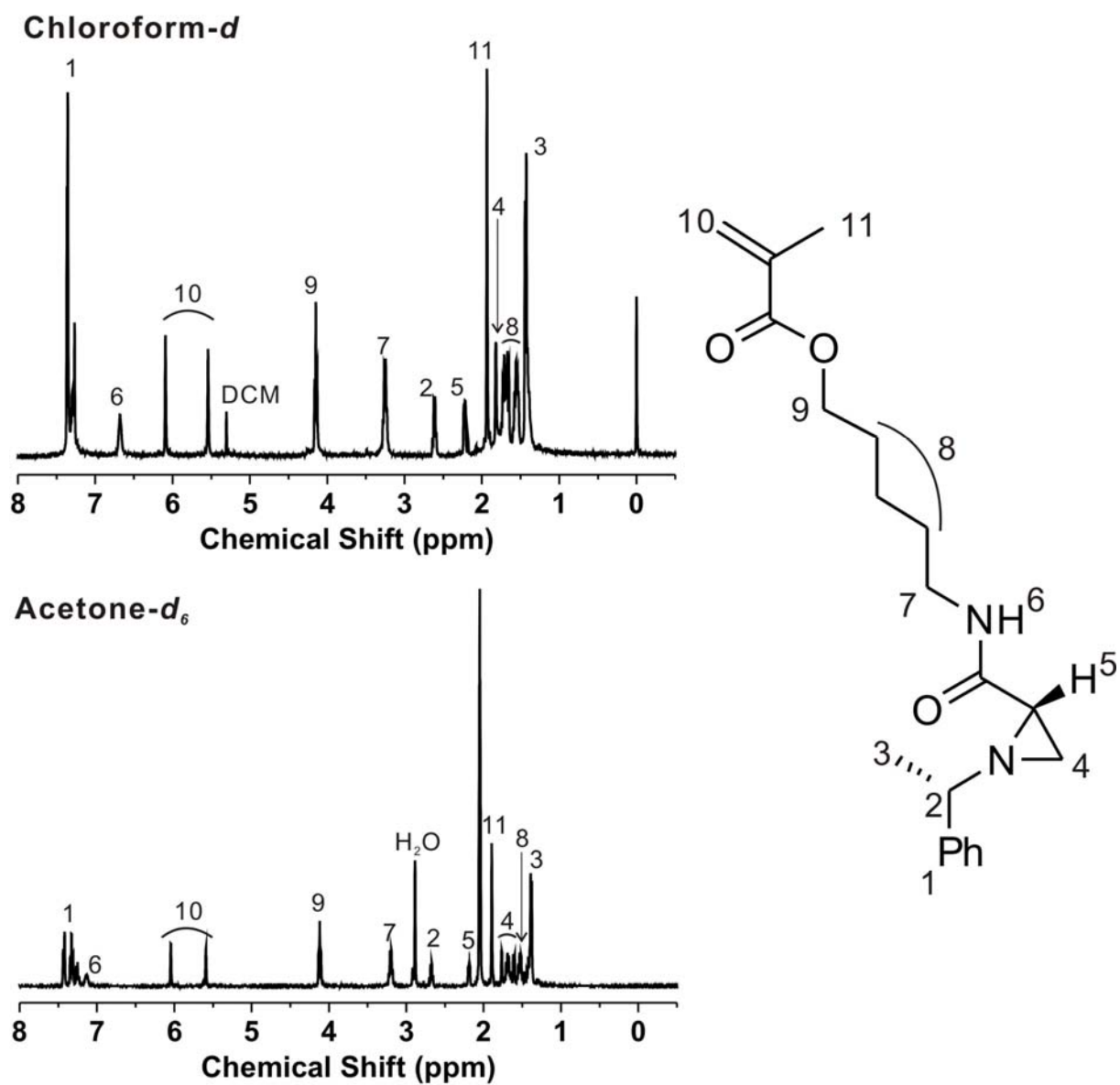


Figure S2. Poly(AziMA-MMA) copolymers prepared from different mole ratios of MMA and AziMA monomers. (a) [AziMA]: [MMA] = 1:3; (b) [AziMA]:[MMA] = 1:6; (c) [AziMA]:[MMA] = 1:9. Ratio of integrations of ^1H NMR peaks at 3.59 (methyl group in the PMMA backbone; it is assigned as “*l*” in spectra below) and 2.61 (“*b*” in the aziridine moiety in poly(AziMA-MMA)) ppm was used to determine the composition of poly(AziMA-MMA)

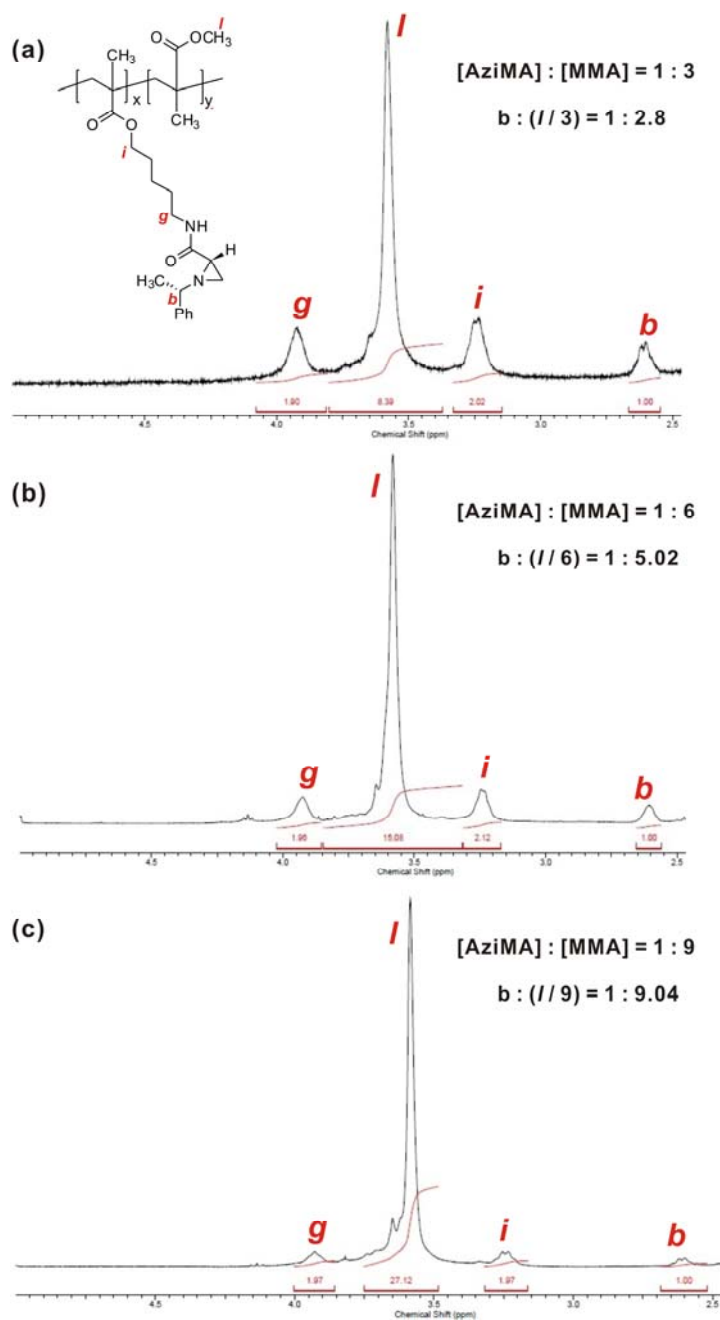


Figure S3. A kinetic plot of copolymerization of aziridine-MA and MMA to poly(AziMA-MMA). Conversion (%) was determined with ^1H NMR spectroscopy.

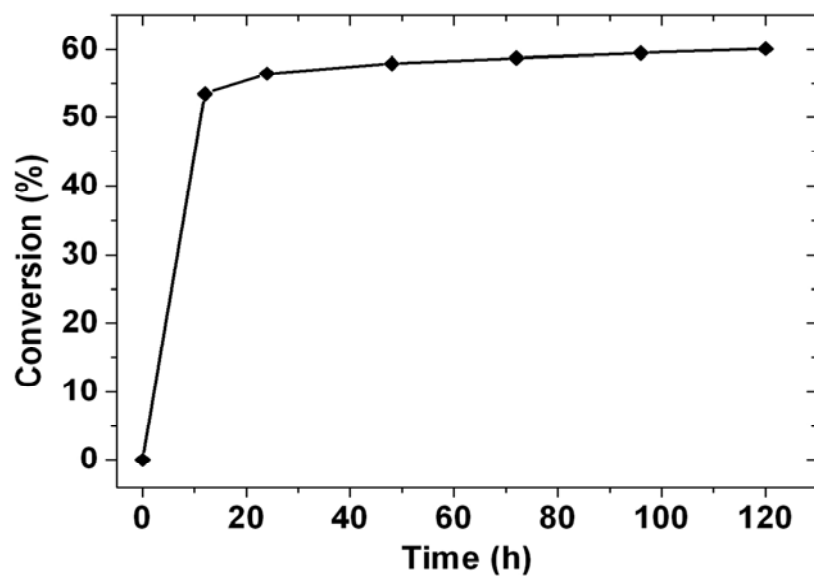


Figure S4. Control experiments with aziridine derivatives. ^1H NMR and ^{13}C NMR spectra of aziridine derivatives before and after ring opening reaction with MeOH in acetone- d_6 .

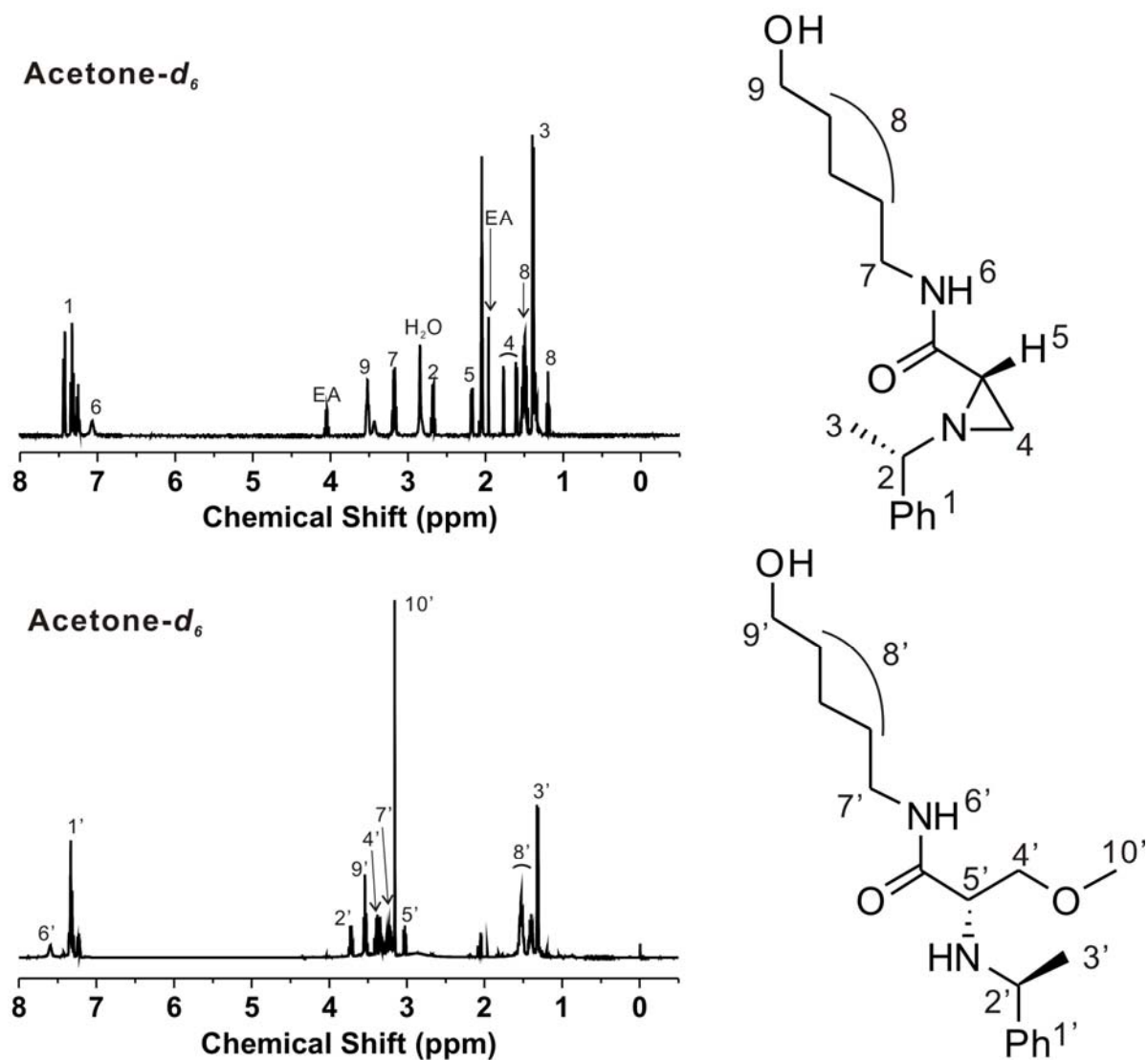


Figure S5. FT-IR spectra for ring-opened poly(AziMA-MMA)s incorporating various alcohol derivatives (ROH).

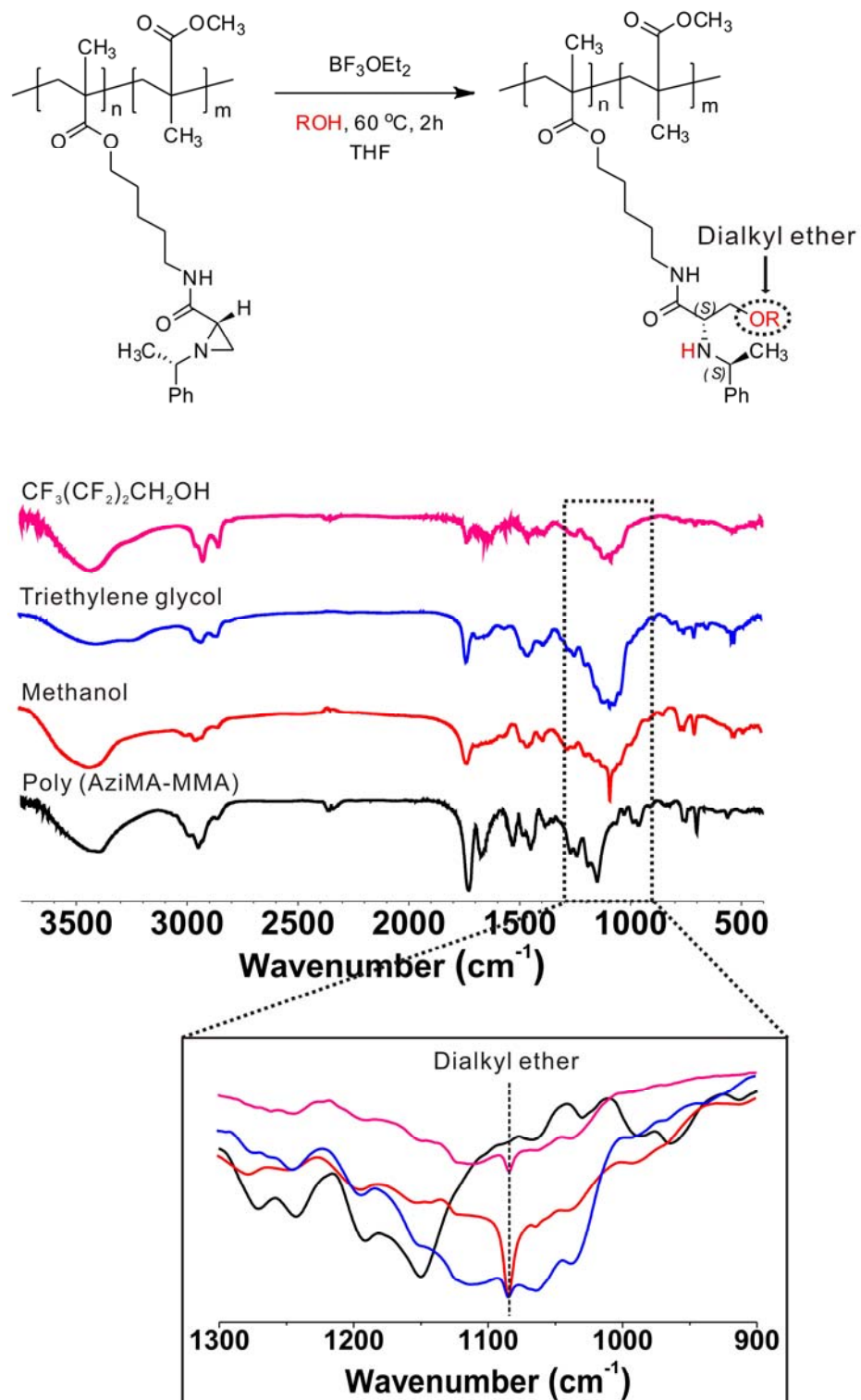


Figure S6. Comparison of optical transparency. UV-vis spectra for thin films of polymethyl methacrylate, PMMA, poly(AziMA-MMA) and ring-opened poly(AziMA-MMA) (by methanol). Thin films were prepared by spin-coating each of polymer solution (in acetone) on glass.

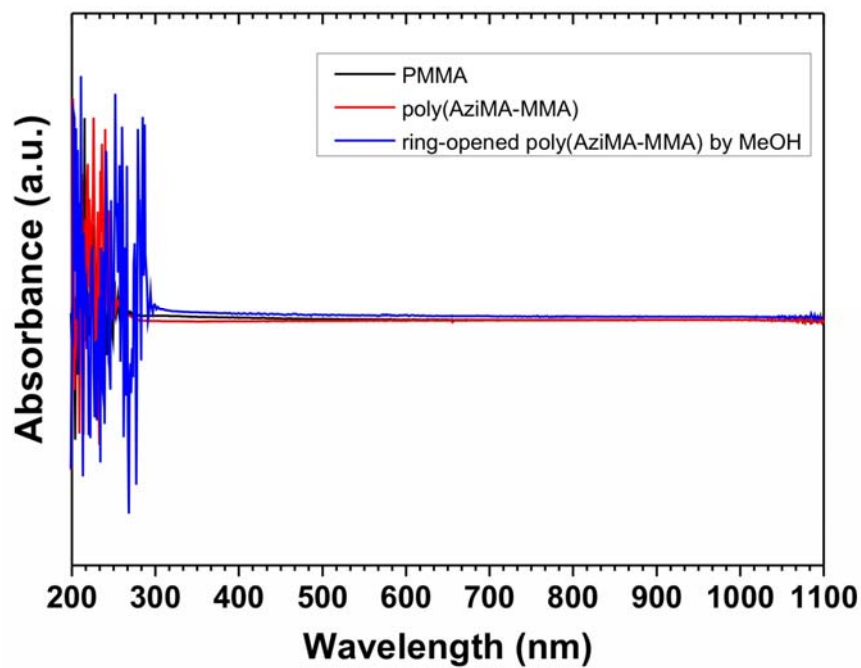


Figure S7. High resolution mass spectrum for AziMA.

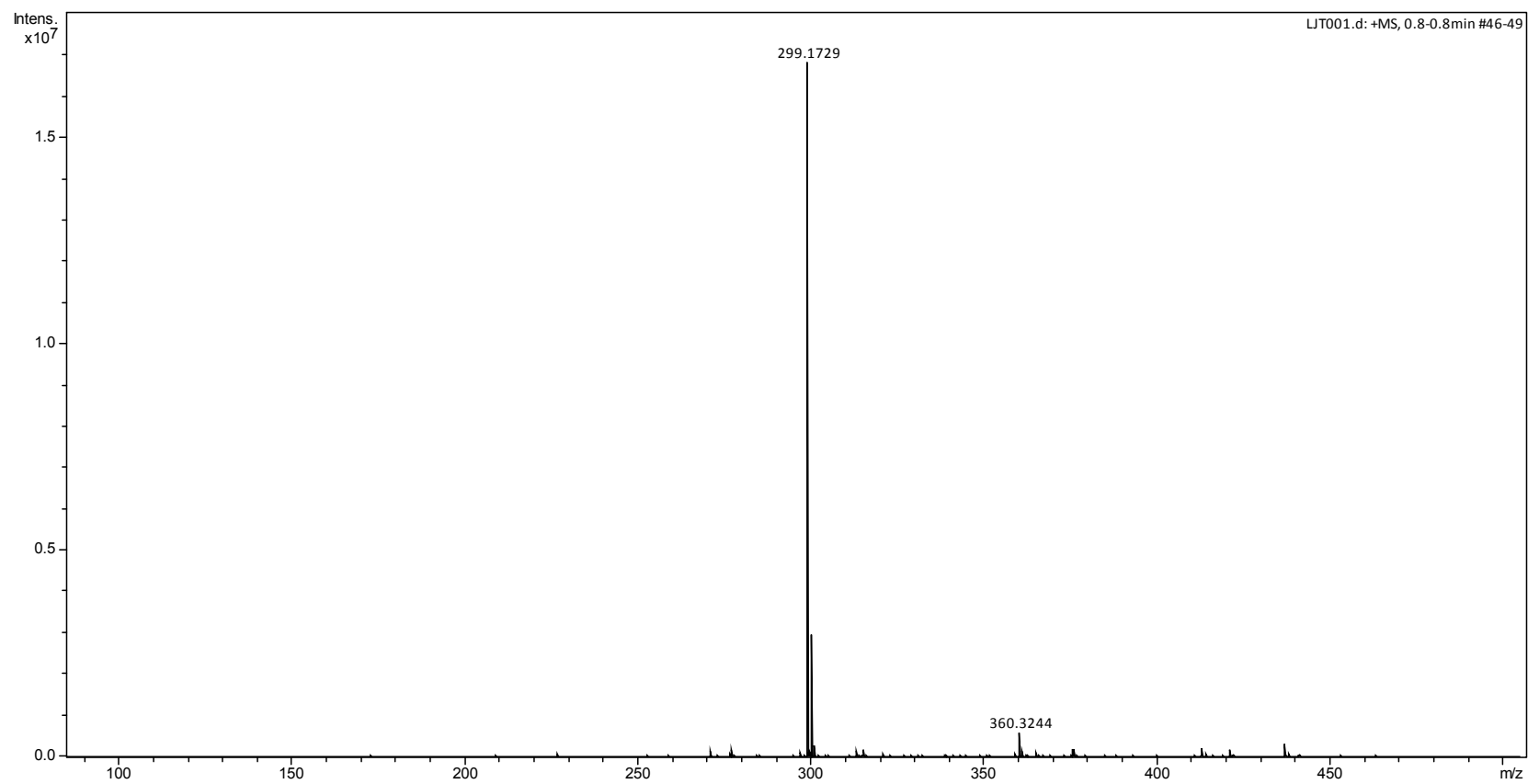


Figure S8. ^{13}C NMR spectra for (*S*)-N-(5-hydroxypentyl)-1-((*S*)-1-phenylethyl)aziridine-2-carboxamide (**S2**).

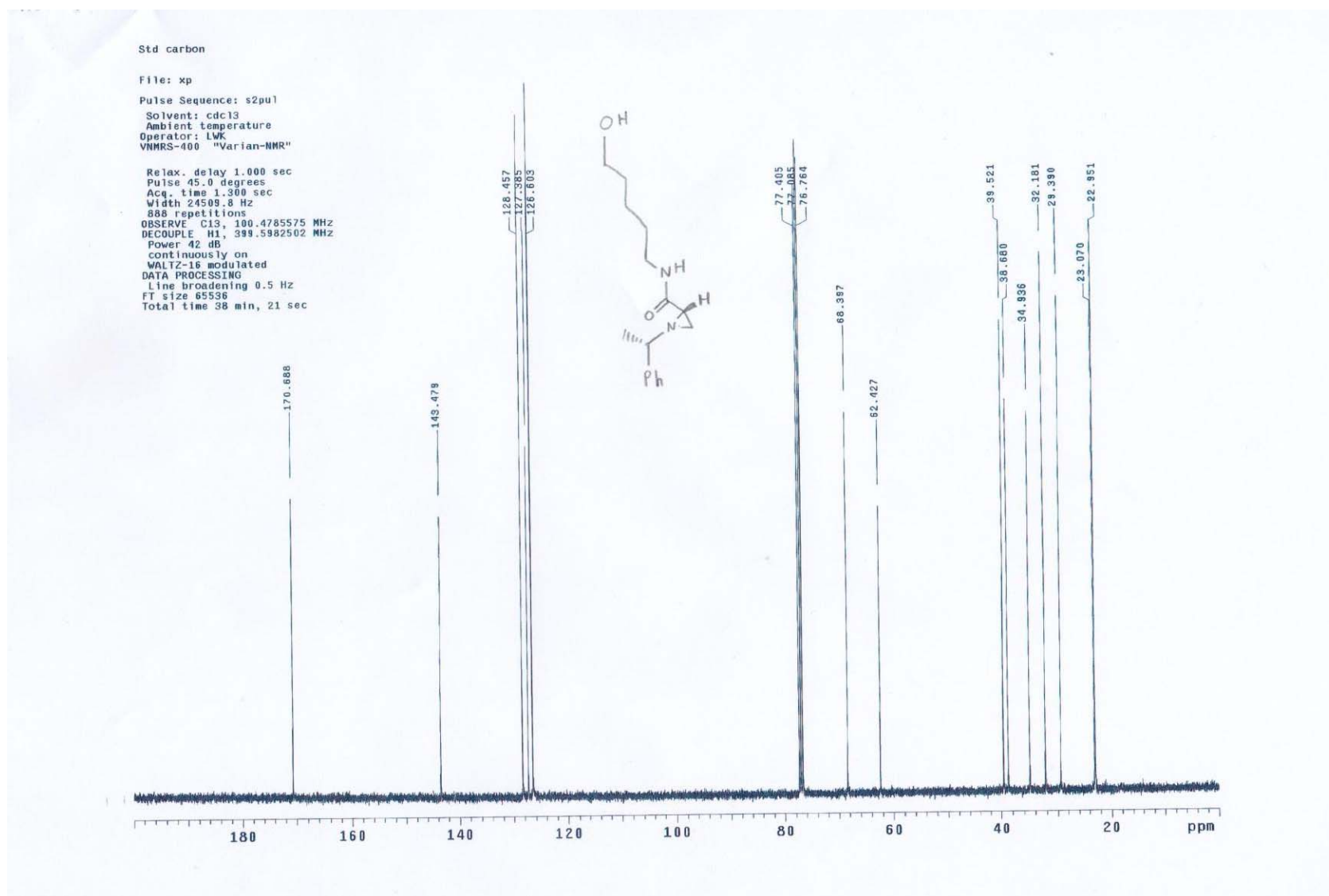
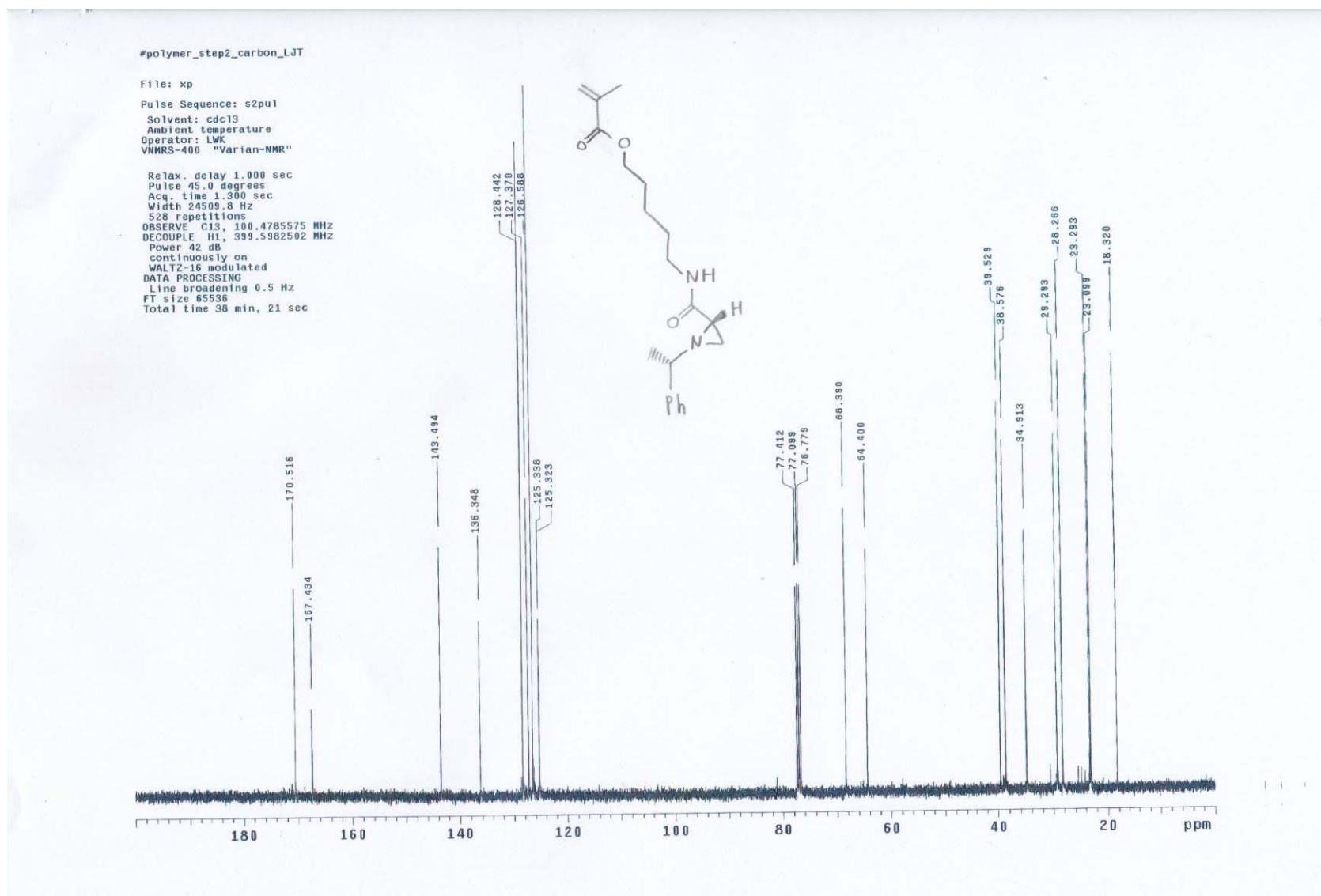


Figure S9. ^{13}C NMR spectra for 5-((*S*)-1-((*S*)-1-phenylethyl)aziridine-2-carboxamido)pentyl methacrylate (**S3**, AziMA).



Reference

- (1) Lim, Y.; Lee, W. K. *Tetrahedron Lett.* **1995**, 36, 8431.