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## Exploring different thermoplastics from lignocellulosic building blocks and monomers

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# Poly(alkanoyl isosorbide methacrylate)s: From Amorphous to Semicrystalline and Liquid Crystalline Biobased Materials

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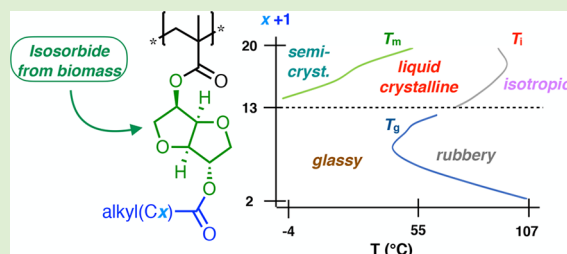


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**ABSTRACT:** We have prepared a series of 12 D-isosorbide-2-alkanoate-5-methacrylate monomers as single regioisomers with different pendant linear C2–C20 alkanoyl chains using biocatalytic and chemical acylations. By conventional radical polymerization, these monomers provided high-molecular-weight biobased poly(alkanoyl isosorbide methacrylate)s (PAIMAs). Samples with C2–C12 alkanoyl chains were amorphous with glass transition temperatures from 107 to 54 °C, while C14–C20 chains provided semicrystalline materials with melting points up to 59 °C. Moreover, PAIMAs with C13–C20 chains formed liquid crystalline mesophases with transition temperatures up to 93 °C. The mesophases were studied using polarized optical microscopy, and rheology showed stepwise changes of the viscosity at the transition temperature. Unexpectedly, a PAIMA prepared from a regioisomeric monomer (C18) showed semicrystallinity but not liquid crystallinity. Consequently, the properties of the PAIMAs were readily tunable by controlling the phase structure and transitions through the alkanoyl chain length and the regiochemistry to form fully amorphous, semicrystalline, or semi/liquid crystalline materials.



## INTRODUCTION

Consumption of finite fossil resources combined with growing environmental concerns is a strong driving force to phase out oil-based chemical processes and utilize renewable biomass as a source for chemicals and plastics.<sup>1</sup> However, it is a great challenge to develop economically viable routes to bioderived plastics that have good processability and fulfill all of the material property requirements for various applications.<sup>2</sup> Biobased polymers with a high glass transition temperature ( $T_g$ ) have been especially challenging to achieve.<sup>3</sup> In this context, rigid bicyclic isosorbide produced from D-glucose on an industrial scale<sup>4</sup> has been identified as one of the platform building blocks with the potential to replace fossil-based counterparts in high- $T_g$  plastics.<sup>5</sup> Isosorbide is a nontoxic, chiral, V-shaped diol, bearing two sterically different secondary hydroxyl groups (with *exo* and *endo* configurations, respectively) and two *cis*-connected tetrahydrofuran rings.<sup>6</sup>

The use of isosorbide has been extensively investigated for the synthesis of step-growth polymers such as polyesters, polycarbonates, polyamides, and polyurethanes, some of which are commercially available.<sup>7,8</sup> Furthermore, diepoxy,<sup>9,10</sup> divinyl,<sup>11,12</sup> and di(meth)acrylate<sup>13–15</sup> monomers of isosorbide have been prepared and their polymerization investigated. In most cases, the *exo* and *endo* hydroxyl groups have not been differentiated and the isosorbide unit has been fully incorporated into the polymer backbone. Far less studied are selective functionalizations where the polymerizable functionality has been attached exclusively on either the *exo* or the *endo* hydroxyl group. In such an arrangement, the isosorbide unit is

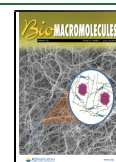
not built into the polymer backbone but instead forms pendant side groups. Thus, the residual free hydroxyl group on the isosorbide unit enables the attachment of various substituents to control properties (e.g., the  $T_g$ ) or to introduce different reactive functionalities, e.g., for use in subsequent cross-linking reactions.

Regioselective synthesis of isosorbide monoesters has been a field of research for decades, mainly because there has been a lack of a universal method for regioselective catalytic acylation of the isosorbide hydroxyl groups. Both chemocatalytic and biocatalytic methods have been investigated. Apart from some early chemical methods based on heavy metal salts,<sup>16</sup> a 4.2:1 *endo* selective Sc(OTf)<sub>3</sub> catalyzed process has been reported by Hillmyer et al.<sup>17</sup> In addition, Aldabbagh and co-workers have developed MeMgCl-mediated conditions to selectively prepare both *exo* and *endo* acetates.<sup>18</sup> However, this method requires equimolar amounts of MeMgCl.<sup>18</sup> Biocatalytic pathways have been studied more intensively.<sup>19–23</sup> For example, a solvent-free Lipzyme-catalyzed procedure has been shown to provide products with high regioselectivity in the case of acyl groups with longer carbon chains but afforded poor results for shorter

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ones.<sup>19</sup> In general, both 2-acylates<sup>22</sup> and 5-acylates<sup>21,24</sup> have been prepared with better results obtained for the latter compound. We have recently reported on a highly regioselective lipase-catalyzed method for the monomethacrylation of isosorbide using either vinyl methacrylate or methacrylic anhydride as the methacryl donor.<sup>24</sup> This readily upscalable approach enables the preparation of both isosorbide-5-methacrylate (5-IMA) and isosorbide-2-methacrylate (2-IMA) with essentially complete regioselectivity (>99:1 for both isomers).

Isosorbide monomethacrylates have been polymerized by both conventional free-radical,<sup>17,24</sup> reversible addition-fragmentation chain transfer (RAFT)<sup>17</sup> and single-electron transfer-living polymerization techniques.<sup>25</sup> Still, the number of studies concerning the effect of different isosorbide substitutions on polymer properties is very limited. Unsubstituted monomer 5-IMA provides a polymethacrylate with  $T_g = 167\text{ }^\circ\text{C}$ , which is soluble in dimethyl sulfoxide (DMSO) but not in other common solvents such as alcohols, water, chlorinated solvents, or tetrahydrofuran (THF).<sup>24</sup> Atactic polymers prepared from acetylated isosorbide methacrylate show  $T_g$  at approximately  $127\text{ }^\circ\text{C}$  and are also soluble in THF, acetonitrile (ACN), and  $\text{CHCl}_3$ . This hints that these polymers may potentially be considered as a biobased alternative to poly(methyl methacrylate) in some applications.

Data on the effects of monomer regiochemistry on polymer properties is very scarce, mostly due to the lack of straightforward and highly regioselective monomethacrylation methodologies. In the case of acetylated isosorbide polymethacrylates, the regiochemistry has no significant impact on the thermal properties of the polymers.<sup>17,24</sup> However, in the case of dodecanoate substitution, the effect is pronounced: the polymer with the pendant dodecanoate chain in the *exo* position shows crystallinity and a high melting point ( $T_m = 83\text{ }^\circ\text{C}$ ), whereas the polymer with the dodecanoate chain in the *endo* position is fully amorphous with  $T_g = 54\text{ }^\circ\text{C}$ .<sup>24</sup> Differences in  $T_g$  values and solubility properties have also been reported in the case of regioisomeric poly(vinyl isosorbide triazoles).<sup>26</sup> These findings imply that the properties of isosorbide polymethacrylates can be conveniently controlled over a wide range by the choice of the pendant substituent. Consequently, this class of materials may then be tuned for different applications, including engineering plastics, optical, and coating applications. This motivates detailed characterizations and studies of different structure–property relationships.

In the present work, we have prepared a range of isosorbide polymethacrylates as single regioisomers substituted with linear alkanooates of different lengths with the main goal to systematically study their phase behavior, thermomechanical and rheological properties, and processability. In addition, we also report on an efficient and upscalable biocatalytic method with which a series of isosorbide-5- and 2-methacrylic diester monomers bearing 12 different alkanooate substituents extending from acetate (C2) to eicosanoate (C20) was synthesized. The monomers were employed in conventional free-radical polymerizations, and the resulting poly(alkanoyl isosorbide methacrylate)s (PAIMAs) were characterized by thermogravimetry, calorimetry, rheology, dynamic mechanical analysis (DMA), and microscopy.

## ■ EXPERIMENTAL SECTION

**Materials.** Reagents and solvents were obtained from commercial sources and used as received. As a precaution, a small amount of a radical scavenger [hydroxyquinone (HQ) or *p*-methoxyphenol (HQMME)] was added to the methacrylate monomers after preparation and the monomers were stored in a refrigerator ( $2\text{--}6\text{ }^\circ\text{C}$ ). The isosorbide acylations were monitored by thin-layer chromatography (TLC, Xtra SIL G/UV<sub>254</sub>), and the plates were visualized by staining with a phosphomolybdic acid solution. Silica gel 60 (0.040–0.063 mm, 230–400 mesh) was used for flash chromatography.

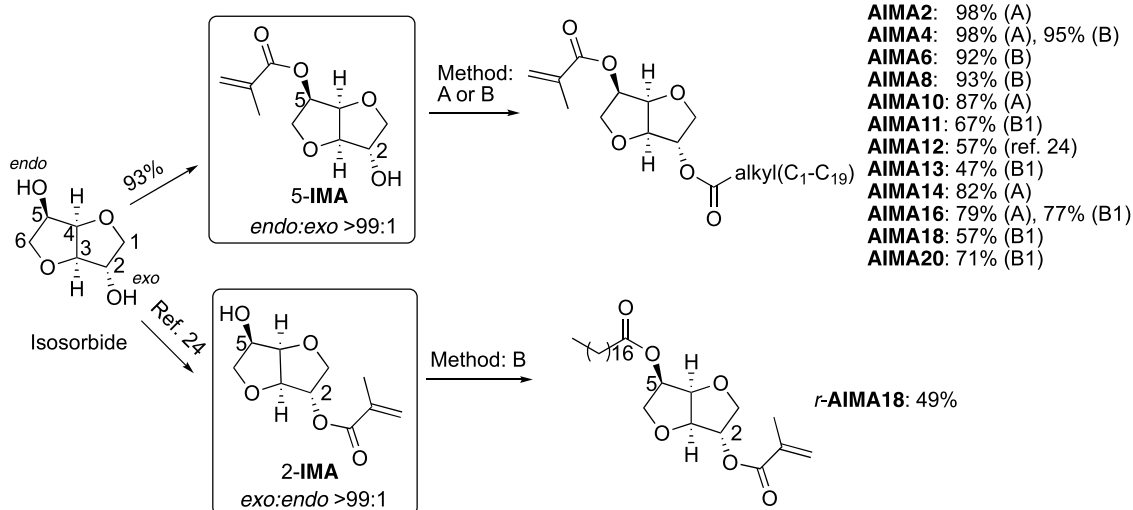
**Structural Characterization.** Monomer and polymer structures were characterized using a Bruker 400 MHz NMR spectrometer with samples dissolved in chloroform-*d*. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured at 400.1 and 100.6 MHz, respectively. The chemical shifts are given in ppm, and residual solvent signals were used for calibration (for  $^1\text{H}$ ,  $\text{CDCl}_3$ :  $\delta = 7.26\text{ ppm}$ , for  $^{13}\text{C}$ ,  $\text{CDCl}_3$ :  $\delta = 77.0\text{ ppm}$ ). The conversions in the polymerization step were measured by comparing the broad non-overlapping polymer signal at 4.90–5.10 or 4.70–4.90 ppm with the remaining double bond signal at approximately 6.15 ppm (*trans*-H) in the monomer. High-resolution mass spectrometry (HRMS) analyses of monomers were carried out on a Thermo Electron LTQ Orbitrap XL analyzer, and Fourier transform infrared (FTIR) analyses were performed on a Shimadzu IRAffinity-1 spectrometer. The molecular weights of the polymers were determined by size-exclusion chromatography (SEC) with THF as the solvent. A Shimadzu Prominence system equipped with three Shodex columns (KF-805, –804, and –802.S, coupled in series) and a refractive index detector (RID-20A) was used. Samples were run at  $40\text{ }^\circ\text{C}$  with an elution rate of  $1\text{ mL min}^{-1}$ . Poly(ethylene oxide) standards ( $M_n = 3860, 12\,600, 49\,640, \text{ and } 96\,100\text{ g mol}^{-1}$ ) were used for calibration, and the results were analyzed using Shimadzu LabSolution software.

**Monomethacrylate Synthesis.** The monomers AIMA2–AIMA20 and *r*-AIMA18 as single regioisomers were prepared from 5-IMA (*endo/exo* > 99:1) and 2-IMA (*exo/endo* > 99:1), respectively, via either biocatalytic (Novozym 435/vinyl alkylate) or chemical (acyl chloride/ $\text{Et}_3\text{N}$ ) acylation in up to 36 g scale. The monomers were purified by a simple extraction/filtration sequence (in case of optimized large-scale synthesis of AIMA2 and AIMA4) or by flash chromatography. Detailed experimental procedures and analytical data for all monomers are presented in the SI.

**Alkanoyl Isosorbide Methacrylate Polymerization.** After removal of the inhibitor (described in the SI), the diester monomer and AIBN (0.5 mol %) were dissolved in EtOAc ( $0.1\text{ g mL}^{-1}$ ) and transferred to the reaction flask. The solution was purged with argon gas for 30–60 min, whereafter the reaction flask was sealed and placed in a preheated oven at  $63\text{ }^\circ\text{C}$  for 24 h. After being allowed to cool, the crude polymer was precipitated in methanol (product concentration  $2\text{ g L}^{-1}$ ). The solids were filtered, washed with an additional amount of methanol, and dried under reduced pressure to obtain the target polymer.

**Thermal Analysis.** Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500. Samples of 1–8 mg were heated to  $600\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen flux ( $60\text{ mL min}^{-1}$ ). The thermal decomposition temperature ( $T_{d,95}$ ) was determined at a 5% loss of the initial weight. Differential scanning calorimetry (DSC) measurements were performed on TA Instruments DSC Q2000. Samples of 1–10 mg were first heated to 120 or  $200\text{ }^\circ\text{C}$  (depending on their respective thermal decomposition temperatures) at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ . They were maintained at this temperature for 2 min, before cooling to  $-50\text{ }^\circ\text{C}$ , and were then maintained isothermally for 2 min, before being heated back to the starting temperature at the same heating rate.

**Dynamic Mechanical Measurements.** Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA Q800. Rectangular bars ( $35 \times 5 \times 1\text{ mm}$ ) of samples P2 and P3 were hot-pressed in a steel mold placed between two Teflon plates using a hydraulic press (Specac, GS15011) at  $150\text{ }^\circ\text{C}$  for 2 min. The samples

Scheme 1. Regioselective Synthesis of the Alkanoyl Isosorbide Monomethacrylates<sup>a</sup>

<sup>a</sup>Method A: corresponding vinyl alkylate, Novozym 435, and ACN/PE. Method B: corresponding acyl chloride, Et<sub>3</sub>N, ACN, or CH<sub>2</sub>Cl<sub>2</sub> (B1).

were then cooled to 100 °C for 5 min and finally to room temperature. Analysis of the samples was carried out at 1 Hz in the temperature range between 25 and 150 °C at a heating rate of 2 °C min<sup>-1</sup>. The measurements were performed in the linear viscoelastic region at a strain of 0.01%. The *T<sub>g</sub>* value was determined by the maximum peak value of the loss modulus (*G''*) in the glass transition region.

**Melt Rheology.** Dynamic rheology measurements were performed with a TA Instruments Advanced Rheometer AR2000 ETC. The experiments were carried out using parallel plates ( $\varnothing$  = 25 mm). Disks of samples PAIMA16, PAIMA18, and PAIMA20 ( $\varnothing$  = 25 mm, *t* = 1 mm) were hot-pressed as described above. A time sweep was carried out on sample PAIMA18 for 40 min at 100 °C, 1 Hz, and 1% strain, which was within the linear viscoelastic region. Moreover, a temperature sweep was performed on PAIMA16, PAIMA18, and PAIMA20 with a strain of 0.01% at 1 Hz. These samples were first cooled from 120 to 75 °C at a rate of 2 °C min<sup>-1</sup> and then heated to 120 °C before being cooled to 75 °C at the same rate.

**Light Microscopy.** The phase behavior and structure of PAIMA20 were observed using an Olympus BX50 microscope under cross-polarized light. The sample was heated and cooled using a Linkam THMS 600 hot stage mounted on the microscope and controlled by a Linkam TMS 93 temperature controller. PAIMA20 was first melted at 120 °C on a 16 mm clear glass stage plate and then covered with another glass plate. The sample was then slowly cooled to room temperature to allow for crystallization. Photographs were taken using a Lumenera INFINITY 2, 2.0 USB Microscope Camera and Lumenera's Infinity Analyse software.

## RESULTS AND DISCUSSION

**Synthesis of Isosorbide Methacrylic Diester Monomers.** An important issue to consider when designing a synthesis is the required scale. At the proof-of-concept level, monomers in quantities up to ca. 2–5 g are commonly needed, and at this scale, there are fewer restrictions regarding processing (including purification) and economy. However, for application tests, where usually preparative synthesis in >30 g scale is required, the development of a readily upscalable procedure normally becomes necessary. For example, the properties of potential byproducts and the choice of an efficient product purification method become crucial if highly reactive monomers need to be produced with high purity on such a scale.

In general, the 5-OH group (*endo*) in isosorbide is sterically shielded but is on the other hand a stronger nucleophile than the 2-OH group (*exo*) due to intramolecular hydrogen bonding. Therefore, the chemical acylation of isosorbide generally favors the sterically less accessible, but chemically more reactive, 5-OH group. Somewhat unexpectedly, such a selectivity toward the 5-OH group has also been observed for most (but not all) of the lipases used to catalyze the regioselective acylation of isosorbide. In the current work, a two-step lipase-catalyzed process was used for the regioselective synthesis of several diester monomers. The first step was methacrylation of the 5-OH group using *Rhizomucor miehei* (RM) lipase as a catalyst. RM lipase should be immobilized on resin; the variant immobilized on imobead was found to be inactive in this application. The procedure applied here is an improved version of our previously reported method<sup>24</sup> and provides 5-IMA in 93% yield (Scheme 1, previously 87%) using a straightforward chromatography-free workup (purity and regioselectivity >99%; see the SI for the detailed procedure).

For the second acylation, both a biocatalytic and a conventional chemical procedure (acyl chloride/Et<sub>3</sub>N) were evaluated. In the biocatalytic reaction (method A, Scheme 1), we utilized *Candida antarctica* lipase B, which is less selective in this system. Consequently, it was able to catalyze the acylation of the 2-OH group in the 5-monoester intermediate with a variety of acyl groups, albeit at a somewhat elevated temperature (45 °C). These syntheses provided highly homogeneous diesters in good to excellent yields (79–98%, Scheme 1). The excess acyl donors (i.e., vinyl esters) with short acyl hydrocarbon chains (C<sub>2</sub>, C<sub>4</sub>) were smoothly separated by distillation at reduced pressure on a rotary evaporator after the reaction was completed. The diester products were purified by decolorization using activated charcoal in ethanol. Such a straightforward separation methodology is particularly important when upscaling the synthesis.

The alkanoyl isosorbide methacrylate monomers in this study are denoted as AIMA<sub>*x*</sub>, where *x* indicates the number of carbon atoms of the pendant alkanoyl substituent. For AIMA2 and AIMA4, we optimized acetylation and butyry-



ylation, respectively, on a ~30 g scale and obtained the target diesters using a chromatography-free process in >98% yield (purity and regioselectivity >99%). For AIMA6, AIMA8, AIMA13, AIMA18, and AIMA20, a conventional acyl chloride/ $\text{Et}_3\text{N}$  procedure was used (method B and B1, Scheme 1). The yields were generally somewhat lower compared to the biocatalytic method. However, no particular optimization was attempted for these monomers, and we focused instead on monomer purification. In general, the choice of a particular synthetic method depends not only on the goal and the scale but also on the availability of a specific acyl donor.

The regioisomeric 2-IMA was prepared according to our previous report,<sup>24</sup> and the subsequent reaction with stearoyl chloride provided *r*-AIMA18 in 49% yield. Monomers with short and medium-size alkanoyl substituents (AIMA2–AIMA13) were viscous liquids, whereas longer alkanoyl-substituted monomers were white crystalline compounds (AIMA14–AIMA20, *r*-AIMA18). The solubility of the monomers was also affected by the length of the alkanoyl chain, and the physical state in the series of monomers changed noticeably between AIMA13 and AIMA14. Monomers with longer alkanoyl chains (AIMA14 and beyond) were soluble in ethereal solvents (THF, diethyl ether) but were insoluble in highly polar DMSO. Monomer AIMA2 is an exception since it was also soluble in ethereal solvents. In general, all of the studied monomers were readily soluble in EtOAc, toluene, ACN,  $\text{CHCl}_3$ , and MeOH, and 5-IMA was also soluble in water (for detailed solubility data, see Table S1).

**Polymerization of Alkanoyl Isosorbide Methacrylate Monomers.** All of the monomers were polymerized in EtOAc solutions at 63 °C for 24 h using conventional free-radical polymerization initiated by AIBN (0.5 mol %), as seen in Scheme 2. Only in the case of AIMA20, a few droplets of  $\text{CH}_2\text{Cl}_2$  were added to the reaction mixture to avoid cloudiness as this monomer had limited solubility in EtOAc. Alternatively, toluene was successfully used as a polymerization medium for AIMA20. The resulting series of poly(alkanoyl isosorbide methacrylate)s were denoted as PAIMA $x$ . MeOH readily

dissolved all of the monomers and was chosen for the precipitation of the polymers from the reaction mixtures. In the case of PAIMA20, the isolated polymer was washed multiple times with MeOH as the residual AIMA20 monomer dissolved slowly in MeOH. All of the isolated polymers were white solids and their structures were confirmed by  $^1\text{H}$  NMR spectroscopy. The number average molecular weight ( $M_n$ ) and polydispersity ( $\bar{D}$ ) were determined by SEC using poly(ethylene oxide) standards (Table 1). The monomer conversions ranged from 56 to 96% (Table 1), and  $M_n$  varied between 32 and 81 kg  $\text{mol}^{-1}$ . In addition to the homopolymers, a 1:1 mixture of AIMA18 and *r*-AIMA18 was also successfully copolymerized [P(AIMA18-*co-r*-AIMA18), entry 14]. The solubility of the polymers was investigated in a wide range of solvents with different solubility parameters ( $\delta$ ) and hydrogen-bonding capacity (Table S2).<sup>27</sup> All polymers with alkanoyl substituents were soluble in EtOAc,  $\text{CHCl}_3$ , and THF. Toluene dissolved all polymers except PAIMA2. Solvents with a strong hydrogen-bonding capacity ( $\text{H}_2\text{O}$ , MeOH, *n*-BuOH) did not dissolve any of the polymers. The polar aprotic DMSO dissolved polymers with short alkanoyl chains (PAIMA2 and PAIMA4), but polymers with longer alkanoyl chains remained insoluble. Acetonitrile, having a  $\delta$  value similar to that of DMSO, dissolved PAIMA2, PAIMA4, and PAIMA6. The *r*-PAIMA18 and P(AIMA18-*co-r*-AIMA18) copolymers had a similar solubility profile as PAIMA18 (Table S2).

**Thermal Stability.** The polymers were analyzed by thermogravimetric analysis (TGA) to study the thermal decomposition of the polymers under a  $\text{N}_2$  atmosphere. The TGA traces in Figure 1a show that the decomposition temperature ( $T_{d,95}$ ) varied between 190 and 259 °C (see Table 1), and the derivatives of the TGA traces in Figure 1b indicate two distinguishable steps. As reported by Matt et al., the first step most likely corresponds to the decomposition of the alkanoyl chains, and the second step to the degradation of the isosorbide units, followed by a gradual decomposition of the polymer backbone.<sup>24</sup> The plot of  $T_{d,95}$  versus the number of carbon atoms in the pendant alkanoyl chain shows an initial decrease from 238 °C for the non-alkanoylated PAIMA0<sup>24</sup> to 190 and 188 °C for PAIMA4 and PAIMA6, respectively. After this decline,  $T_{d,95}$  increases almost linearly with the alkanoyl chain length up to 259 °C for PAIMA20. This variation may possibly be explained by the high  $T_g$  (high melt viscosity) of the material without alkanoyl chains ( $x = 0$ ), resulting in high  $T_{d,95}$  values. With increasing chain length ( $x = 2$  and 4),  $T_g$  decreased, and consequently,  $T_{d,95}$  decreased to 190 °C. As the chain length increased further ( $x = 6$ –20), the gradual increase in  $T_{d,95}$  may be explained by the dilution of the heat-sensitive isosorbide in the samples as the alkanoyl chain length and content increased (Figure 2).

**Fully Amorphous Materials.** Differential scanning calorimetry (DSC) showed a large variation in phase behavior depending on the length of the pendant alkanoyl chain. PAIMA0, with unsubstituted 2-OH, is a fully amorphous material with a high  $T_g$  (167 °C) because of the hydrogen bonding of the hydroxyl groups.<sup>24</sup> As seen in Figure 3a, the DSC traces of polymers substituted with short alkanoyl chain lengths indicated only glass transitions and were thus also fully amorphous materials. As expected, the  $T_g$  decreased with increasing chain length because of the increasing internal plasticization by the flexible alkanoyl chain. Thus, the  $T_g$  decreased from 107 °C for PAIMA2 to 80 °C for PAIMA4, whereafter the value seemingly stabilized between 57 and 52

**Scheme 2.** Polymerization of the Alkanoyl Isosorbide Methacrylates by Conventional Radical Polymerization

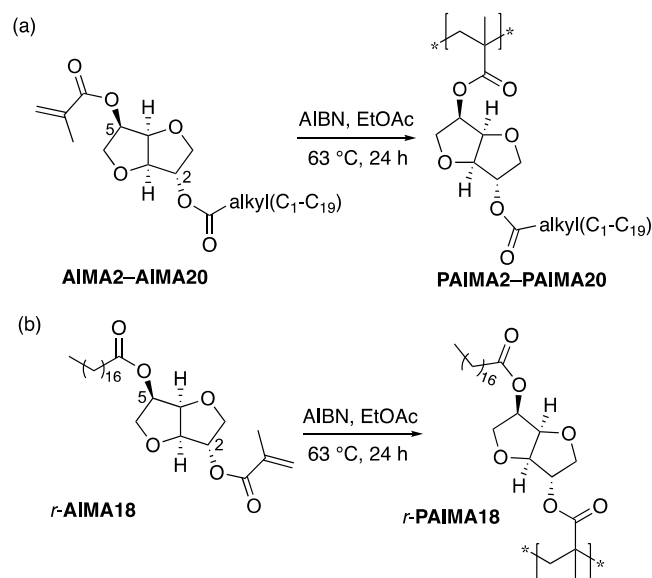


Table 1. Polymerization and Thermal Data of the PAIMAx Samples

entry	sample	monomer conv. (%) <sup>b</sup>	$M_n$ ( $\text{kg mol}^{-1}$ ) <sup>c</sup>	$\bar{D}$ <sup>c</sup>	$T_{d95}$ ( $^{\circ}\text{C}$ ) <sup>d</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>e</sup>	$T_m$ ( $^{\circ}\text{C}$ ) <sup>e</sup>	$T_c$ ( $^{\circ}\text{C}$ ) <sup>e</sup>	$\Delta H_m$ ( $\text{J g}^{-1}$ ) <sup>e</sup>	$T_i$ ( $^{\circ}\text{C}$ ) <sup>f</sup>	$T_a$ ( $^{\circ}\text{C}$ ) <sup>g</sup>	$\Delta H_i$ ( $\text{J g}^{-1}$ ) <sup>e</sup>
1	PAIMA0 <sup>a</sup>	96	n.a	n.a	238	167						
2	PAIMA2	85	32	2.97	208	107						
3	PAIMA4	84	60	1.78	190	80						
4	PAIMA6	63	56	2.11	188	57						
5	PAIMA8	76	38	2.16	199	46						
6	PAIMA10	56	47	2.06	201	52						
7	PAIMA11	79	56	2.27	209	56						
8	PAIMA12 <sup>a</sup>	87	43	2.70	226	66						
9	PAIMA13	81	32	2.23	228					75	65	2.2
10	PAIMA14	82	61	2.23	233		−4	−10	5.5	82	73	2.0
11	PAIMA16	82	58	2.11	231	76	19	10	20	92	79	2.7
12	PAIMA18	75	62	2.63	254	79	32	26	16	97	90	1.5
13	r-PAIMA18	58	49	2.06	251		30	23	33			
14	P(AIMA18-co-r- AIMA18)	75	81	2.14	247		41	35	41	69	59	0.5
15	PAIMA20	81	46	2.57	259	74	55	46	53	94	88	2.1

<sup>a</sup>Data taken from ref 24. <sup>b</sup>Determined by  $^1\text{H}$  NMR spectroscopy. <sup>c</sup>Measured by SEC in THF using poly(ethylene oxide) standards. <sup>d</sup>Measured by TGA at 5% weight loss under  $\text{N}_2$ . <sup>e</sup>Determined by DSC. <sup>f</sup>Isotropization temperature measured during heating. <sup>g</sup>Anisotropization temperature measured during cooling.

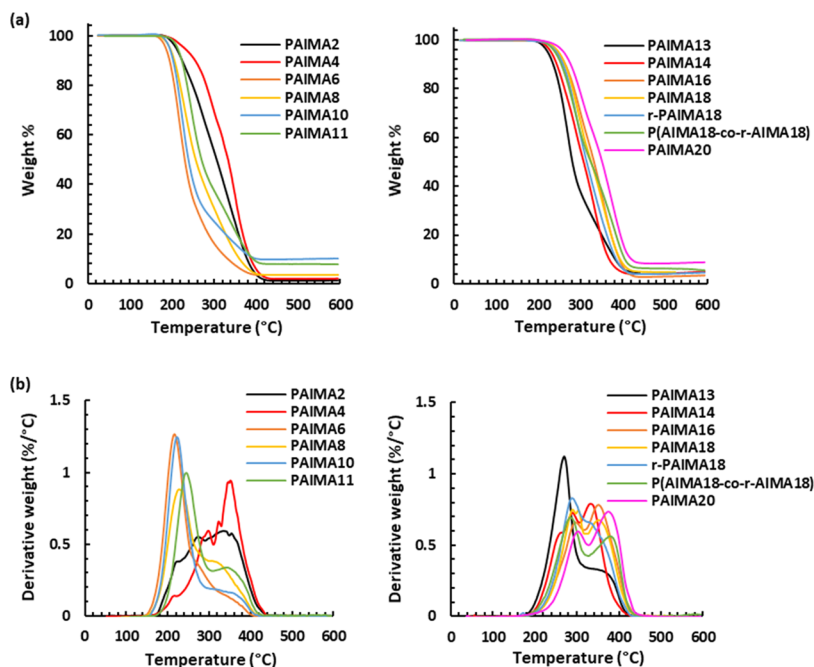


Figure 1. TGA (a) and corresponding differential TGA (b) profiles of the PAIMAx series recorded under a  $\text{N}_2$  atmosphere at  $10\text{ }^{\circ}\text{C min}^{-1}$ .

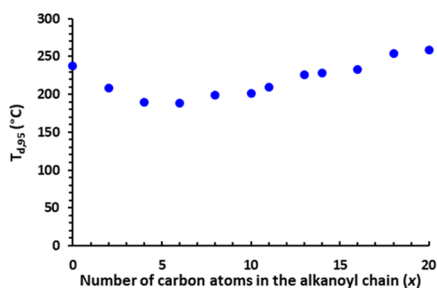
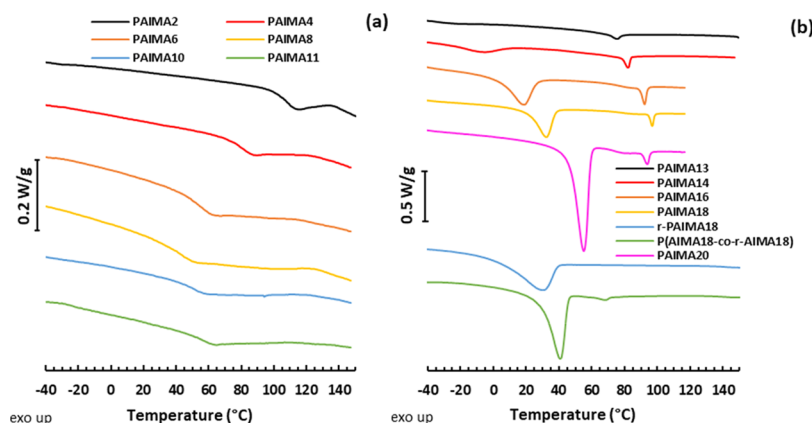


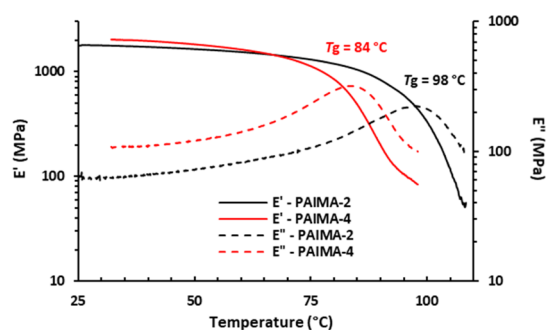
Figure 2. Variation of  $T_{d95}$  with the number of carbon atoms in the alkanoyl chain in the PAIMAx series with  $x = 0\text{--}20$ .

$^{\circ}\text{C}$  for PAIMA6, -8, -10, -11, and -12 (notably, the  $T_g$  of PAIMA8 is  $46\text{ }^{\circ}\text{C}$  but may be explained by the quite low  $M_n$  of this sample). The  $T_g$  values of both PAIMA0 and PAIMA2 reached above  $100\text{ }^{\circ}\text{C}$ , which makes these materials interesting for high-temperature applications such as “hot-fill” applications in packaging.

Dynamic mechanical analysis (DMA) was carried out on hot-pressed samples of PAIMA2 and PAIMA4 to study the mechanical stiffness and glass transitions of these materials. Figure 4 shows the storage ( $E'$ ) and loss ( $E''$ ) moduli as a function of temperature in the linear viscoelastic region. As expected, the materials had a high mechanical stiffness at the glassy plateau, which then decreased as the glass transition was reached. Hence, for PAIMA2 and PAIMA4, the storage



**Figure 3.** DSC heating traces of the polymers in the **PAIMAx** series: (a)  $x = 2$ –11 and (b)  $x = 13$ –20, also including the samples *r*-PAIMA18 and P(AIMA18-*co*-*r*-AIMA18).

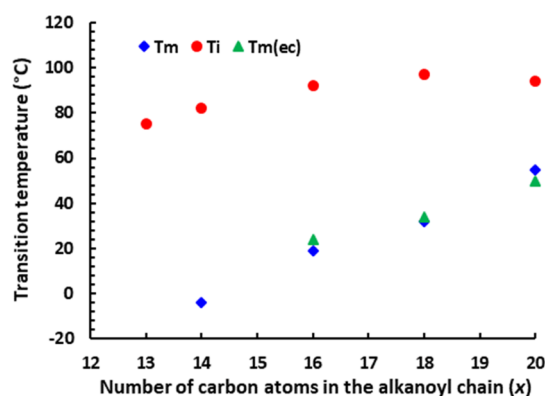


**Figure 4.** Storage ( $E'$ ) and loss ( $E''$ ) moduli of **PAIMA2** and **PAIMA4** measured by DMA at  $2$  °C  $\text{min}^{-1}$  in the linear viscoelastic region (0.01% strain, 1 Hz).

modulus only went below 1 GPa at temperatures above 86 and 77 °C, respectively. The  $T_g$  values (taken at the local maximum of the loss modulus) were found at 98 and 84 °C for **PAIMA2** and **PAIMA4**, respectively. These values may be compared with 107 and 80 °C, respectively, measured by DSC.

**Semicrystalline and Liquid Crystalline Materials.** As the length of the pendant alkanoyl chain was increased to above  $x = 13$ , the polymers in the **PAIMAx** series became semicrystalline (Table 1). Consequently, **PAIMA14** showed a first-order transition attributed to crystalline melting (Figure 5). The melting point ( $T_m$ ) then increased with alkanoyl chain length from  $-4$  for **PAIMA14** to 55 °C for **PAIMA20** (Figure 5). Concurrently, the melt enthalpy ( $\Delta H_m$ ) increased from 5.5 to  $53 \text{ J g}^{-1}$  (Table 1). Glass transitions were detected at 74–79 °C for **PAIMA16**, **–18**, and **–20**, i.e., at significantly higher values than for **PAIMA6**, **–8**, **–10**, **–11**, and **–12** (Table 1). This increase of  $T_g$  with the alkanoyl chain length may indicate that the polymethacrylate backbone is not plasticized by the flexible alkanoyl chains, which in turn suggests that these two components were phase-separated when  $x$  exceeded a certain number between 12 and 16.

The  $T_g$  and  $T_m$  values of the **PAIMAx** series may be compared to those of corresponding poly(*n*-alkyl methacrylate)s. For example, high-molecular-weight poly(octadecyl methacrylate) shows  $T_g$  and  $T_m$  values of  $-100$ <sup>28</sup> and 37.5 °C,<sup>29</sup> respectively. In addition, the  $T_m$  of the **PAIMAs** with the longest alkanoyl chains ( $x = 16$ –20) matched the values of corresponding ethyl carboxylates (Figure 5). Hence, the  $T_m$  values of the ethyl esters of hexadecanoic, octadecanoic, and eicosanoic acid are 24, 34, and 50 °C, respectively.<sup>30–32</sup>

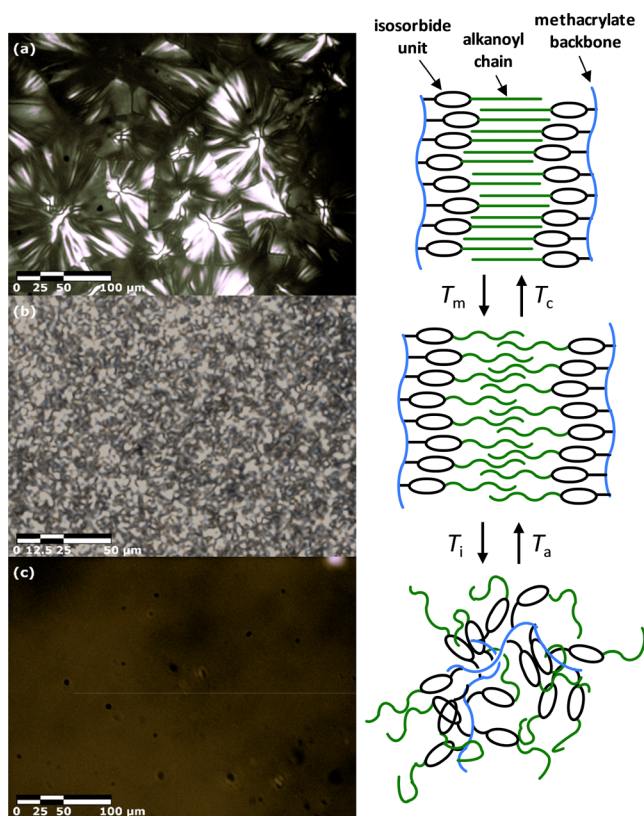


**Figure 5.** Variation of the crystalline melting point ( $T_m$ ) and the isotropization temperature ( $T_i$ ) in the **PAIMAx** series with  $x = 13$ –20 compared with the crystalline melting point of ethyl carboxylates [ $T_m(\text{ec})$ ] with  $x = 16$ –20.

Another first-order transition was observed by DSC well above  $T_m$  for samples with a pendant alkanoyl chain length above 12 carbon atoms (Figure 5). For **PAIMA14**, this transition occurred at an isotropization temperature of  $T_i = 82$  °C during heating, i.e., 86 °C above  $T_m$  ( $-4$  °C). The transition enthalpy ( $\Delta H_i$ ) varied between 1.5 and  $2.7 \text{ J g}^{-1}$ , well below that of  $\Delta H_m$ , seemingly independent of the alkanoyl chain length. We interpreted this as an order-to-disorder transition that appeared in connection with the formation of a liquid crystalline mesophase after crystalline melting. The transition temperature seemed to increase with the alkanoyl chain length (small variations may be explained by differences in molecular weight) from  $T_i = 82$  for **PAIMA14** to 97 and 94 °C for **PAIMA18** and **PAIMA20**, respectively (Figure 5). The corresponding anisotropization temperature ( $T_a$ ) recorded during cooling was between 6 and 10 °C below  $T_i$ , revealing a reversible hysteresis behavior (Table 1).

To observe the phase transitions and further confirm the formation of a liquid crystalline mesophase, **PAIMA20** was studied during heating ( $10$  °C  $\text{min}^{-1}$ ) by optical microscopy under cross-polarized light. Typical micrographs of the optical textures at different temperature regimes are shown in Figure 6. First, the micrograph taken at 22.5 °C (i.e., below  $T_m$ ) displays the typical spherulitic texture of a semicrystalline polymer (Figure 6a). In this case, the spherulites had an average diameter of  $\sim 100 \mu\text{m}$ . Upon heating, the crystallites





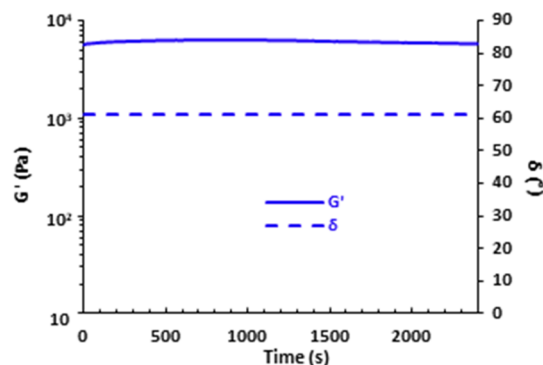
**Figure 6.** Cross-polarized optical micrographs of **PAIMA20** showing a semicrystalline spherulitic texture at 22.5 °C (a), a fine grainy texture indicating a liquid crystalline mesophase at 52.2 °C (b), and the absence of any texture at 113 °C to indicate a fully isotropic polymer melt (c). The illustration shows a simplified representation of the polymers and the different phase structures.

started to melt, and the spherulitic texture completely disappeared at around 50 °C. Instead, a fine granular texture started to appear, indicating the formation of a mesophase, most probably a nematic liquid crystalline phase (see Figure 6b). When the sample was further heated, this texture became finer and then gradually disappeared. No texture was observed above 95 °C, which indicated a fully isotropic polymer melt (Figure 6c). Consequently, all of the results and conclusions from the DSC study concerning the phase behavior of **PAIMA20** were corroborated by optical microscopy observations.

As far as we know, no mesophases have been reported for poly(*n*-alkyl methacrylate)s. Hence, the liquid crystallinity of the **PAIMA $x$**  series was most probably induced by the stiff and stereoregular isobornide units, which acted as mesogenic groups. He et al. have previously reported on the use of isobornide as the core units of liquid crystalline materials.<sup>33</sup> Moreover, Zhang and co-workers have prepared and studied side-chain cholesteric liquid crystalline polymers containing aromatic mesogenic groups and isobornide as a chiral center.<sup>34</sup> However, to the best of our knowledge, the present work demonstrates for the first time the use of isobornide as a mesogenic group, giving rise to order–disorder transitions close to 100 °C. The polymers discussed up to this point were all based on 5-methacrylic 2-diester monomers. To study the influence of the isobornide substitution, we prepared and studied *r*-**PAIMA18** (based on 2-methacrylic 5-diester monomer, Scheme 2). Both polymers with  $x = 18$  showed

semicrystallinity with  $T_m$  at approximately 30 °C (Table 1). However, whereas **PAIMA18** showed a clear transition at  $T_i = 97$  °C, *r*-**PAIMA18** showed no such transition, indicating the absence of any mesophase (Figure 3). In addition, a copolymer was prepared from monomers **AIMA18** and *r*-**AIMA18** (Scheme 1) (50:50, mol/mol). This copolymer showed a crystalline melting point at 41 °C and a very small ( $\Delta H_m = 0.5$  J g<sup>−1</sup>) endothermic order–disorder transition at 69 °C, well below that of **PAIMA18** (97 °C). Hence, the small mesophase detected for the copolymer may likely be exclusively formed by 5-methacrylic diester monomer residues. In conclusion, it seemed like **PAIMA $x$**  samples based on 5-methacrylic diester monomers with sufficiently long alkanoyl chains ( $x > 12$ ) form mesophases, while the corresponding *r*-**PAIMAs** based on 2-methacrylic diester monomers were unable to form such phases. Thus, the precise substitution and orientation of the isobornide units in the polymethacrylates seem to be crucial for liquid crystallinity in these materials. This also implies that the degree of liquid crystallinity of the **PAIMA** materials can be readily controlled. Previous studies have shown that the stereochemistry of isobornide units in polymer structures can have a large influence on physicochemical properties, e.g., solubility and transition temperatures.<sup>26</sup>

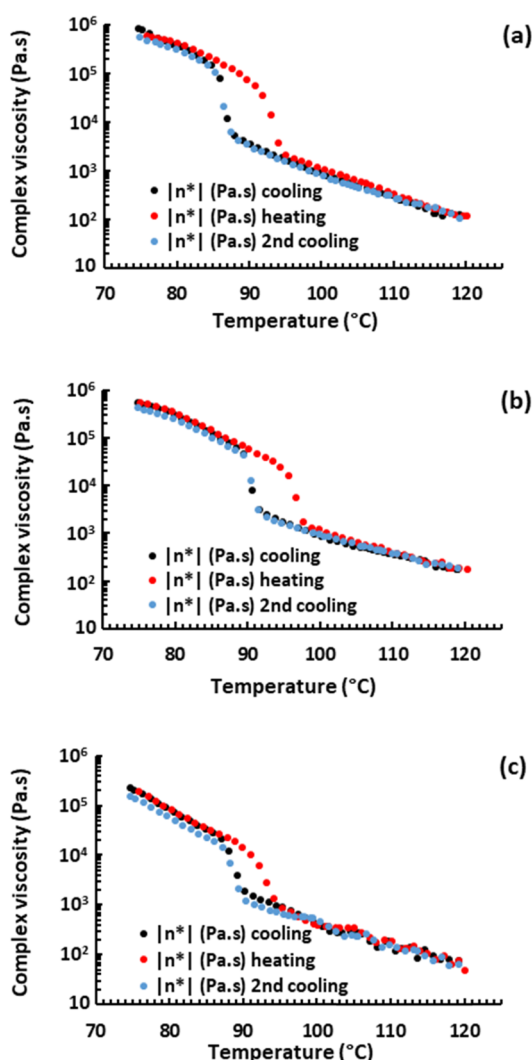
The influence of the dynamics of the order–disorder transition and its influence on the viscosity of **PAIMA16**, **PAIMA18**, and **PAIMA20** was studied by melt rheology in a plate–plate geometry. To verify that the polymers were thermally stable under the measurement conditions, a time sweep was initially performed on **PAIMA18** at 100 °C (slightly above its  $T_i$ ) for 40 min. If the sample degraded via cross-linking or chain scission reactions, the phase angle ( $\delta$ ) was expected to decrease or increase, respectively, and the shear storage modulus ( $G'$ ) would change. However, in the present case, both  $\delta$  and  $G'$  remained constant over time to indicate high stability in the melt state (see Figure 7). This finding also implied that **PAIMA18** may be melt-processed without degradation.



**Figure 7.** Variation of the melt shear storage modulus ( $G'$ ) and phase shift ( $\delta$ ) during a time sweep of **PAIMA18** at 100 °C, as measured at 1 Hz and 0.01% strain.

In the next step, temperature sweeps were carried out on **PAIMA16**, **PAIMA18**, and **PAIMA20** at 1 Hz in the temperature region around the order–disorder transition. Hence, the samples were first heated to 120 and then cooled to 75 °C at a rate of 2 °C min<sup>−1</sup>. Next, the polymers were heated to 120 °C before being cooled to 75 °C again at the same rate. Figure 8 shows the complex viscosity as a function of temperature, and the results indicate a stepwise 10–25-fold





**Figure 8.** Complex viscosity  $|\eta^*|$  of PAIMA16 (a), PAIMA18 (b), and PAIMA20 (c) as a function of temperature (0.01% strain, 1 Hz, 2 °C min<sup>-1</sup>) showing reversible stepwise changes and hysteresis effects at the order–disorder transitions.

decrease of the complex viscosity at the isotropic transition during heating, followed by a corresponding increase upon subsequent cooling. These steps were reversible and displayed a hysteresis of 4–6 °C. The results thus showed that the viscosity of the liquid crystalline mesophase was higher than that of the isotropic melt phase, most probably because of a higher state of aggregation in the former case.

## CONCLUSIONS

We have successfully prepared and systematically explored a series of 12 isosorbide-based AIMA monomers with different pendant linear alkanoyl chains having lengths spanning from C2 to C20. The monomers were synthesized in up to 36 g scale as single regioisomers through biocatalytic and chemical acylation pathways, and were subsequently polymerized by conventional radical polymerization to produce the corresponding series of PAIMA samples. As expected, the alkanoyl chain length had a profound influence on the phase behavior, transition temperatures, and properties of these materials. Hence, PAIMAs tethered with C2–C12 alkanoyl chains were fully amorphous, stiff, and transparent materials with  $T_g$  values

in the range of 107–66 °C. When the chain length exceeded C13, the polymers in the series became semicrystalline materials with  $T_m$  between –4 (C14) and 59 °C (C20). In addition, PAIMAs with C13–C20 chains formed mesophases above  $T_m$  and displayed order–disorder transition (ODT) temperatures between 75 (C13) and 94 °C (C20). The appearance of the liquid crystalline mesophases was verified by polarized optical microscopy, and melt rheology showed sharp and reversible changes in the complex viscosity at the ODT during heating–cooling cycles. These measurements also indicated that melt processing is possible without noticeable signs of degradation. Notably, *r*-PAIMA prepared from a regioisomeric C18-monomer showed semicrystallinity but no liquid crystallinity, indicating the crucial role of isosorbide stereochemistry in mesophase formation. The overall study demonstrated that the phase behavior and transition temperatures of the PAIMAs can be controlled by the choice of the alkanoyl chain length and the regiochemistry of the monomer. We envisage that the properties may be further extended and modified using cyclic or branched alkanoyl pendant groups. Hence, the PAIMA class of biobased polymers has the potential to be tailored into viable alternatives in many applications within, e.g., the plastic and coating sectors.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.biomac.0c01474>.

Detailed descriptions of monomer and polymer synthesis; solubility properties; and SEC chromatograms and NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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## Supporting Information

### Poly(alkanoyl isosorbide methacrylate)s: From Amorphous to Semi-Crystalline and Liquid Crystalline Biobased Materials

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## Synthesis of monomers

### *D*-Isosorbide 5-methacrylate **5-IMA**

**The enzymatic synthesis.** Into a 0.5 L flask were introduced: D-isosorbide (21.92 g, 0.15 mol), methyl tert-butyl ether (MTBE; 300 mL), vinyl methacrylate (33.64 g, 0.30 mol, 2 eq.), and Lipozyme RM (2.5 g; *Rhizomucor miehei* lipase immobilized on resin; product of Novozymes AS). The mixture was slowly stirred at 20 °C for 60 h. The progress of the synthesis, up to reaching the conversion rate of ca 95-99%, was monitored by TLC. The synthesis was terminated by filtering off the enzyme. Hydroquinone (HQ; 4 mg) was added and the filtrate was evaporated. The residual crude product was dissolved in EtOAc (400 mL), and washed with saturated NaHCO<sub>3</sub> solution (2x 50 mL), and brine (2x 30 mL). The collected water washings were united and extracted with EtOAc (3 x 30 mL), the extract was washed with saturated NaHCO<sub>3</sub> solution (2x 15 mL) and brine (2x 10 mL). The extracts were united, HQ (4 mg) was added and the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The oily crude product was dissolved in EtOH (95.6% EtOH/H<sub>2</sub>O; 200 mL), activated charcoal powder (2.0 g) was added and the mixture was stirred at 20 °C for 18 h. The charcoal was filtered off using a glass filter (P4) covered with a filter aid Hyflo® Super Cel® layer. An additional 2 mg of HQ was added to the solution before evaporation, which afforded 29.92 g (yield: 93.1%) of colourless target D-isosorbide 5-methacrylate. The purity of the product was >99% as determined by <sup>1</sup>H NMR spectroscopy. The product contained only traces of EtOH and HQ.

### General acylation method B1

**The chemical synthesis.** D-Isosorbide 5-methacrylate (1.0–1.4 g) in round-bottomed flask was closed with the rubber septum, purged with Ar and dissolved in dry dichloromethane (15–25 mL). Solution was cooled down on ice bath. Then acyl chloride solution (1.5–1.7 eq) in dichloromethane (2 – 5 mL) and triethylamine (1.5–2 eq) were added dropwise. After addition of the reagents, ice bath was removed and mixture was let to stir for overnight at room temperature. The completion of reaction was estimated by TLC or NMR. Reaction was quenched with saturated NaHCO<sub>3</sub> solution (15–50 mL). Organic phases were collected, dried over anhydrous MgSO<sub>4</sub> and filtrated. The solvent was evaporated and the crude product was purified by column chromatography (eluent: 10% EtOAc in petroleum ether). Fractions were collected and concentrated under reduced pressure to obtain the target product. Liquid products were stored in solution at 2–6 °C with a small amount of hydroquinone (1–2 mg).

### *D*-Isosorbide-2-Acetate-5-Methacrylate **AIMA2**

**The enzymatic synthesis.** D-Isosorbide 5-methacrylate (27.85 g, 0.13 mol) that contains a trace amount of HQ was dissolved in EtOAc (250 mL). Vinyl acetate (44.77 g; 48.1 mL; 0.52 mol; 4 eq.) was added followed by Novozym® 435 (2.5 g). The mixture was stirred slowly at 45 °C for 96 hours, until the conversion was complete by TLC. The reaction was terminated by filtering off the enzyme using a filter aid Hyflo® Super Cel® layer on a glass filter (P4). The filtrate was evaporated on a rotary evaporator; the residual substance was dissolved in EtOAc (350 mL) and washed with saturated NaHCO<sub>3</sub> solution (3x 30 mL) and brine (2x 30 mL). The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and HQ (4 mg) was added. The solution was evaporated and the target diester was dissolved in EtOH (200 mL). Activated charcoal powder (2.0 g) was added to the solution and the mixture gained was stirred for 18 hours. Then the charcoal was filtered off using a glass filter (P4) covered with a layer of filter aid Hyflo® Super Cel®. An additional portion (2 mg) of HQ was added and EtOH was evaporated on a rotary evaporator. The target diester was obtained (32.75 g; yield: 98.3%) as a chemically highly pure (>99%) product.

This compound has been characterized in previous publication.<sup>1</sup>

#### *D-Isosorbide-2-Butanoate-5-Methacrylate AIMA4*

**The enzymatic synthesis.** Isosorbide 5-methacrylate (27.85 g, 0.13 mol) that contains a trace amount of HQ was dissolved in acetonitrile (250 mL). Vinyl butyrate (44.5 g; 49.5 mL; 0.39 mol; 3 eq.) was added followed by Novozym® 435 (3.0 g). The mixture was stirred slowly at 45 °C for 120 hours, until the conversion was complete by TLC. The reaction was terminated by filtering off the enzyme using a glass filter (P4) covered with a layer of filter aid Hyflo® Super Cel®. The filtrate was evaporated on a rotary evaporator; the residual substance was dissolved in EtOAc (350 mL) and washed with saturated NaHCO<sub>3</sub> solution (3x 30 mL) and brine (2x 30 mL). The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and HQ (4 mg) was added. The solution was evaporated and the residue was dissolved in EtOH (200 mL). Activated charcoal powder (2.0 g) was added to the solution and the mixture was stirred for 18 hours. Then the charcoal was filtered off using a glass filter (P4) covered with a layer of filter aid Hyflo® Super Cel®. An additional portion (2 mg) of HQ was added and EtOH was evaporated on a rotary evaporator; the flask was additionally evacuated via a cold trap (-78 °C) in order to eliminate traces of EtOH. The target diester was obtained in near-by quantitative yield (36.29 g; yield: 98.3%) and as a chemically highly pure (>99%) product.

#### *D-Isosorbide-2-Butanoate-5-Methacrylate AIMA4*

**The chemical synthesis.** Isosorbide 5-methacrylate (1.714 g; 8 mmol) was dissolved in acetonitrile (20 mL), triethylamine (1.42 g; 1.95 mL; 14 mmol) was added on stirring at RT, followed by butyryl chloride (1.28 g; 1.25 mL; 12 mmol). The mixture was stirred at RT for 12 hours; the completion of reaction was estimated by TLC. Methanol (0.2 mL; 5 mmol) was added and stirring was continued for additional 4 hours. Reaction mixture was evaporated, the residue was dissolved in EtOAc (80 mL) and washed with sat. NaHCO<sub>3</sub> (2x25 mL) and brine (2x15 mL). EtOAc solution was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, hydroquinone (2 mg) was added and the solvent was evaporated. The product was purified by flash-chromatography (eluent PE/EtOAc 10/1.5) to afford homogeneous isosorbide 2-butyrate-5-methacrylate (2.177 g; yield: 95.7%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>5(x)</sub>, 1H), 5.20 (m, CH<sub>2(n)</sub>, 1H), 4.88 (m, CH<sub>4(x)</sub>, 1H), 4.49 (m, CH<sub>3(x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.29 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.63 (m, CH<sub>2(A3)</sub>, 2H), 0.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A4)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.69 (CO<sub>(A1)</sub>), 166.64 (CO<sub>(7)</sub>), 135.64 (C<sub>(8)</sub>), 126.32 (CH<sub>2(9)</sub>), 86.03 (CH<sub>(3)</sub>), 80.86 (CH<sub>(4)</sub>), 77.78 (CH<sub>(2)</sub>), 74.10 (CH<sub>(5)</sub>), 73.45 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 35.98 (CH<sub>2(A2)</sub>), 18.32 (CH<sub>2(A3)</sub>), 18.27 (CH<sub>3(10)</sub>), 13.56 (CH<sub>3(A4)</sub>).

[α]<sub>D</sub><sup>20</sup> +82.4 (c 0.19 M, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.32 (eluent: petroleum ether/EtOAc 10/2). HRMS (ESI): calcd for C<sub>14</sub>H<sub>20</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 285.1333, found 285.1329

#### *D-Isosorbide-2-Hexanoate-5-Methacrylate AIMA6*

**The chemical synthesis.** Isosorbide 5-methacrylate (1.714 g; 8 mmol) was dissolved in acetonitrile (30 mL), triethylamine (1.42 g; 1.95 mL; 14 mmol) was added on stirring at RT followed by caproyl chloride (1.104 g; 1.14 mL; 8.2 mmol). The mixture was stirred at RT for 12 hours; the completion of reaction was estimated by TLC. Methanol (64.08 mg; 0.081 mL;

<sup>1</sup> Matt, L.; Parve, J.; Parve, O.; Pehk, T.; Pham, T. H.; Liblikas, I.; Vares, L.; Jannasch, P. Enzymatic Synthesis and Polymerization of Isosorbide-Based Monomethacrylates for High- Tg Plastics. *ACS Sustain. Chem. Eng.* **2018**, 6 (12), 17382–17390. <https://doi.org/10.1021/acssuschemeng.8b05074>

2 mmol) was added and stirring was continued for additional 2 hours. The reaction mixture was evaporated, EtOAc (80 mL) added to the residue and the solution washed with sat. NaHCO<sub>3</sub> (2x15 mL) and brine (2x15 mL). The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated. The product was purified by flash chromatography over silica gel (eluent: PE/EtOAc 10/1.2) to afford 2.309 g of the target compound (92.4%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2E</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2Z</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.93 (m, CH<sub>2(6n)</sub>, 1H), 2.31 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.29 (m, CH<sub>2(A4-A5)</sub>, 4H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(6a)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.91 (CO<sub>(A1)</sub>), 166.66 (CO<sub>(7)</sub>), 135.64 (C<sub>(8)</sub>), 126.34 (CH<sub>2(9)</sub>), 86.04 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.15 (CH<sub>2(A2)</sub>), 31.20 (CH<sub>2(A3)</sub>), 24.51 (CH<sub>2(4A)</sub>), 22.25 (CH<sub>2(5A)</sub>), 18.30 (CH<sub>3(10)</sub>), 13.87 (CH<sub>3(A6)</sub>). [α]<sub>D</sub><sup>20</sup> +81.2 (c 50 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.55 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for C<sub>16</sub>H<sub>24</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 313.1646, found 313.1644

#### *D-Isosorbide-2-Octanoate-5-Methacrylate AIMA8*

**The chemical synthesis.** Isosorbide 5-methacrylate (1.714 g; 8 mmol) was dissolved in acetonitrile (30 mL), triethylamine (1.42 g; 1.95 mL; 14 mmol) was added on stirring at RT followed by capryloyl chloride (1.334 g; 1.42 mL; 8.2 mmol).

The mixture was stirred at RT for 14 hours; methanol (64 mg; 0.081 mL; 2 mmol) was added and stirring was continued for an additional hour. Reaction mixture was evaporated, EtOAc (80 mL) added to the residue and the solution was washed with sat. NaHCO<sub>3</sub> and brine (both: 2x15 mL). The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated. The product was purified by flash chromatography over silica gel (eluent: PE/EtOAc 10/1) to afford 2.552 g of the target diester (yield: 93.7%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A7)</sub>, 8H), 0.87 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A8)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.89 (CO<sub>(A1)</sub>), 166.65 (CO<sub>(7)</sub>), 135.66 (C<sub>(8)</sub>), 126.30 (CH<sub>2(9)</sub>), 86.05 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.14 (CH<sub>2(A2)</sub>), 31.59 (CH<sub>2(3A)</sub>), 28.89 (CH<sub>2(4A)</sub>), 28.86 (CH<sub>2(5A)</sub>), 24.72 (CH<sub>2(6A)</sub>), 22.60 (CH<sub>2(7A)</sub>), 18.32 (CH<sub>3(10)</sub>), 14.07 (CH<sub>3(8A)</sub>).

[α]<sub>D</sub><sup>20</sup> +60.1 (c 77 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.61 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for C<sub>18</sub>H<sub>28</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 341.1959, found 341.1952

#### *D-Isosorbide-2-Decanoate-5-Methacrylate AIMA10*

**The enzymatic synthesis.** Isosorbide 5-methacrylate (1.714 g; 8 mmol) was dissolved in acetonitrile (20 mL), vinyl decanoate (2.38 g; 2.7 mL; 12 mmol) and Novozym 435 (0.2 g) were added. After 48 h stirring at 40-45 °C an additional amount of vinyl decanoate (1.19 g; 1.35 mL; 6 mmol) was added. Stirring was continued for additional 48 hours, the completion of reaction was estimated by TLC. The enzyme was filtered off and the filtrate evaporated. The residue was dissolved in EtOAc (80 mL) and washed with sat. NaHCO<sub>3</sub> and brine (both: 2x15 mL). The product was further purified by flash chromatography over silica gel (eluent: PE/EtOAc 10/0.8) to afford 2.572 g of the target diester (87.2%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m,

CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A9)</sub>, 12H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A10)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.87 (CO<sub>(A1)</sub>), 166.61 (CO<sub>(7)</sub>), 135.61 (C<sub>(8)</sub>), 126.28 (CH<sub>2(9)</sub>), 85.99 (CH<sub>(3)</sub>), 80.84 (CH<sub>(4)</sub>), 77.75 (CH<sub>(2)</sub>), 74.07 (CH<sub>(5)</sub>), 73.41 (CH<sub>2(1)</sub>), 70.57 (CH<sub>2(6)</sub>), 34.11 (CH<sub>2(A2)</sub>), 33.82 (CH<sub>2(A3)</sub>), 29.32 (CH<sub>2(A4)</sub>), 29.18 (CH<sub>2(A5)</sub>), 29.17 (CH<sub>2(A6)</sub>), 29.01 (CH<sub>2(A7)</sub>), 24.78 (CH<sub>2(A8)</sub>), 22.60 (CH<sub>2(A9)</sub>), 18.21 (CH<sub>3(10)</sub>), 14.03 (CH<sub>3(A10)</sub>). [α]<sub>D</sub><sup>20</sup> +66.9 (c 18 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.61 (eluent: 20% EtOAc/PE). HRMS (ESI): calcd for C<sub>20</sub>H<sub>42</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 369.2272, found 369.2255

#### *D-Isosorbide-2-Undecanoate-5-Methacrylate AIMA11*

**The chemical synthesis.** This monomer was synthesized according to general method B1. The product (1.603 g) was obtained in the form of transparent viscous liquid (yield: 67.0 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>= 1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A10)</sub>, 14H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A11)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.89 (CO<sub>(A1)</sub>), 166.65 (CO<sub>(7)</sub>), 135.66 (C<sub>(8)</sub>), 126.30 (CH<sub>2(9)</sub>), 86.05 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.10 (CH<sub>2(A2)</sub>), 31.80 (CH<sub>2(A3)</sub>), 29.46 (CH<sub>2(A4)</sub>), 29.35 (CH<sub>2(A5)</sub>), 29.21 (CH<sub>2(A6)</sub>), 29.14 (CH<sub>2(A7)</sub>), 28.99 (CH<sub>2(A8)</sub>), 24.77 (CH<sub>2(A9)</sub>), 22.59 (CH<sub>2(A11)</sub>), 18.21 (CH<sub>3(9)</sub>), 14.02 (CH<sub>3(A11)</sub>).

[α]<sub>D</sub><sup>20</sup> +61.1 (c 44 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.61 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for C<sub>21</sub>H<sub>34</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 383.2428, found 383.2425.

#### *D-Isosorbide-2-Tridecanoate-5-Methacrylate AIMA13*

**The chemical synthesis.** This monomer was synthesized according to general method B1. The product (1.556 g) was obtained in the form of a transparent viscous liquid (isolated yield: 47.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>= 1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(3a)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(4-12a)</sub>, 18H), 0.86 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(13a)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.89 (CO<sub>(A1)</sub>), 166.65 (CO<sub>(7)</sub>), 135.66 (C<sub>(8)</sub>), 126.30 (CH<sub>(9)</sub>), 86.05 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.16 (CH<sub>2(A2)</sub>), 31.91 (CH<sub>2(A3)</sub>), 29.65 (CH<sub>2(A4)</sub>), 29.56 (CH<sub>2(A5)</sub>), 29.47+ (CH<sub>2(A6)</sub>), 29.41 (CH<sub>2(A7)</sub>), 29.34 (CH<sub>2(A8)</sub>), 29.21 (CH<sub>2(A9)</sub>), 28.90 (CH<sub>2(A10)</sub>), 24.68 (CH<sub>2(A11)</sub>), 22.52 (CH<sub>2(A12)</sub>), 18.13 (CH<sub>3(10)</sub>), 13.94 (CH<sub>3(A13)</sub>).

[α]<sub>D</sub><sup>20</sup> +53.5 (c 69 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.61 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for C<sub>23</sub>H<sub>38</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 411.27412, found 411.27488.

#### *D-Isosorbide-2-Tetradecanoate-5-Methacrylate AIMA14*

**The enzymatic synthesis.** Isosorbide 5-methacrylate (1.285 g; 6 mmol) was dissolved in acetonitrile (10 mL), petroleum ether (10 mL) was added followed by vinyl myristate (3.05 g; 3.51 mL; 12 mmol) and Novozym 435 (0.2 g). The mixture was stirred slowly at 40-45 °C for 120 hours. After that the mixture was filtered and the solvent was evaporated. Acetonitrile (40 mL) was added to the residue; after careful shaking the mixture was filtered and the



solvent was evaporated. The product was purified by short column chromatography over silica gel (eluent: PE/EtOAc 10/0.5) to afford 2.105 g of the target compound (yield: 82.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A13)</sub>, 20H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A14)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.89 (CO<sub>(A1)</sub>), 166.65 (CO<sub>(7)</sub>), 135.66 (C<sub>(8)</sub>), 126.30 (CH<sub>2(9)</sub>), 86.05 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.16 (CH<sub>2(A2)</sub>), 31.91 (CH<sub>2(A3)</sub>), 29.65 (CH<sub>2(A4)</sub>), 29.60-29.63 (CH<sub>2(A5-A6)</sub>), 29.56 (CH<sub>2(A7)</sub>), 29.41 (CH<sub>2(A8)</sub>), 29.34 (CH<sub>2(A9)</sub>), 29.21 (CH<sub>2(A10)</sub>), 29.06 (CH<sub>2(A11)</sub>), 24.84 (CH<sub>2(A12)</sub>), 22.68 (CH<sub>2(A13)</sub>), 18.28 (CH<sub>3(10)</sub>), 14.10 (CH<sub>3(A14)</sub>). [α]<sub>D</sub><sup>20</sup> +56.6 (c 13 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.61 (eluent: 20% EtOAc/PE). HRMS (ESI): calcd for C<sub>24</sub>H<sub>40</sub>O<sub>6</sub>Na [M + Na]<sup>+</sup> 447.2717, found 447.2695.

#### *D-Isosorbide-2-Hexadecanoate-5-Methacrylate AIMA16*

**The enzymatic synthesis.** Isosorbide 5-methacrylate (1.285 g; 6 mmol) was dissolved in acetonitrile (10 mL), petroleum ether (10 mL) was added, followed by vinyl palmitate (3.39 g; 12 mmol) and Novozym 435 (0.2 g). The mixture was slowly stirred at 40-45°C for 120 hours. Then, the mixture was filtered and evaporated. Acetonitrile (40 mL) was added to the residue; after careful shaking the mixture was filtered and the solvent was evaporated. The product was purified by short column chromatography over silica gel (eluent: PE/EtOAc 10/0.5) to afford 2.159 g of the target compound (yield: 79.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A15)</sub>, 24H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A16)</sub>, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 172.89 (CO<sub>(A1)</sub>), 166.65 (CO<sub>(7)</sub>), 135.66 (C<sub>(8)</sub>), 126.30 (CH<sub>2(9)</sub>), 86.05 (CH<sub>(3)</sub>), 80.88 (CH<sub>(4)</sub>), 77.81 (CH<sub>(2)</sub>), 74.11 (CH<sub>(5)</sub>), 73.46 (CH<sub>2(1)</sub>), 70.61 (CH<sub>2(6)</sub>), 34.16 (CH<sub>2(A2)</sub>), 31.91 (CH<sub>2(A3)</sub>), 29.65 (CH<sub>2(A4)</sub>), 29.60-29.63 (CH<sub>2(A5-A8)</sub>), 29.56 (CH<sub>2(A9)</sub>), 29.41 (CH<sub>2(A10)</sub>), 29.34 (CH<sub>2(A11)</sub>), 29.21 (CH<sub>2(A12)</sub>), 29.06 (CH<sub>2(A13)</sub>), 24.84 (CH<sub>2(A14)</sub>), 22.68 (CH<sub>2(A15)</sub>), 18.28 (CH<sub>3(10)</sub>), 14.10 (CH<sub>3(A16)</sub>). [α]<sub>D</sub><sup>20</sup> +48.6 (c 21 mM, CHCl<sub>3</sub>). TLC: R<sub>f</sub> = 0.62 (eluent: 20% EtOAc/PE). HRMS (ESI): calcd for C<sub>26</sub>H<sub>44</sub>O<sub>6</sub>H [M + H]<sup>+</sup> 453.3211, found 453.3189

#### *D-Isosorbide-2-Hexadecanoate-5-Methacrylate AIMA16*

**The chemical synthesis.** This monomer was synthesized according to general method B1. The product (2.17 g) was gained in the form of white crystals (yield: 77.7 %).

#### *D-Isosorbide-2-Octadecanoate-5-Methacrylate AIMA18*

**The chemical synthesis.** This monomer was synthesized according to general method B1. The product (1.75 g) was obtained in the form of white crystals (yield: 57.3 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.16 (dq, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>2(9E)</sub>, 1H), 5.62 (dd, <sup>2</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=1.5, CH<sub>2(9Z)</sub>, 1H), 5.21 (m, CH<sub>(5x)</sub>, 1H), 5.20 (m, CH<sub>(2n)</sub>, 1H), 4.88 (m, CH<sub>(4x)</sub>, 1H), 4.48 (m, CH<sub>(3x)</sub>, 1H), 3.97 (m, CH<sub>2(1n)</sub>, 1H), 3.96 (m, CH<sub>2(6x)</sub>, 1H), 3.95 (m, CH<sub>2(1x)</sub>, 1H), 3.89 (m, CH<sub>2(6n)</sub>, 1H), 2.30 (m, CH<sub>2(A2)</sub>, 2H), 1.96 (dd, <sup>4</sup>J<sub>HH</sub>=1.5 Hz, <sup>4</sup>J<sub>HH</sub>=0.9 Hz, CH<sub>3(10)</sub>, 3H), 1.59 (m, CH<sub>2(A3)</sub>, 2H), 1.23-1.26 (m, CH<sub>2(A4-A17)</sub>, 28H), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3(A18)</sub>,

3H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ )  $\delta$ : 172.89 ( $\text{CO}_{(\text{A}1)}$ ), 166.65 ( $\text{CO}_{(7)}$ ), 135.66 ( $\text{C}_{(8)}$ ), 126.30 ( $\text{CH}_{2(9)}$ ), 86.05 ( $\text{CH}_{(3)}$ ), 80.88 ( $\text{CH}_{(4)}$ ), 77.81 ( $\text{CH}_{(2)}$ ), 74.11 ( $\text{CH}_{(5)}$ ), 73.46 ( $\text{CH}_{2(1)}$ ), 70.61 ( $\text{CH}_{2(6)}$ ), 34.16 ( $\text{CH}_{2(\text{A}2)}$ ), 31.91 ( $\text{CH}_{2(\text{A}3)}$ ), 29.6-29.7 ( $\text{CH}_{2(\text{A}4-\text{A}10)}$ ), 29.58 ( $\text{CH}_{2(\text{A}11)}$ ), 29.42 ( $\text{CH}_{2(\text{A}12)}$ ), 29.34 ( $\text{CH}_{2(\text{A}13)}$ ), 29.21 ( $\text{CH}_{2(\text{A}14)}$ ), 29.06 ( $\text{CH}_{2(\text{A}15)}$ ), 24.84 ( $\text{CH}_{2(\text{A}16)}$ ), 22.68 ( $\text{CH}_{2(\text{A}17)}$ ), 18.28 ( $\text{CH}_{3(10)}$ ), 14.10 ( $\text{CH}_{3(\text{A}18)}$ ).

$[\alpha]^{20}_{\text{D}}$  +47.9 (*c* 80 mM,  $\text{CHCl}_3$ ). TLC:  $R_f$  = 0.63 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{48}\text{O}_6\text{H} [\text{M} + \text{H}]^+$  481.3524, found 481.3504

#### *D*-Isosorbide-5-Octadecanoate-2-Methacrylate **r-AIMA18**

**The chemical synthesis.** This monomer was synthesized according to general method B1, except *D*-Isosorbide 2-methacrylate was used as starting material. The synthesis afforded 0.21 g of **r-AIMA18** as white crystals (yield: 49.2%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.07 (dq,  $^2J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=0.9$  Hz,  $\text{CH}_{2(9\text{E})}$ , 1H), 5.56 (dd,  $^2J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=1.5$ ,  $\text{CH}_{2(9\text{Z})}$ , 1H), 5.21 (m,  $\text{CH}_{(2\text{n})}$ , 1H), 5.11 (m,  $\text{CH}_{(5\text{x})}$ , 1H), 4.82 (m,  $\text{CH}_{(4\text{x})}$ , 1H), 4.49 (m,  $\text{CH}_{(3\text{x})}$ , 1H), 3.97 (m,  $\text{CH}_{2(1\text{n})}$ , 1H), 3.96 (m,  $\text{CH}_{2(1\text{x})}$ , 1H), 3.91 (m,  $\text{CH}_{2(6\text{x})}$ , 1H), 3.78 (m,  $\text{CH}_{2(6\text{n})}$ , 1H), 2.32 (m,  $\text{CH}_{2(\text{A}2)}$ , 2H), 1.88 (dd,  $^4J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=0.9$  Hz,  $\text{CH}_{3(10)}$ , 3H), 1.60 (m,  $\text{CH}_{2(\text{A}3)}$ , 2H), 1.20-1.23 (m,  $\text{CH}_{2(\text{A}4-\text{A}17)}$ , 18H), 0.83 (t,  $^3J_{\text{HH}}=7.1$  Hz,  $\text{CH}_{3(\text{A}18)}$ , 3H).

$^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.06 ( $\text{CO}_{(\text{A}1)}$ ), 166.16 ( $\text{CO}_{(7)}$ ), 135.58 ( $\text{C}_{(8)}$ ), 126.35 ( $\text{CH}_{2(9)}$ ), 85.79 ( $\text{CH}_{(3)}$ ), 80.64 ( $\text{CH}_{(4)}$ ), 78.14 ( $\text{CH}_{(2)}$ ), 73.66 ( $\text{CH}_{(5)}$ ), 73.23 ( $\text{CH}_{2(1)}$ ), 70.21 ( $\text{CH}_{2(6)}$ ), 33.82 ( $\text{CH}_{2(\text{A}2)}$ ), 31.81 ( $\text{CH}_{2(\text{A}3)}$ ), 29.5-29.6 ( $\text{CH}_{2(\text{A}4-\text{A}10)}$ ), 29.45 ( $\text{CH}_{2(\text{A}11)}$ ), 29.33 ( $\text{CH}_{2(\text{A}12)}$ ), 29.25 ( $\text{CH}_{2(\text{A}13)}$ ), 29.14 ( $\text{CH}_{2(\text{A}14)}$ ), 28.95 ( $\text{CH}_{2(\text{A}15)}$ ), 24.76 ( $\text{CH}_{2(\text{A}16)}$ ), 22.57 ( $\text{CH}_{2(\text{A}17)}$ ), 18.03 ( $\text{CH}_{3(10)}$ ), 14.06 ( $\text{CH}_{3(\text{A}18)}$ ).

$[\alpha]^{20}_{\text{D}}$  +59.7 (*c* 8 mM,  $\text{CHCl}_3$ ). TLC:  $R_f$  = 0.62 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{48}\text{O}_6\text{H} [\text{M} + \text{H}]^+$  481.3524, found 481.3507.

#### *D*-Isosorbide-2-Eicosanoate-5-Methacrylate **AIMA20**

**The chemical synthesis.** This monomer was synthesized by general method B1. Reaction afforded 2.28 g of **AIMA20** as white crystals (yield: 71.0 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.16 (dq,  $^2J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=0.9$  Hz,  $\text{CH}_{2(9\text{E})}$ , 1H), 5.62 (dd,  $^2J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=1.5$ ,  $\text{CH}_{2(9\text{Z})}$ , 1H), 5.21 (m,  $\text{CH}_{(5\text{x})}$ , 1H), 5.20 (m,  $\text{CH}_{(2\text{n})}$ , 1H), 4.88 (m,  $\text{CH}_{(4\text{x})}$ , 1H), 4.48 (m,  $\text{CH}_{(3\text{x})}$ , 1H), 3.97 (m,  $\text{CH}_{2(1\text{n})}$ , 1H), 3.96 (m,  $\text{CH}_{2(6\text{x})}$ , 1H), 3.95 (m,  $\text{CH}_{2(1\text{x})}$ , 1H), 3.89 (m,  $\text{CH}_{2(6\text{n})}$ , 1H), 2.30 (m,  $\text{CH}_{2(\text{A}2)}$ , 2H), 1.96 (dd,  $^4J_{\text{HH}}=1.5$  Hz,  $^4J_{\text{HH}}=0.9$  Hz,  $\text{CH}_{3(10)}$ , 3H), 1.59 (m,  $\text{CH}_{2(\text{A}3)}$ , 2H), 1.23-1.26 (m,  $\text{CH}_{2(\text{A}4-\text{A}19)}$ , 30H), 0.87 (t,  $^3J_{\text{HH}}=7.0$  Hz,  $\text{CH}_{3(\text{A}20)}$ , 3H).

$^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ )  $\delta$ : 172.89 ( $\text{CO}_{(\text{A}1)}$ ), 166.65 ( $\text{CO}_{(7)}$ ), 135.66 ( $\text{C}_{(8)}$ ), 126.30 ( $\text{CH}_{2(9)}$ ), 86.05 ( $\text{CH}_{(3)}$ ), 80.88 ( $\text{CH}_{(4)}$ ), 77.81 ( $\text{CH}_{(2)}$ ), 74.11 ( $\text{CH}_{(5)}$ ), 73.46 ( $\text{CH}_{2(1)}$ ), 70.61 ( $\text{CH}_{2(6)}$ ), 34.16 ( $\text{CH}_{2(\text{A}2)}$ ), 31.91 ( $\text{CH}_{2(\text{A}3)}$ ), 29.6-29.7 ( $\text{CH}_{2(\text{A}4-\text{A}12)}$ ), 29.58 ( $\text{CH}_{2(\text{A}13)}$ ), 29.42 ( $\text{CH}_{2(\text{A}14)}$ ), 29.34 ( $\text{CH}_{2(\text{A}15)}$ ), 29.21 ( $\text{CH}_{2(\text{A}16)}$ ), 29.06 ( $\text{CH}_{2(\text{A}17)}$ ), 24.83 ( $\text{CH}_{2(\text{A}18)}$ ), 22.67 ( $\text{CH}_{2(\text{A}19)}$ ), 18.28 ( $\text{CH}_{3(10)}$ ), 14.10 ( $\text{CH}_{3(\text{A}20)}$ ).

$[\alpha]^{20}_{\text{D}}$  +52.6 (*c* 33 mM,  $\text{CHCl}_3$ ). TLC:  $R_f$  = 0.63 (eluent: 20% EtOAc/PE).

HRMS (ESI): calcd for  $\text{C}_{30}\text{H}_{56}\text{O}_6\text{Na} [\text{M} + \text{Na}]^+$  531.3656, found 531.3633.

## Synthesis of polymers

**Inhibitor removal prior polymerization.** It was crucial to completely remove the stabilizers (HQ or HQMME) prior the polymerization to ensure the high conversion and repeatability. In case of **AIMA2-AIMA10**, the monomers dissolved in EtOAc were washed few times with 1-2% aqueous NaOH. The Na-salt of HQ and HQMME have a purple color, which made it easy to monitor the inhibitor removal. However, for monomers with longer alkyl tail (**AIMA11-AIMA18**), a short silica column was used as the wash with 1% NaOH caused some hydrolysis of alkyl ester. Due to higher polarity, HQ was easier to remove compared to HQMME. For **AIMA20**, no inhibitor was used.

### General Procedure for Free Radical Polymerization of Isosorbide methacrylates.

Isosorbide monomethacrylate (0.1–2.3 g) was dissolved in EtOAc (1–23 mL) and placed into the pressure tube depending on the volume of the reaction mixture (4; 8; 30 mL). Thereafter was added azobisisobutyronitril solution in EtOAc (AIBN; 0.5 mol % in 50–100  $\mu$ L EtOAc). The mixture was sparged with Ar for 30-60 minutes, a pressure tube was closed tightly and placed into a preheated oven at 63 °C for 24 hours. After the reaction, the crude mixture was let to cool down, small drop from the mixture was taken for the NMR analysis in CDCl<sub>3</sub> to determine the conversion. Polymer was precipitated in the MeOH (0.1–1 L), filtrated using P3 glass-filter and washed 1-2 times with small amount of MeOH to remove traces of the monomer. Polymer, as white powder, was carefully collected from the glass-filter and dried under reduced pressure. The dried product was characterized by NMR, SEC, DSC and TGA.

#### *Polymer of D-Isosorbide-2-Butanoate-5-Methacrylate* **PAIMA2**

**PAIMA2:** 0.73 g, white powder (conversion: 85%, isolated yield: 66.0%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.14 (bm, CH<sub>(5x)</sub>), 4.98 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.70 (bm, CH<sub>2(6n)</sub>), 2.06 (bm, CH<sub>3(A2)</sub>), 1.91 (bm, CH<sub>2(9)</sub>), 1.02 (bm, CH<sub>3(10)</sub>).

#### *Polymer of D-Isosorbide-2-Butanoate-5-Methacrylate* **PAIMA4**

**PAIMA4:** 0.78 g, white powder (conversion: 84%, isolated yield: 65.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.18 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.73 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.72 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.63 (bm, CH<sub>2(A3)</sub>), 1.12 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.93 (bm, CH<sub>3(A4)</sub>).

#### *Polymer of D-Isosorbide-2-Hexanoate-5-Methacrylate* **PAIMA6**

**PAIMA6:** 113 mg, white powder (conversion: 63%, isolated yield: 51.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.26-1.25 (bm, CH<sub>2(A4-A5)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.89 (bm, CH<sub>3(A6)</sub>).

#### *Polymer of D-Isosorbide-2-Octanoate-5-Methacrylate* **PAIMA8**

**PAIMA8:** 78 mg, white powder (conversion 76%, isolated yield 60.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>),

2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.28-1.34 (bm, CH<sub>2(A4-A7)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.88 (bm, CH<sub>3(A8)</sub>).

*Polymer of D-Isosorbide-2-Decanoate-5-Methacrylate* **PAIMA10**

**PAIMA10:** 115 mg, white powder, (conversion 56%, isolated yield 51.1%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.28-1.34 (bm, CH<sub>2(A4-A9)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.88 (bm, CH<sub>3(A10)</sub>).

*Polymer of D-Isosorbide-2-Undecanoate-5-Methacrylate* **PAIMA11**

**PAIMA11:** 0.51 g, white powder (conversion 87%, isolated yield 67.9%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.21-1.28 (bm, CH<sub>2(A4-A11)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (bm, CH<sub>3(A11)</sub>).

*Polymer of D-Isosorbide-2-Tridecanoate-5-Methacrylate* **PAIMA13**

**PAIMA13:** 76 mg, white (conversion 81%, isolated yield 53.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.21-1.28 (bm, CH<sub>2(A4-A12)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (bm, CH<sub>3(A13)</sub>).

*Polymer of D-Isosorbide-2-Tetradecanoate-5-Methacrylate* **PAIMA14**

**PAIMA14:** 160 mg, white powder (conversion: 82%, isolated yield: 66.4%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.21-1.28 (bm, CH<sub>2(A4-A13)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (bm, CH<sub>3(A14)</sub>).

*Polymer of D-Isosorbide-2-Hexadecanoate-5-Methacrylate* **PAIMA16**

**PAIMA16:** 161 mg, white powder (conversion: 82%, isolated yield: 71.6 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.21-1.28 (bm, CH<sub>2(A4-A15)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (bm, CH<sub>3(A16)</sub>).

*Polymer of D-Isosorbide-2-Octadecanoate-5-Methacrylate* **PAIMA18**

**PAIMA18:** 0.52 g, white powder (conversion 75%, isolated yield 61.4%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.28-1.34 (bm, CH<sub>2(A4-A17)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.88 (bm, CH<sub>3(A18)</sub>).

*Polymer of D-Isosorbide-5-Octadecanoate-2-Methacrylate* **r-PAIMA18**

**r-PAIMA18:** 71 mg, white powder (conversion 58%, isolated yield 39.7%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.21 (bm, CH<sub>(2n)</sub>), 5.04 (bm, CH<sub>(5x)</sub>), 4.86 (bm, CH<sub>(4x)</sub>), 4.51 (bm, CH<sub>(3x)</sub>), 3.97 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(1x)</sub>), 3.92 (bm, CH<sub>2(6x)</sub>), 3.82 (bm, CH<sub>2(6n)</sub>),



2.39 (bm, CH<sub>2(A2)</sub>), 1.66 (bm, CH<sub>2(A3)</sub>), 1.21-1.30 (bm, CH<sub>2(A4-A17)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.91 (bm, CH<sub>3(A18)</sub>).

*Copolymer of D-Isosorbide-2-Octadecanoate-5-Methacrylate and D-Isosorbide-5-Octadecanoate-2-Methacrylate P(AIMA18-co-r-AIMA18)*

Standard polymerization procedure was used, except *r*-PAIMA18 and PAIMA18 regioisomers in 1:1 ratio were used as monomers.

**P(AIMA18-co-r-PAIMA18)**: 160 mg, white powder (conversion 75%, isolated yield: 64.3 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.30; 5.18, 5.01, 4.72, 4.46, 3.9-4.0, 3.73-3.77, 2.30-2.35, 1.60, 1.20-1.35 (CH<sub>2(A4-A18)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (CH<sub>3(A18)</sub>)

*Polymer of D-Isosorbide-2-Eicosanoate-5-Methacrylate PAIMA20*

**PAIMA20**: 1.68 g, white powder (conversion 81%, isolated yield 73.9 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.27 (bm, CH<sub>(5x)</sub>), 4.99 (bm, CH<sub>(2n)</sub>), 4.72 (bm, CH<sub>(4x)</sub>), 4.46 (bm, CH<sub>(3x)</sub>), 3.95 (bm, CH<sub>2(1n)</sub>), 3.94 (bm, CH<sub>2(6x)</sub>), 3.92 (bm, CH<sub>2(1x)</sub>), 3.73 (bm, CH<sub>2(6n)</sub>), 2.30 (bm, CH<sub>2(A2)</sub>), 1.59 (bm, CH<sub>2(A3)</sub>), 1.21-1.28 (bm, CH<sub>2(A4-A19)</sub>), 1.10 (bm, CH<sub>2(9)</sub>), 1.01 (bm, CH<sub>3(10)</sub>), 0.87 (bm, CH<sub>3(A20)</sub>).

## Evaluation of Solubility of AIMA's and PAIMA's

The solubility of the different isosorbide methacrylate monomers and polymers were determined by mixing small samples (about 5 mg) with a range of selected solvents (1 mL). The mixture was stirred up to 30 minutes. The results of the solubility test were divided into two categories, soluble and insoluble, based on visual inspection. If the samples were found to be completely dissolved, they considered as soluble; if not, they were considered as insoluble.

**Table S1.** Monomer solubility<sup>a</sup>

Monomer	H <sub>2</sub> O δ = 48 (s)	MeOH δ = 43 (s)	<i>n</i> -BuOH δ = 23 (s)	DMSO δ = 25 (m)	THF δ = 19 (m)	Et <sub>2</sub> O δ = 15 (m)	ACN δ = 24 (p)	CHCl <sub>3</sub> δ = 19 (p)	toluene δ = 18 (p)	EtOAc δ = 19 (p)	Physical state <sup>b</sup>
5-IMA	+	+	+	+	+	+	+	+	+	+	l
AIMA2	-	+	+	+	+	+	+	+	+	+	l
AIMA4	-	+	+	+	-	-	+	+	+	+	l
AIMA6	-	+	+	+	-	-	+	+	+	+	l
AIMA8	-	+	+	+	-	-	+	+	+	+	l
AIMA10	-	+	+	+	-	-	+	+	+	+	l
AIMA11	-	+	+	+	-	-	+	+	+	+	l
AIMA12	-	+	+	+	-	-	+	+	+	+	l
AIMA13	-	+	+	+	-	-	+	+	+	+	l
AIMA14	-	+	+	-	+	+	+	+	+	+	s
AIMA16	-	+	+	-	+	+	+	+	+	+	s
AIMA18	-	+	-	-	+	+	+	+	+	+	s
<i>r</i> -AIMA18	-	+	-	-	+	+	+	+	+	+	s
AIMA20	-	+	-	-	+	+	+	+	+	+	s

<sup>a</sup>The symbols "+" and "-" indicate solubility and nonsolubility, respectively. Solubility parameters (d, MPa<sup>1/2</sup>) were obtained from the *Polymer Handbook* (J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. Bloch. *Polymer Handbook*, 4th ed., John Wiley and Sons, New York, 1999), and the letters s, m, and p denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.

<sup>b</sup> l – viscous oily liquid, s – white solid

**Table S2.** Polymer solubility<sup>a</sup>

Polymer	H <sub>2</sub> O $\delta = 48$	MeOH $\delta = 43$	n-BuOH $\delta = 23$	DMSO $\delta = 25$	THF $\delta = 19$	Et <sub>2</sub> O $\delta = 15$	ACN $\delta = 24$	CHCl <sub>3</sub> $\delta = 19$	toluene $\delta = 18$	EtOAc $\delta = 19$	Physical state
<b>PAIMA0</b>	-	-	-	+	-	-	-	-	-	-	s
<b>PAIMA2</b>	-	-	-	+	+	-	+	+	-	+	s
<b>PAIMA4</b>	-	-	-	+	+	-	+	+	+	+	s
<b>PAIMA6</b>	-	-	-	-	+	-	+	+	+	+	s
<b>PAIMA8</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA10</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA11</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA12</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA13</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA14</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA16</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA18</b>	-	-	-	-	+	-	-	+	+	+	s
<b><i>r</i>-PAIM18</b>	-	-	-	-	+	-	-	+	+	+	s
<b>P(AIMA18- co- <i>r</i>-AIMA18)</b>	-	-	-	-	+	-	-	+	+	+	s
<b>PAIMA20</b>	-	-	-	-	+	-	-	+	+	+	s

<sup>a</sup>The symbols "+" and "-" indicate solubility and nonsolubility, respectively. Solubility parameters ( $\delta$ , MPa<sup>1/2</sup>) were obtained from the *Polymer Handbook* (J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. Bloch. *Polymer Handbook*, 4th ed., John Wiley and Sons, New York, 1999), and the letters s, m, and p denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.

<sup>b</sup> l – viscous oily liquid, s – white solid

### SEC curves

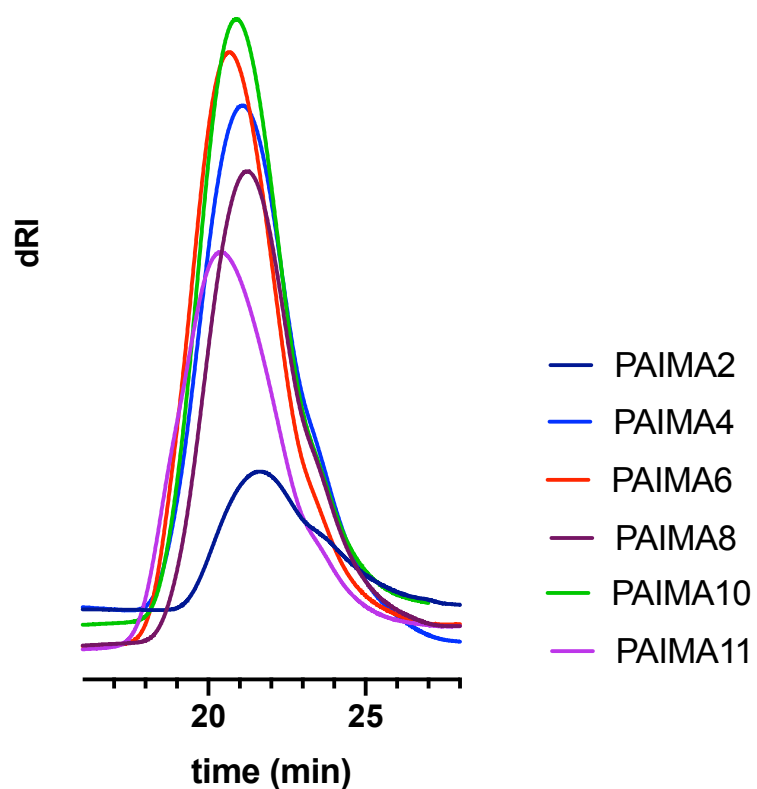


Figure S1. SEC curves of PAIMA2-PAIMA11 polymers

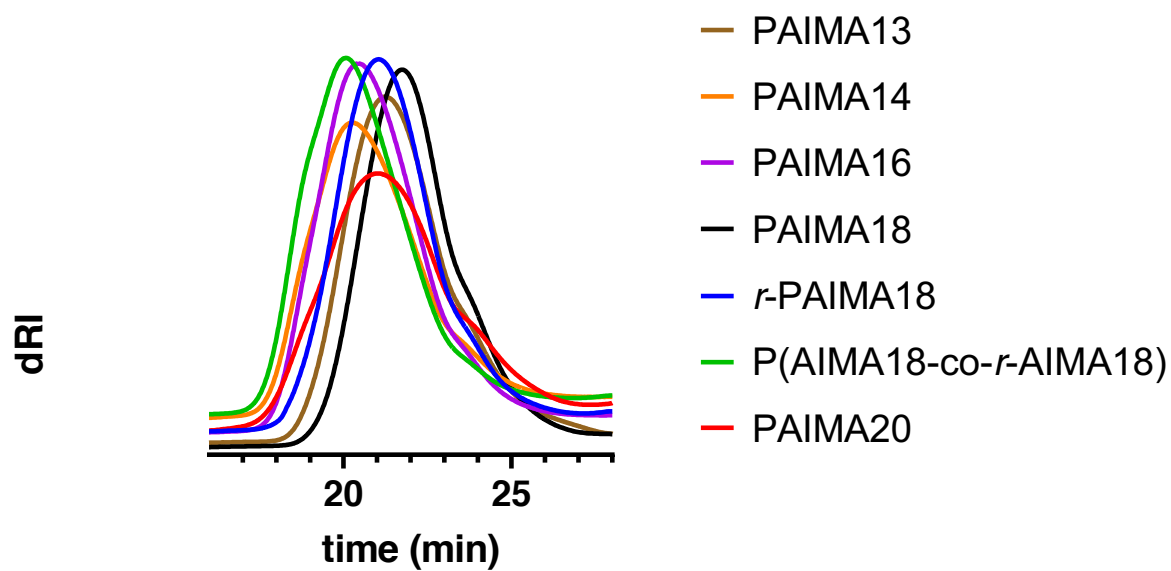


Figure S2. SEC curves of PAIMA13-PAIMA20 polymers

## NMR Spectra

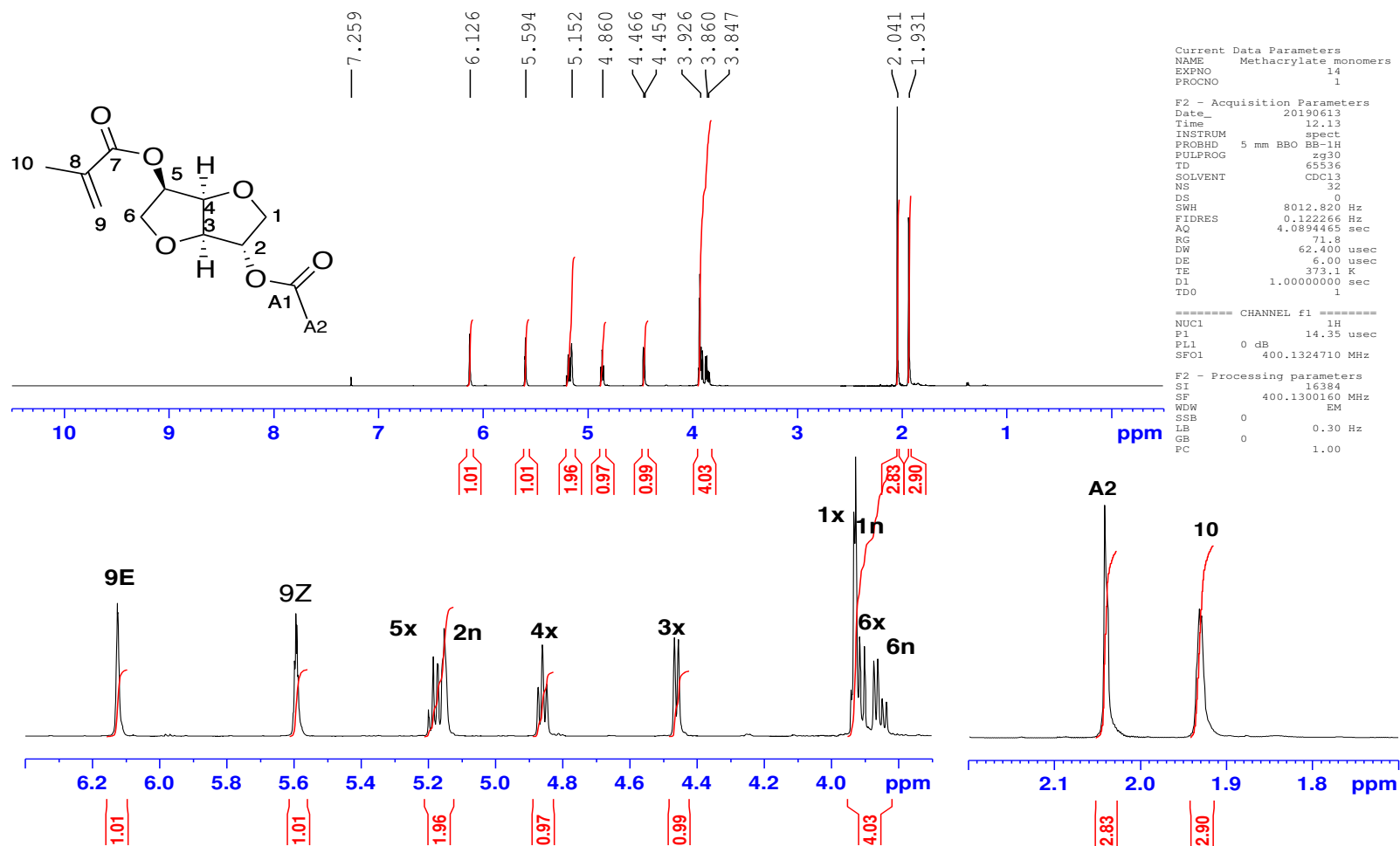
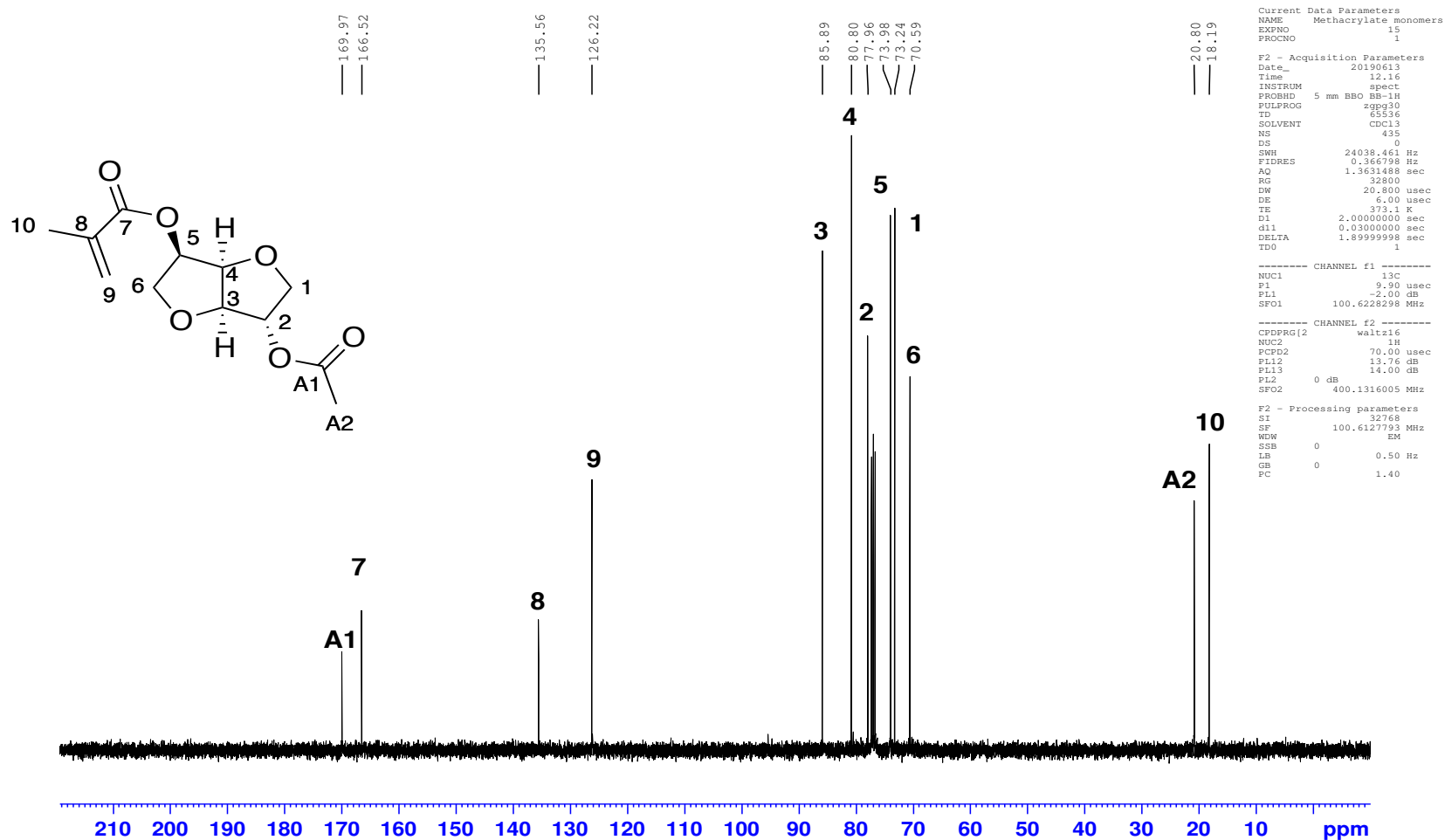
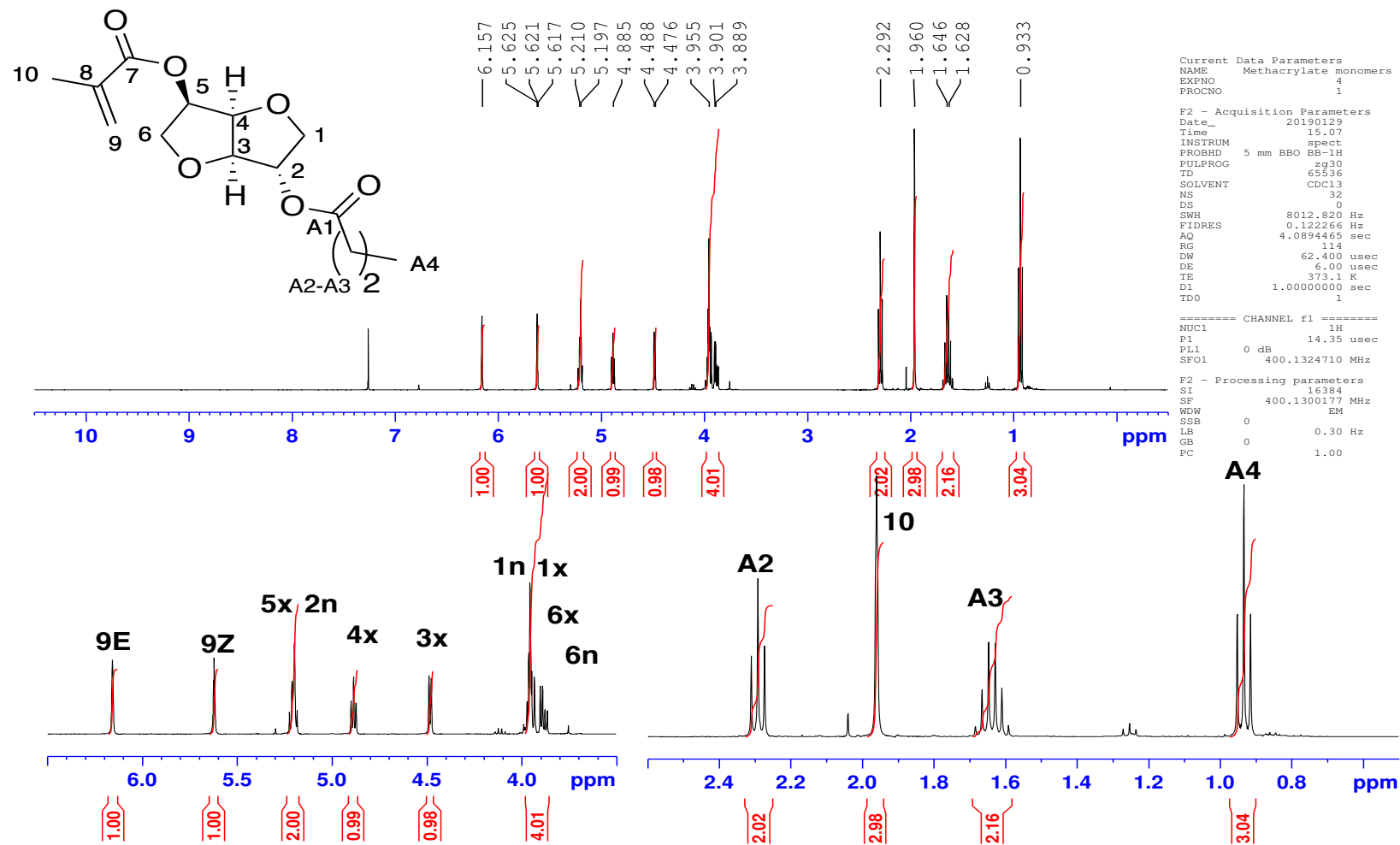


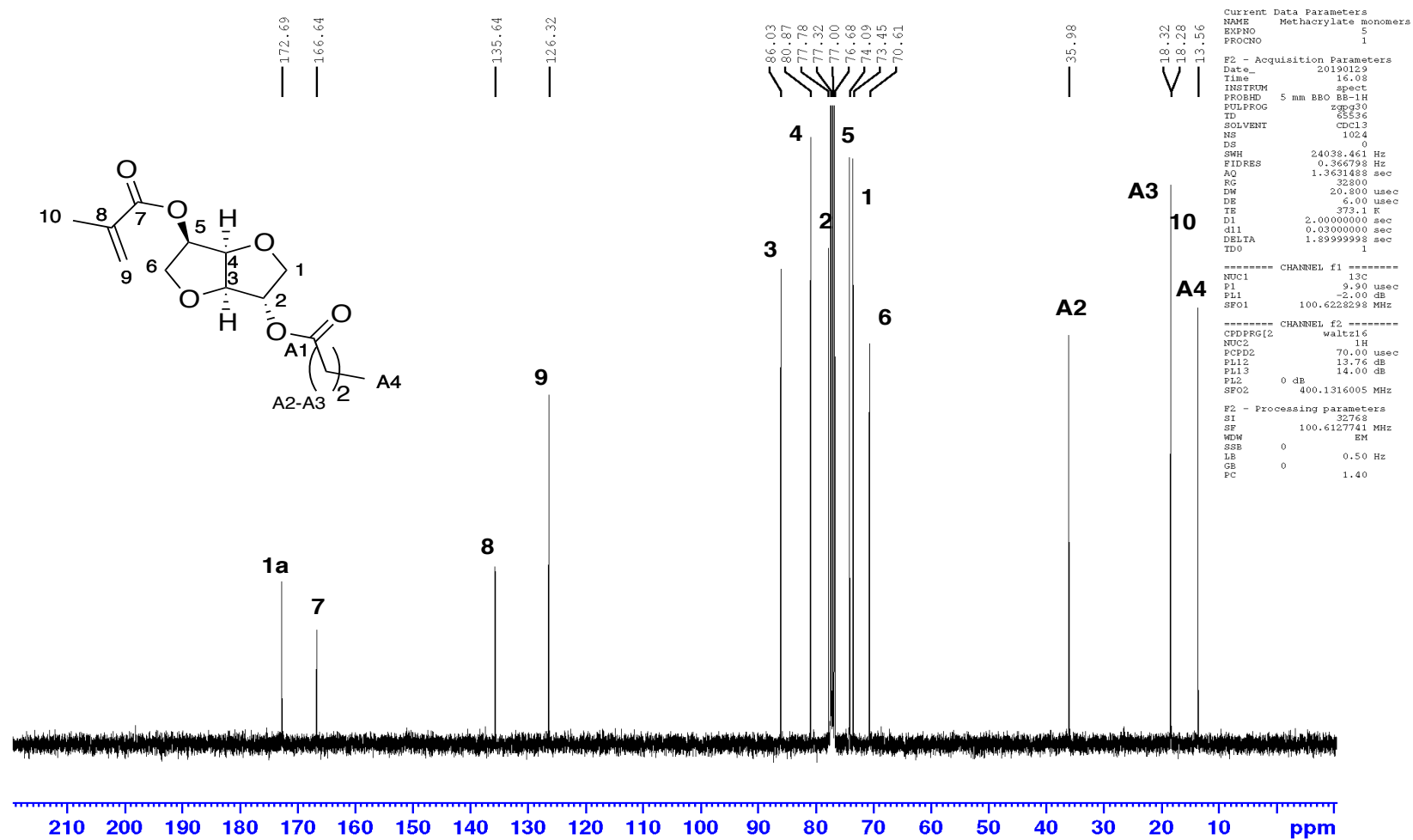
Figure S3.  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-acetate-5-methacrylate AIMA2



**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-acetate-5-methacrylate AIMA2

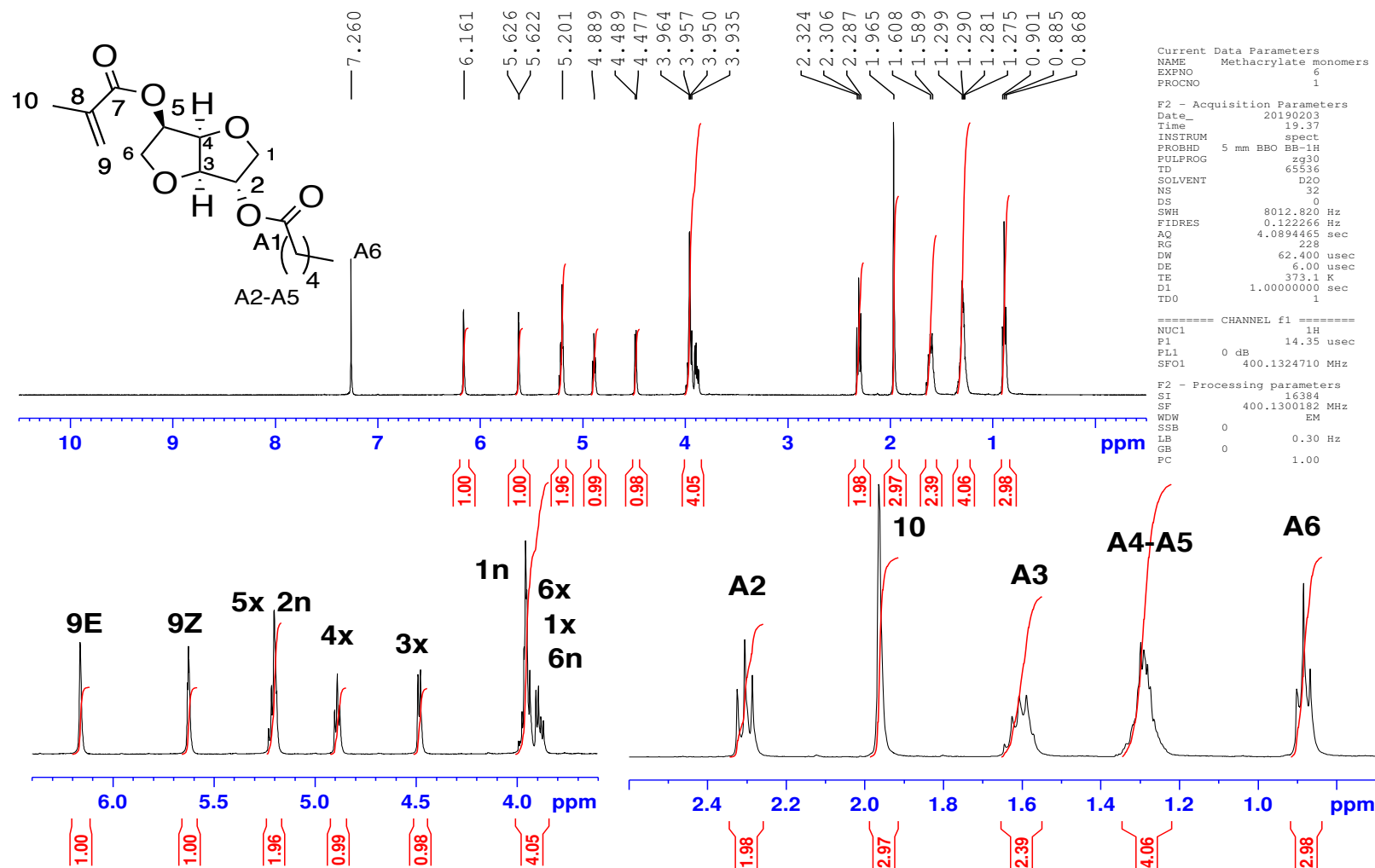


**Figure S5.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-butanoate-5-methacrylate AIMA4

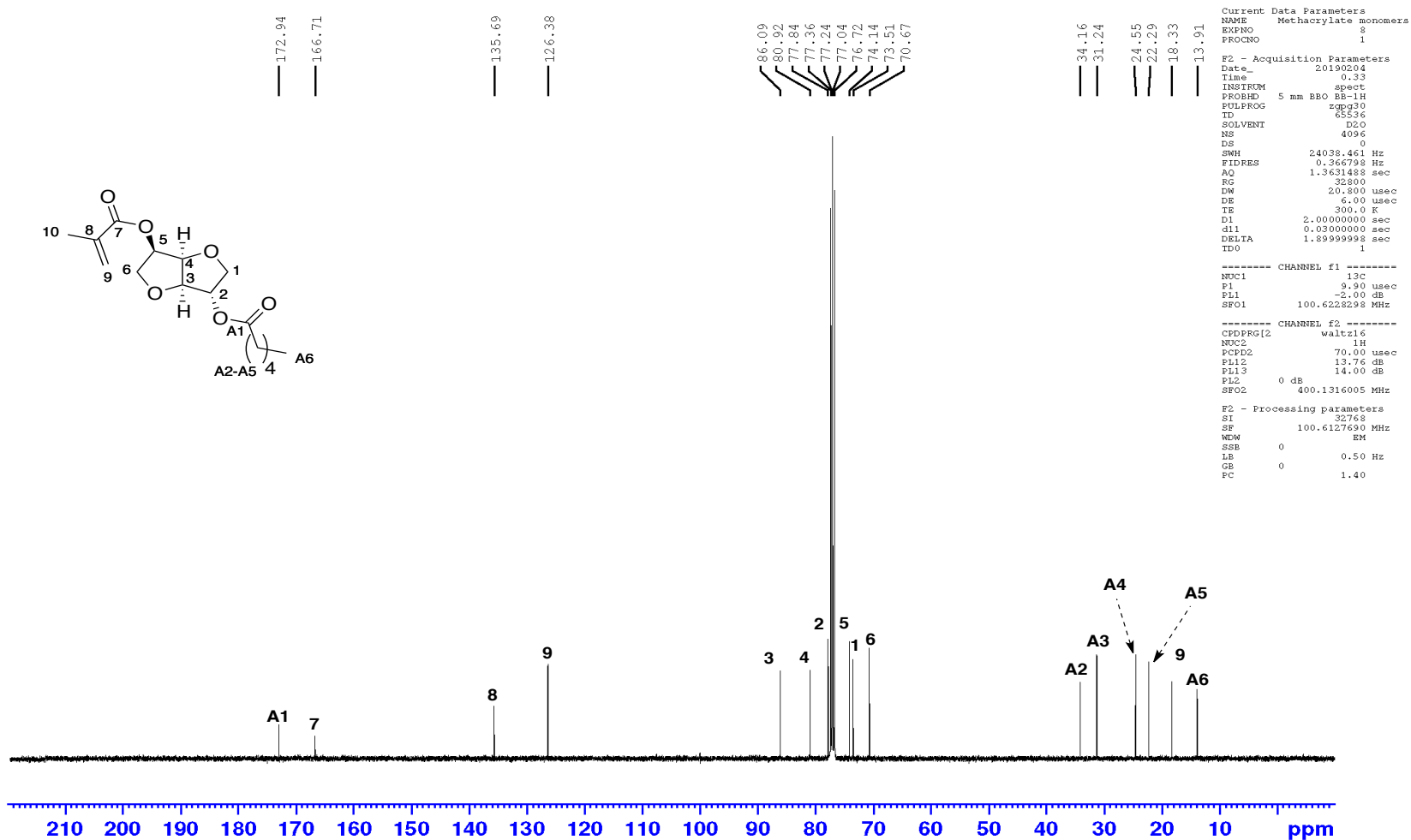


**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-butanoate-5-methacrylate AIMA4

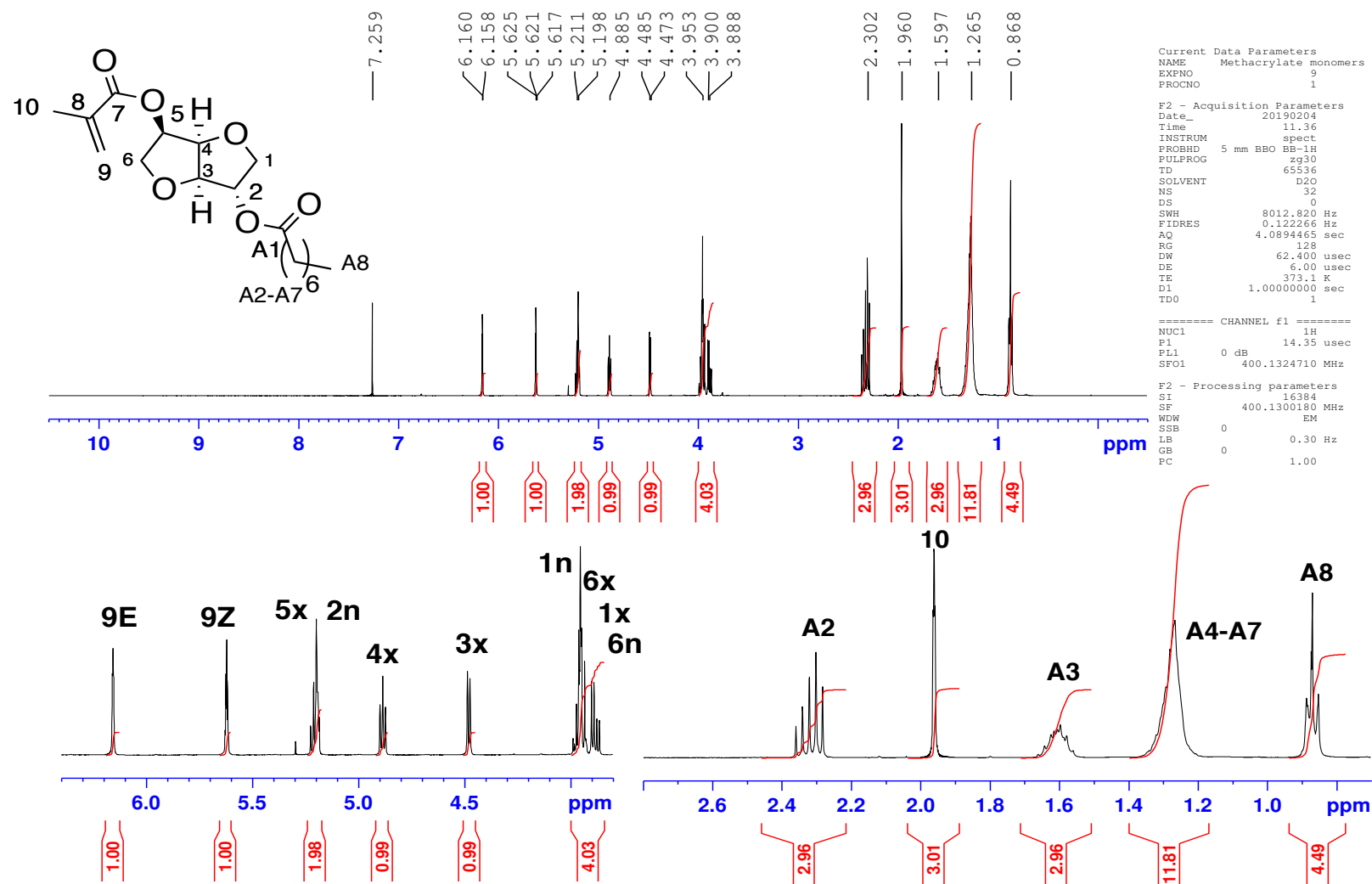




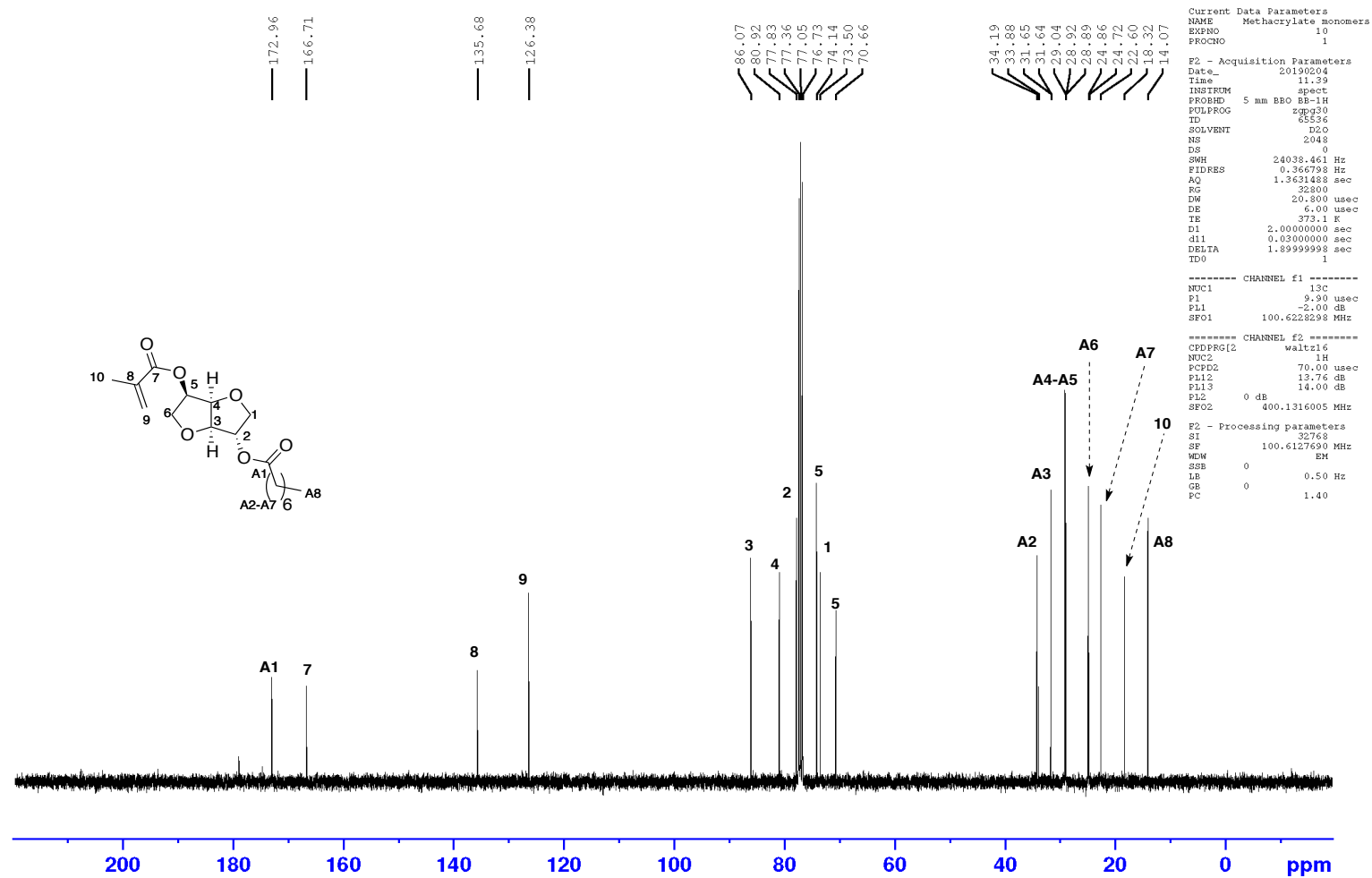
**Figure S7.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-hexanoate-5-methacrylate AIMA6



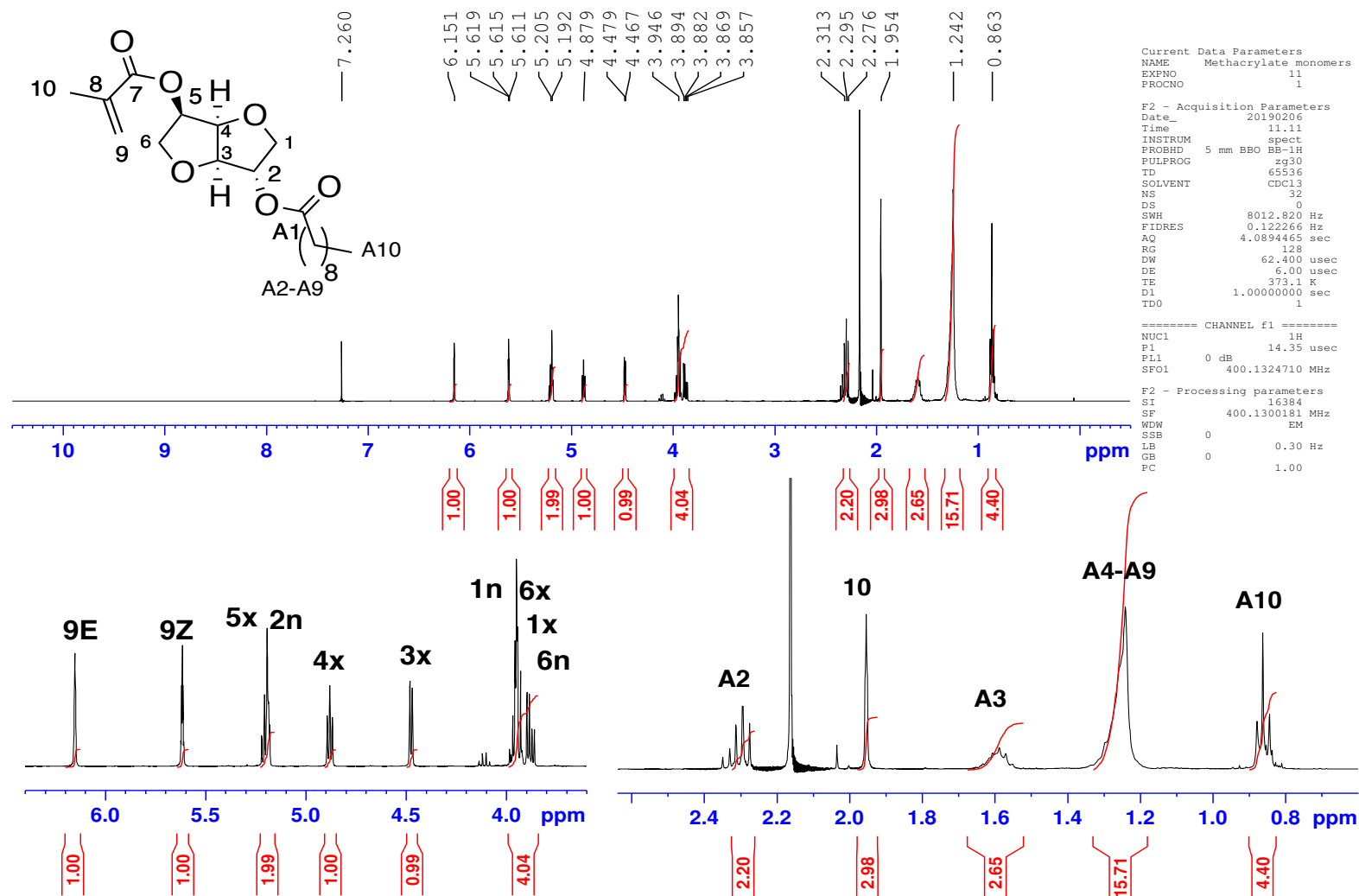
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-hexanoate-5-methacrylate AIMA6



**Figure S9.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-octanoate-5-methacrylate AIMA8



**Figure S10.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-octanoate-5-methacrylate AIMA8



**Figure S11.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-decanoate-5-methacrylate AIMA10



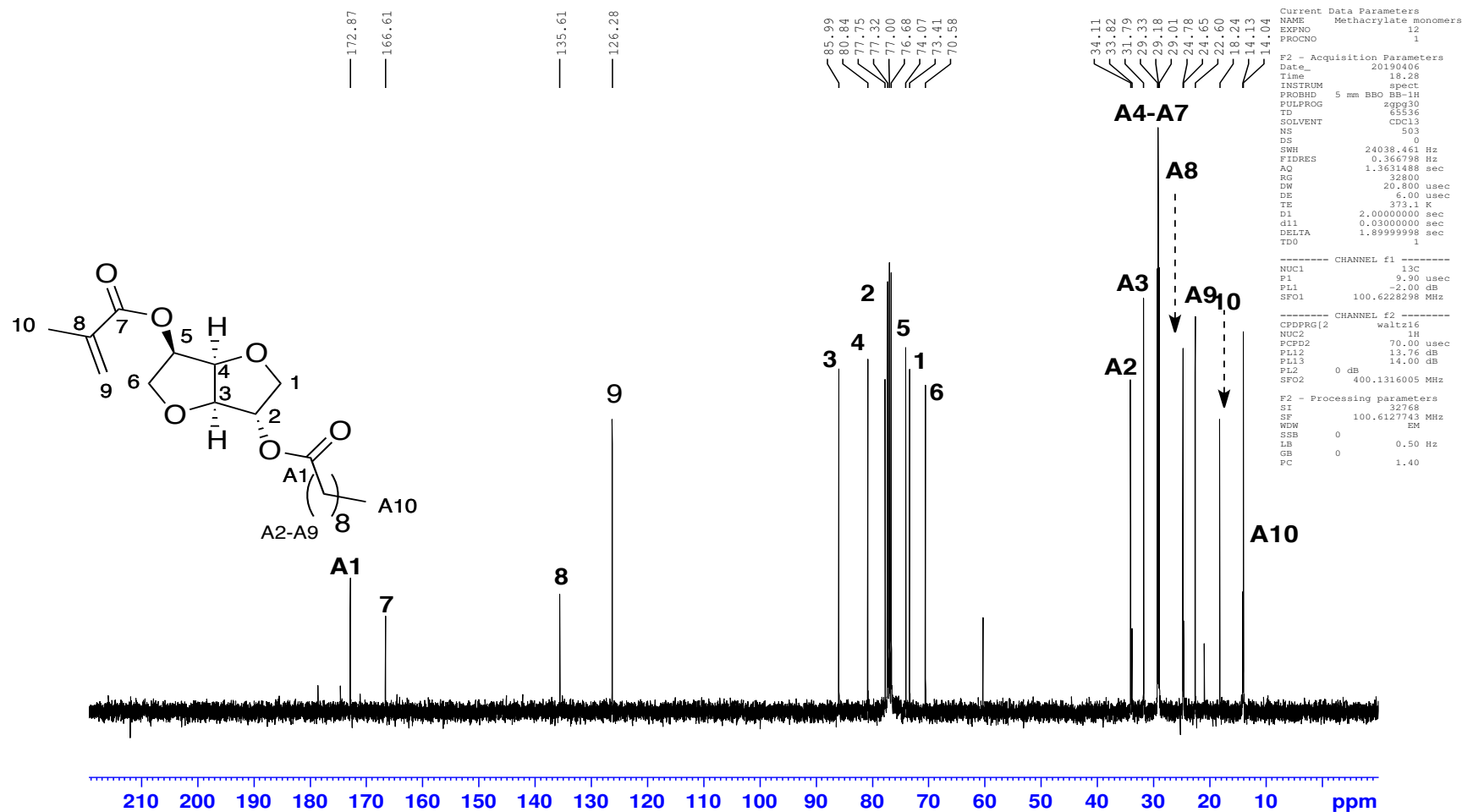
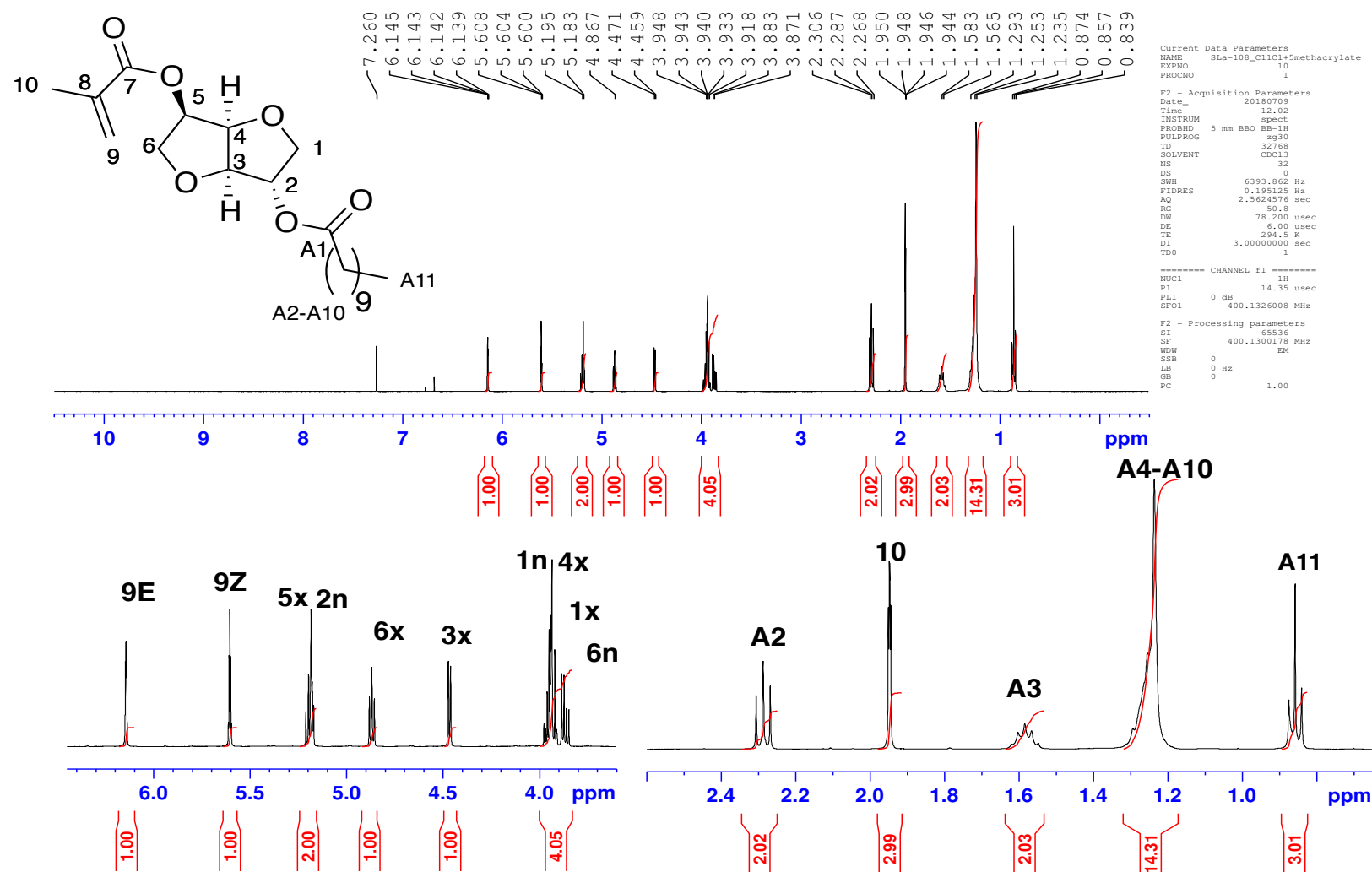
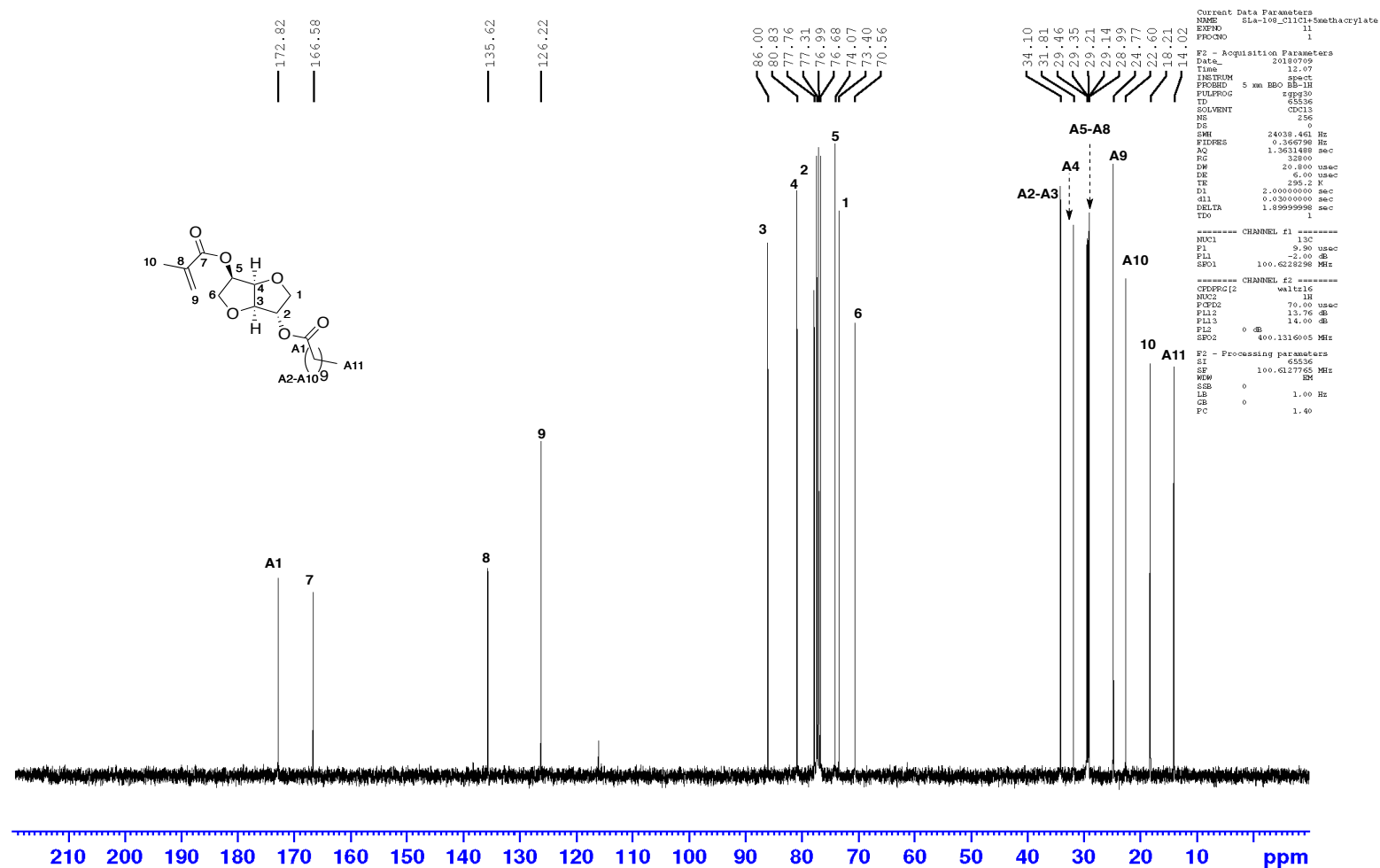


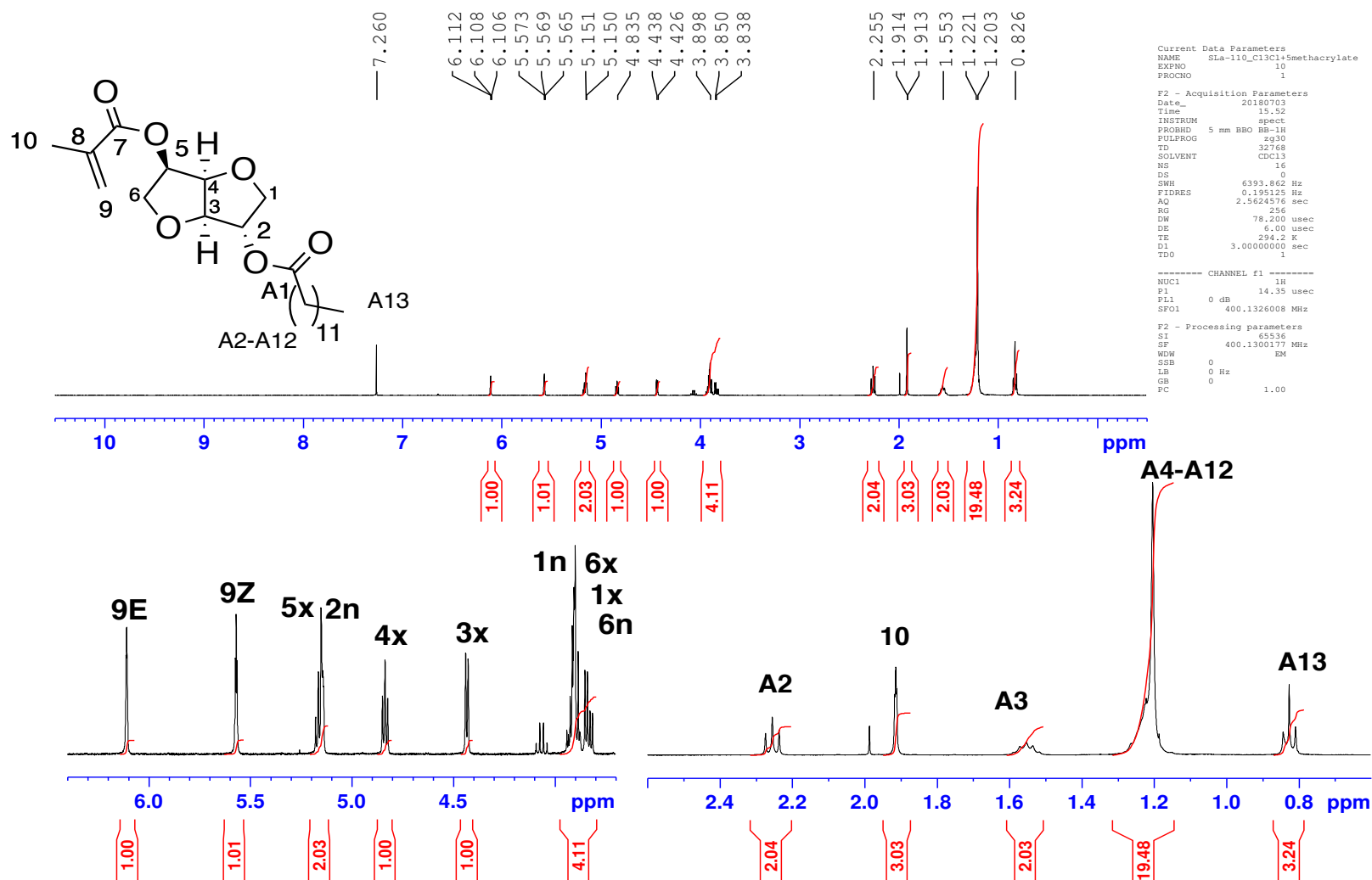
Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-decanoate-5-methacrylate AIMA10



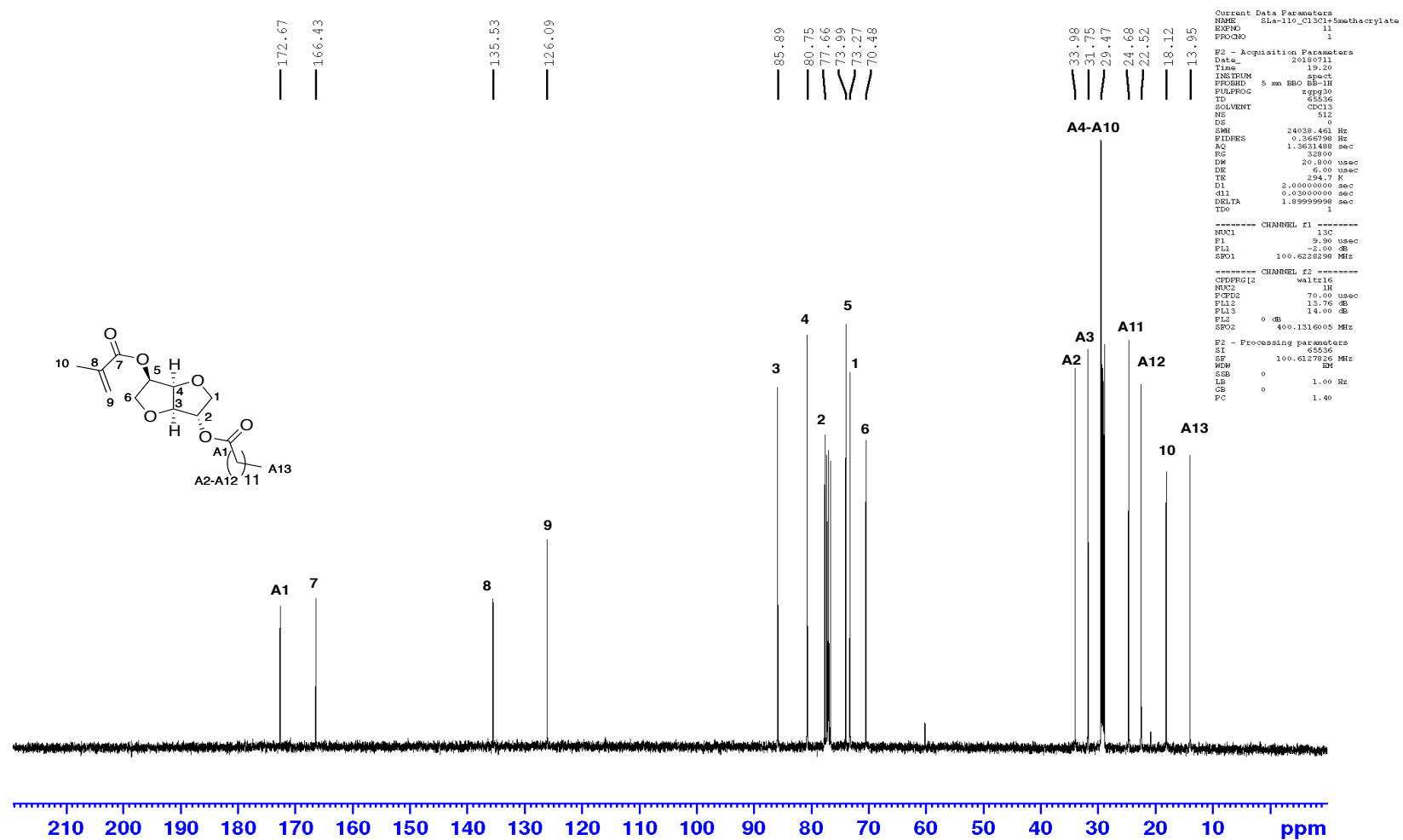
**Figure S13.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-undecanoate-5-methacrylate AIMA11



**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-undecanoate-5-methacrylate AIMA11

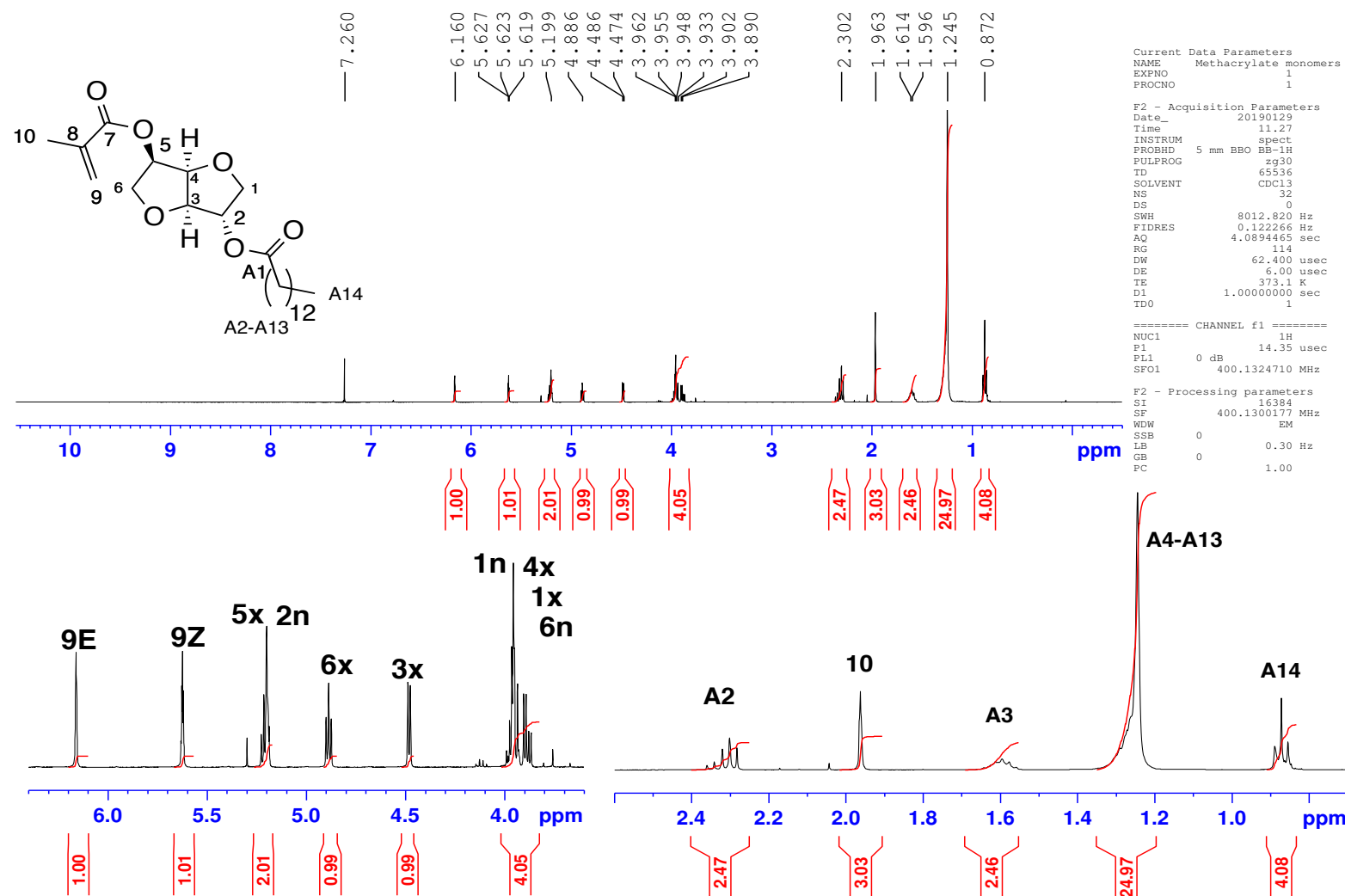


**Figure S15.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-tridecanoate-5-methacrylate AIMA13

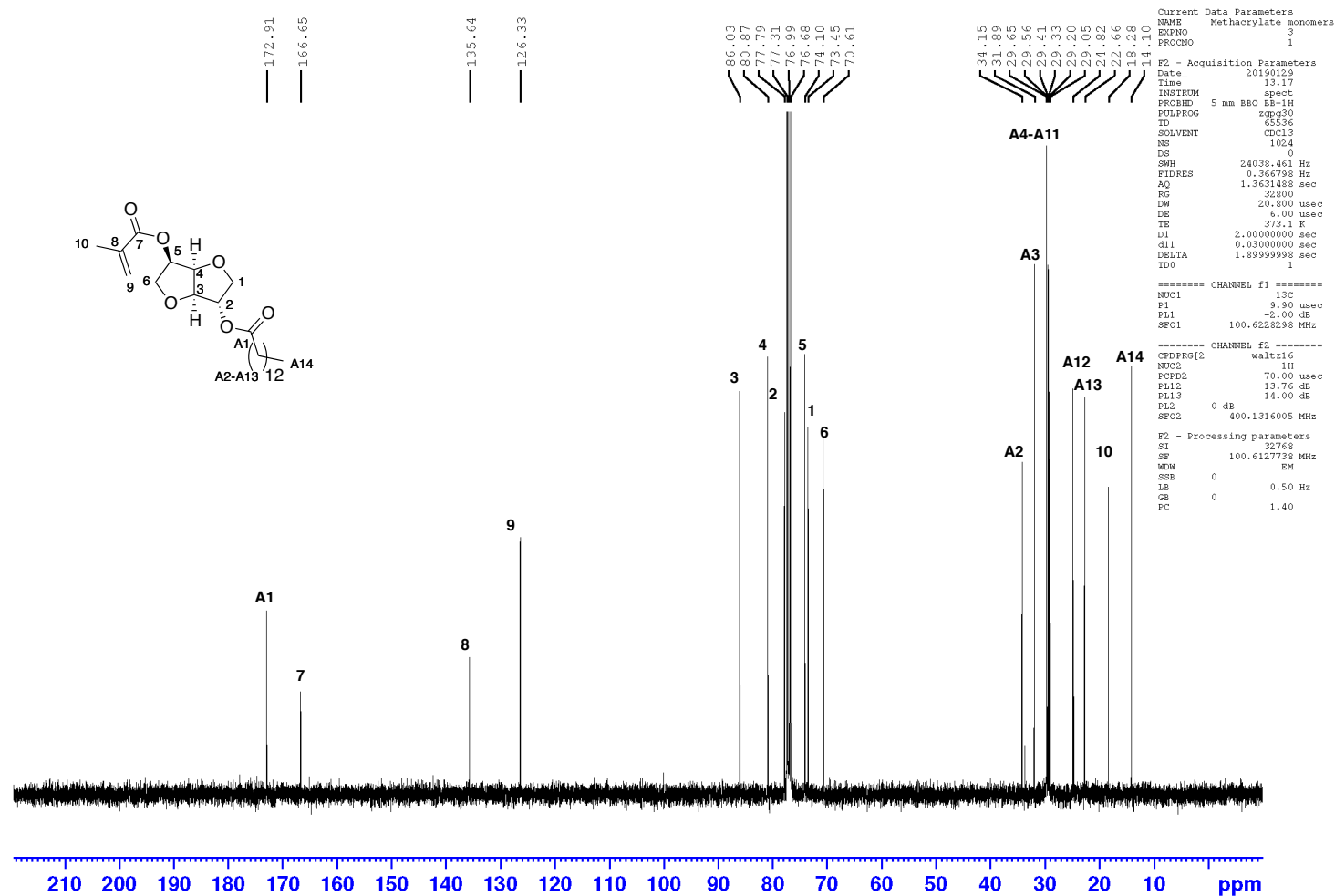


**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-tridecanoate-5-methacrylate AIMA13





**Figure S17.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-tetradecanoate-5-methacrylate AIMA14



**Figure S18.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-tetradecanoate-5-methacrylate AIMA14

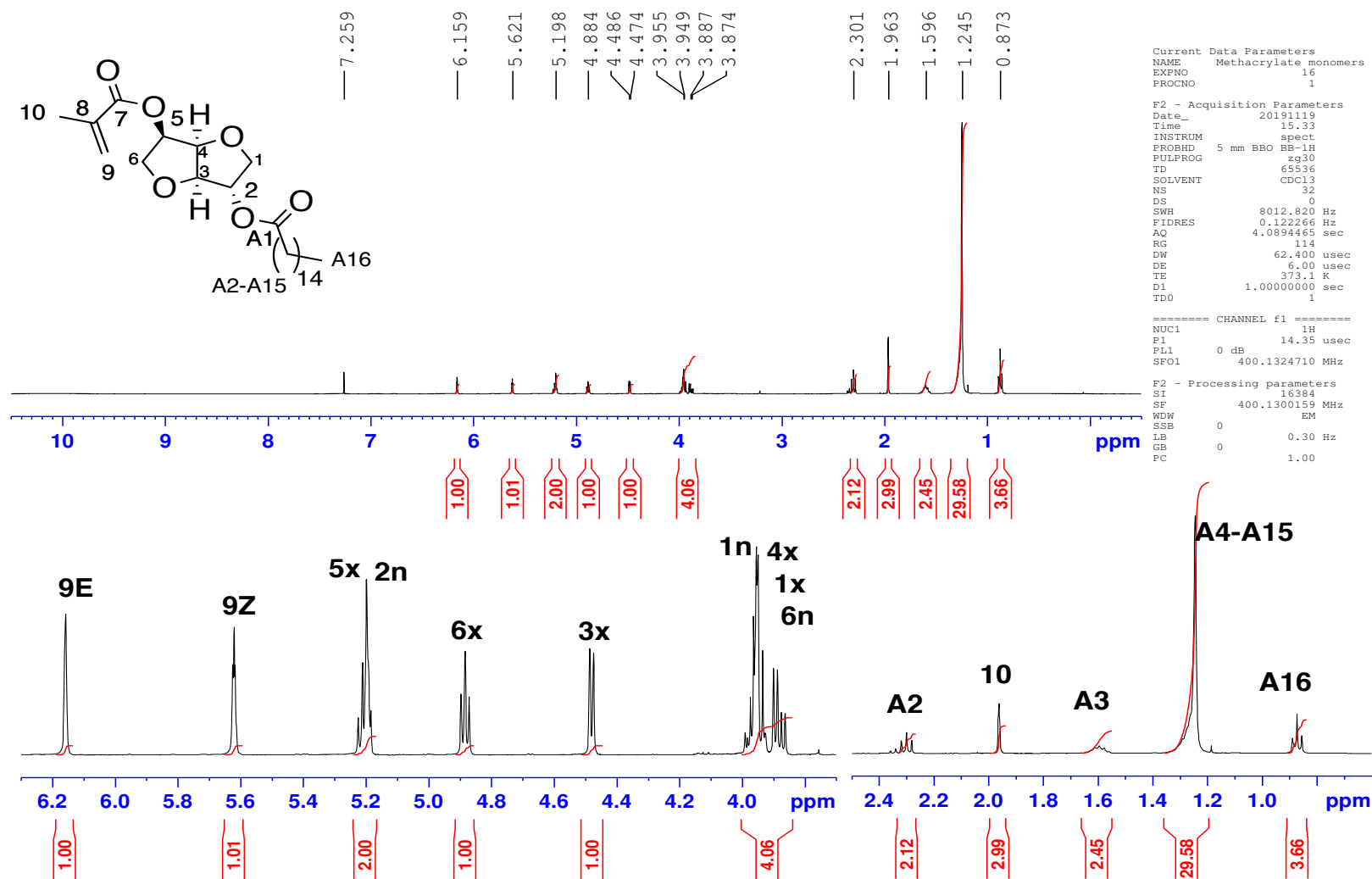
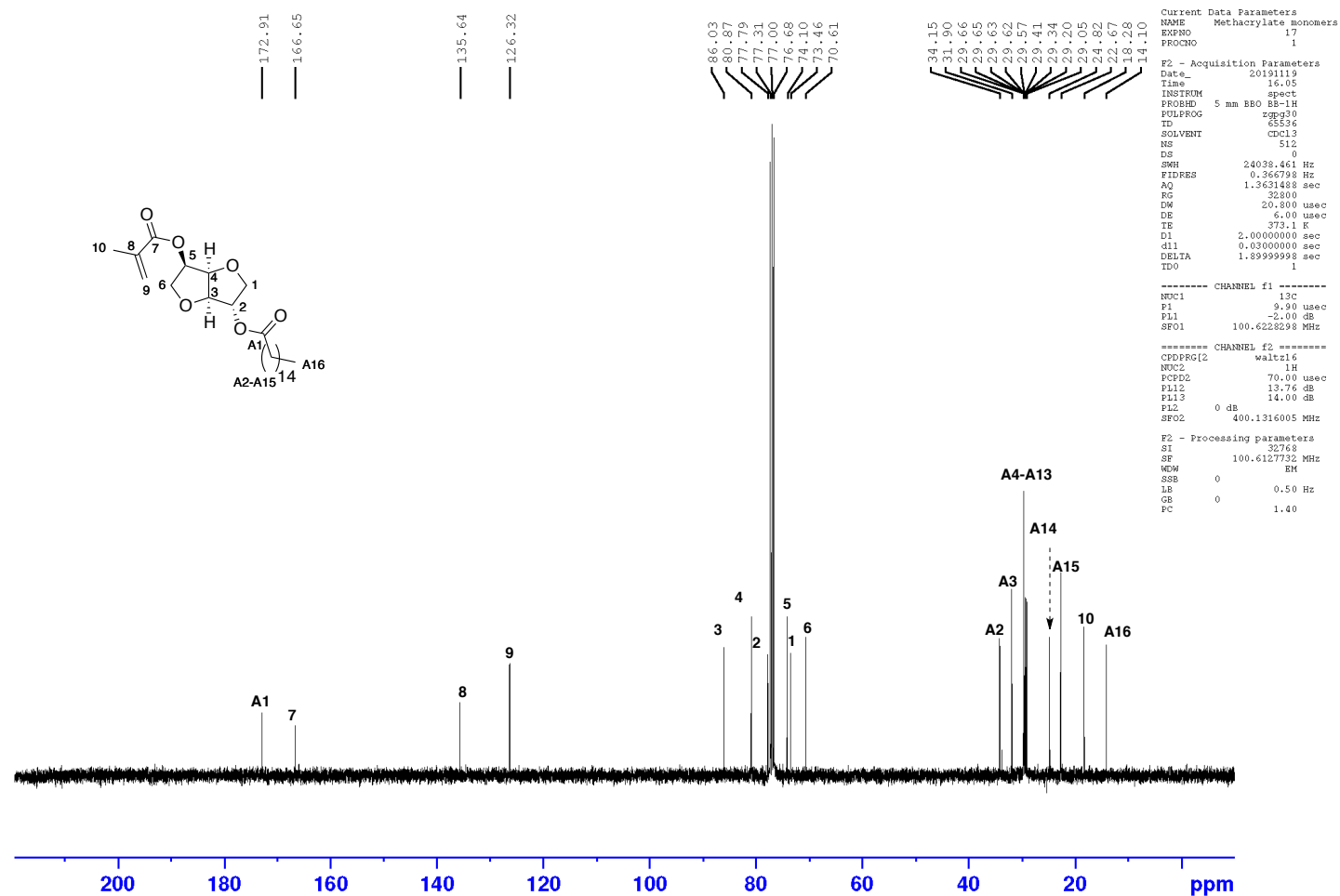
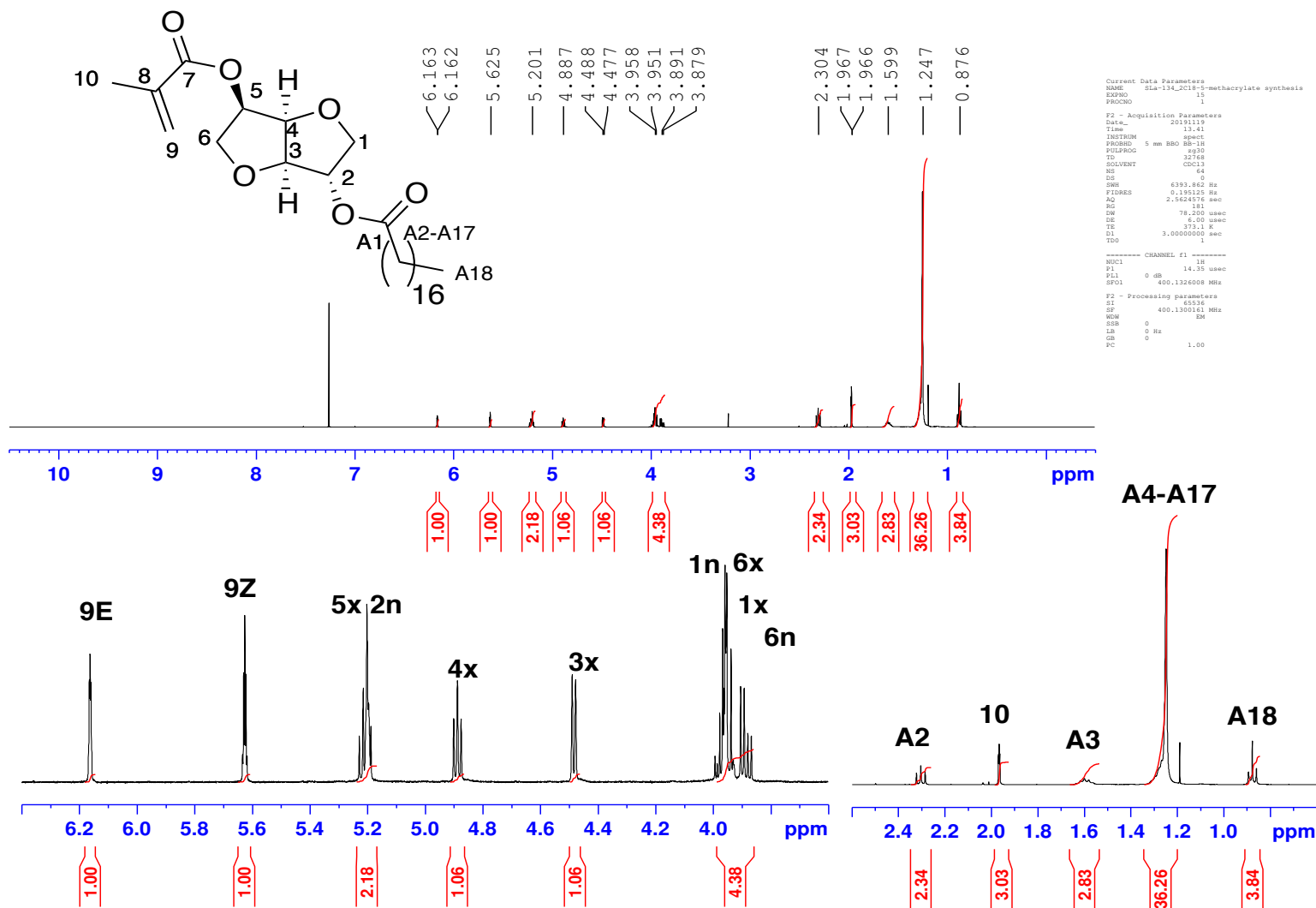


Figure S19. <sup>1</sup>H{<sup>13</sup>C} spectrum of D-isosorbide-2-hexadecanoate-5-methacrylate AIMA16

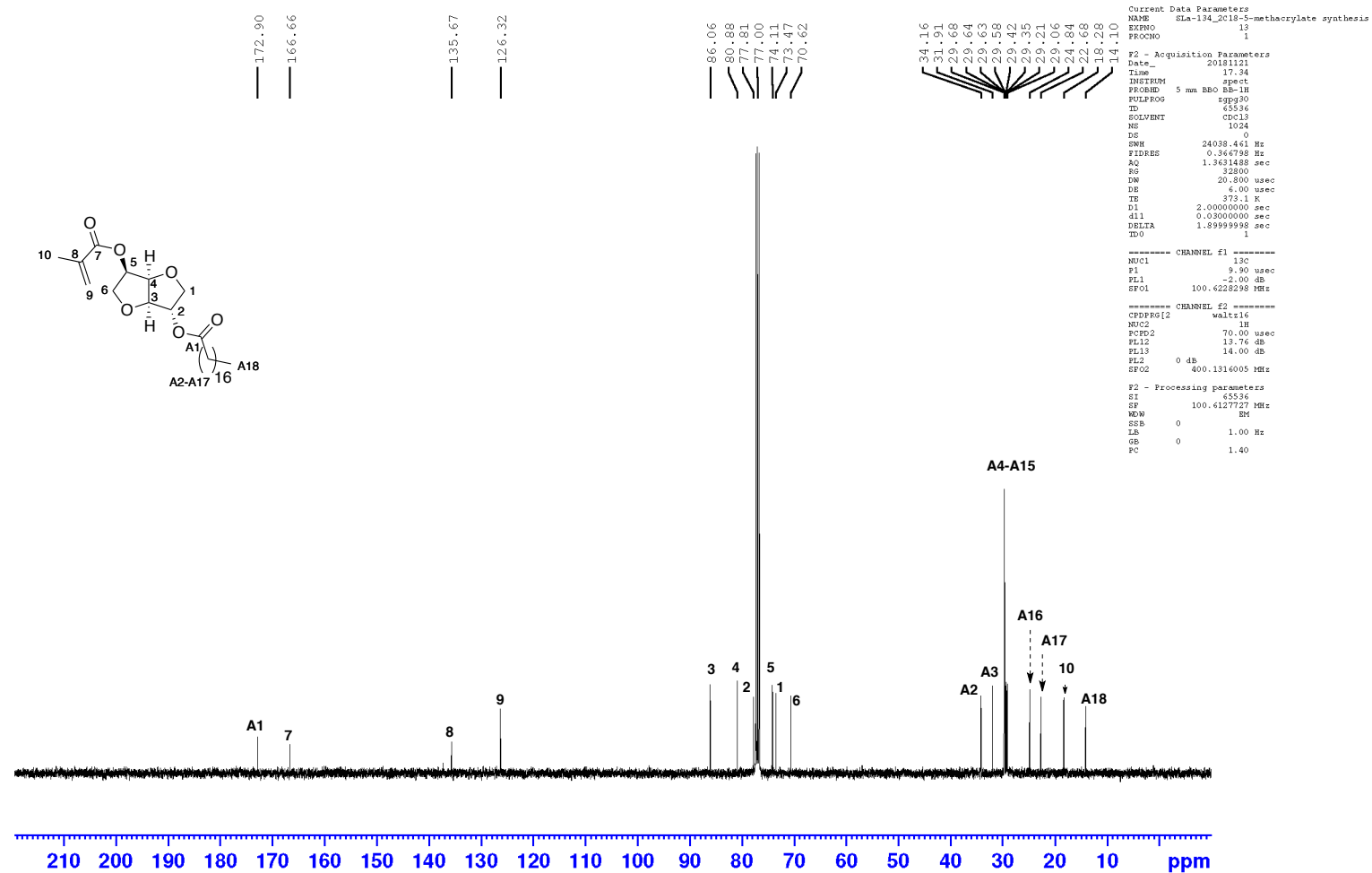


**Figure S20.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-hexadecanoate-5-methacrylate AIMA16

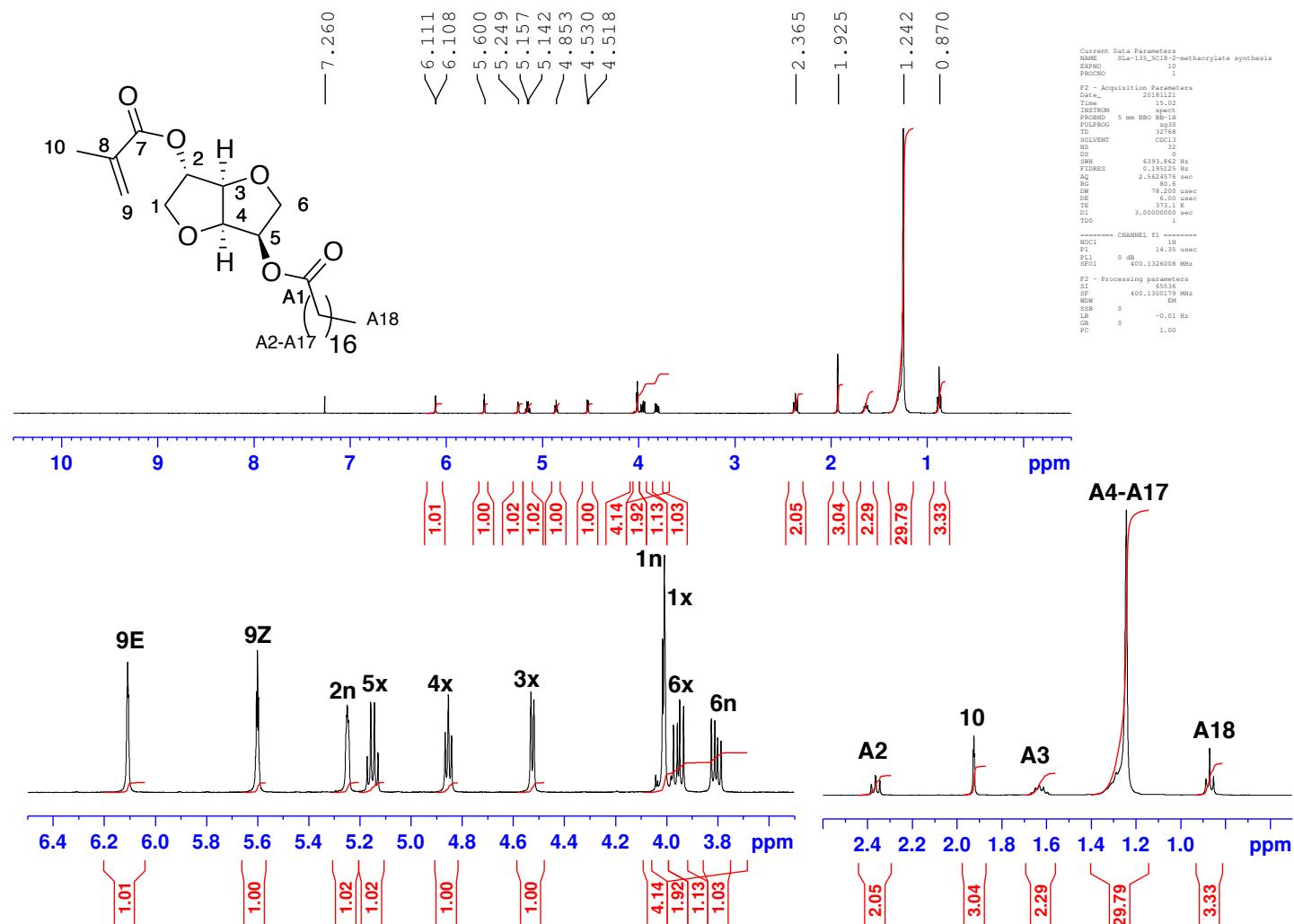


**Figure S21.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-octadecanoate-5-methacrylate AIMA18





**Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-octadecanoate-5-methacrylate AIMA18



**Figure S23.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-5-octadecanoate-2-methacrylate *r*-AIMA18

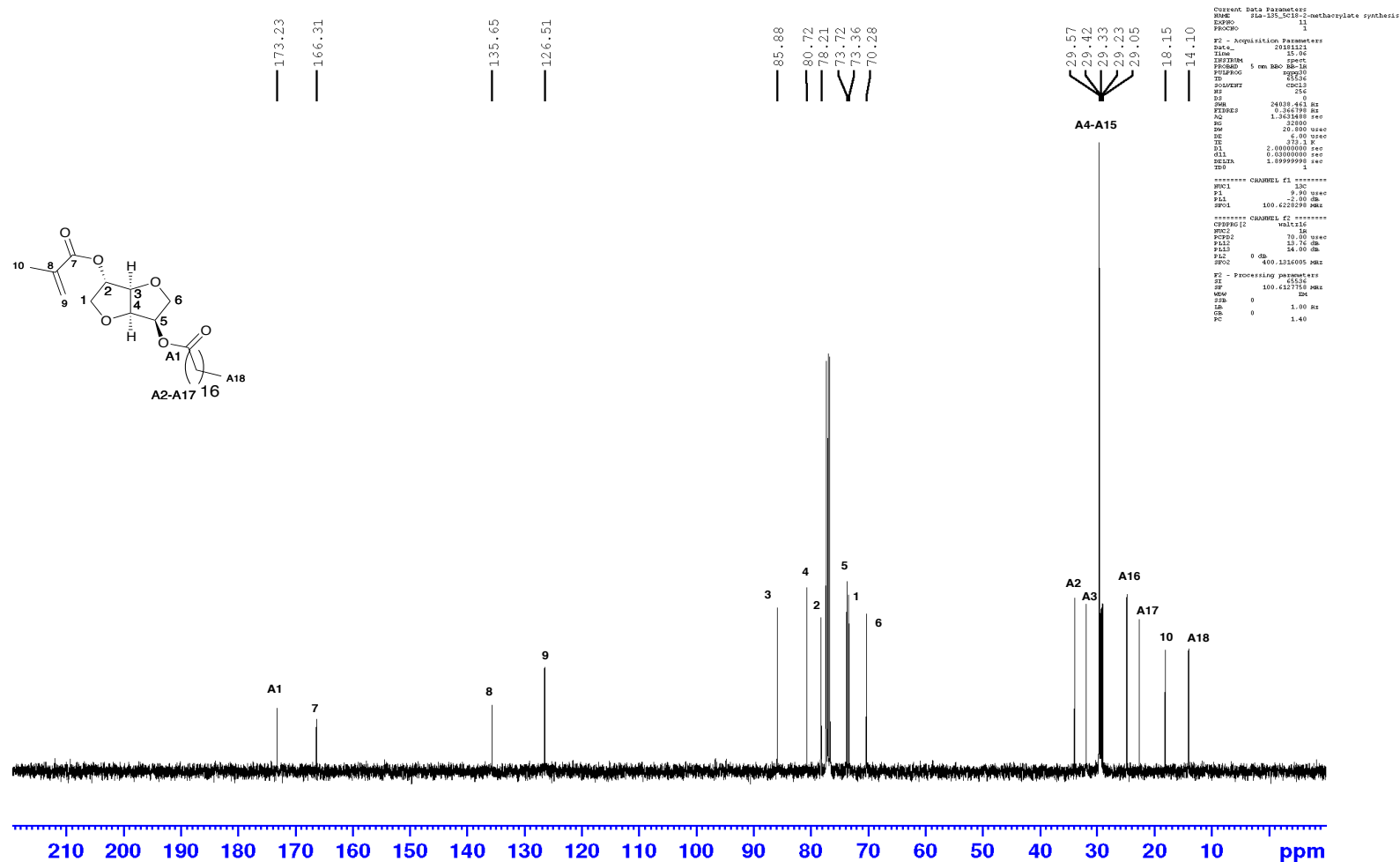
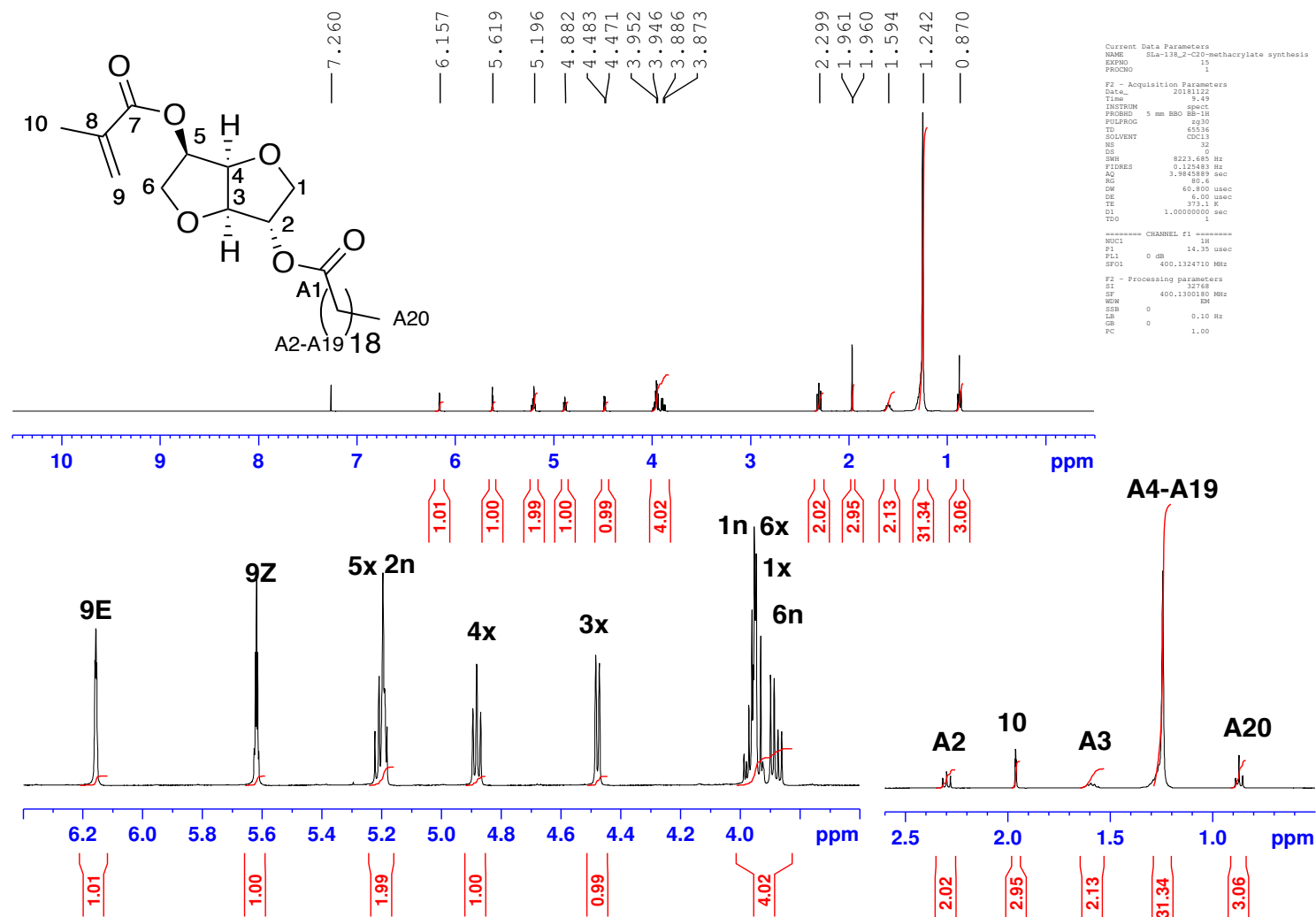
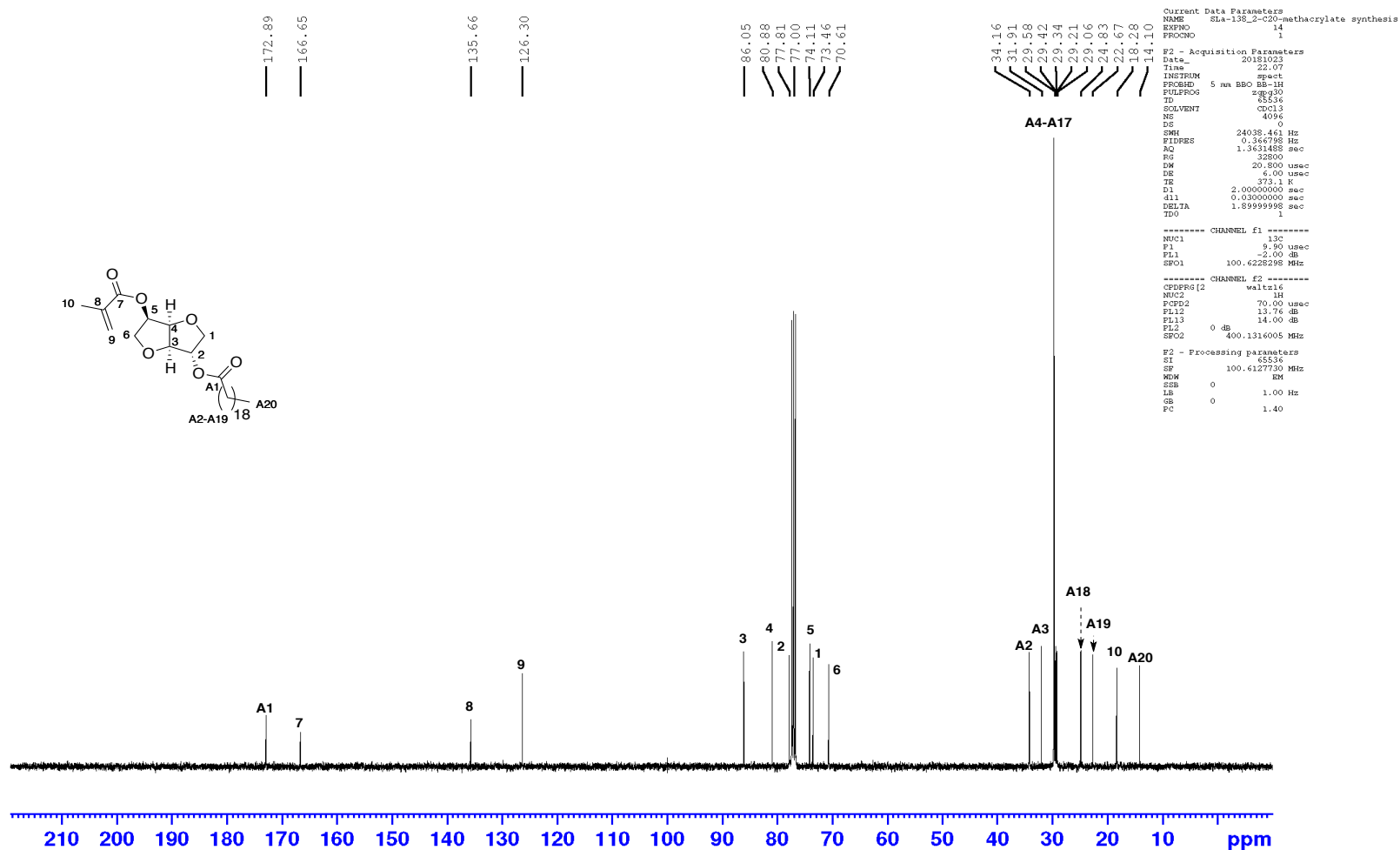


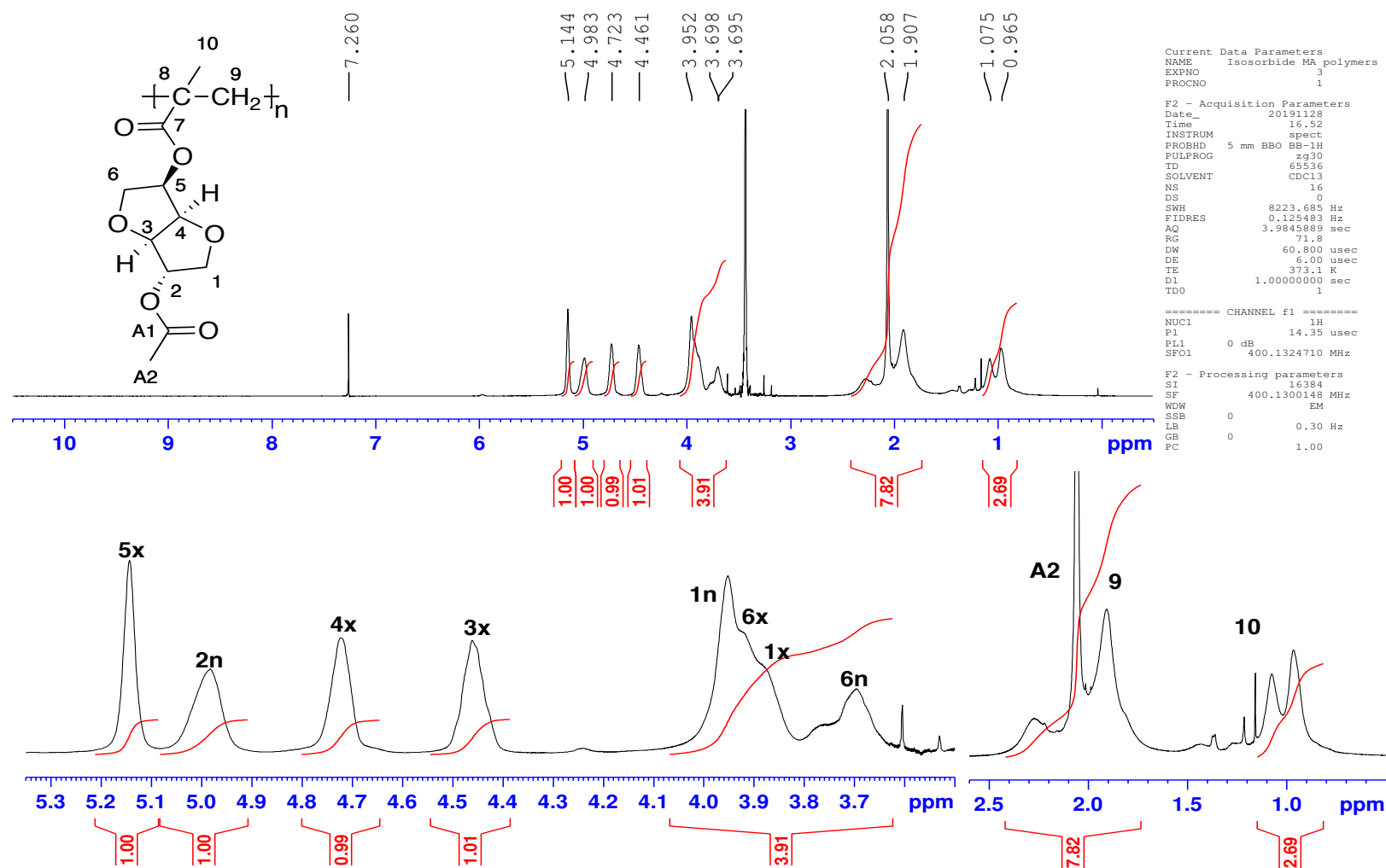
Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-5-octadecanoate-2-methacrylate *r*-AIMA18



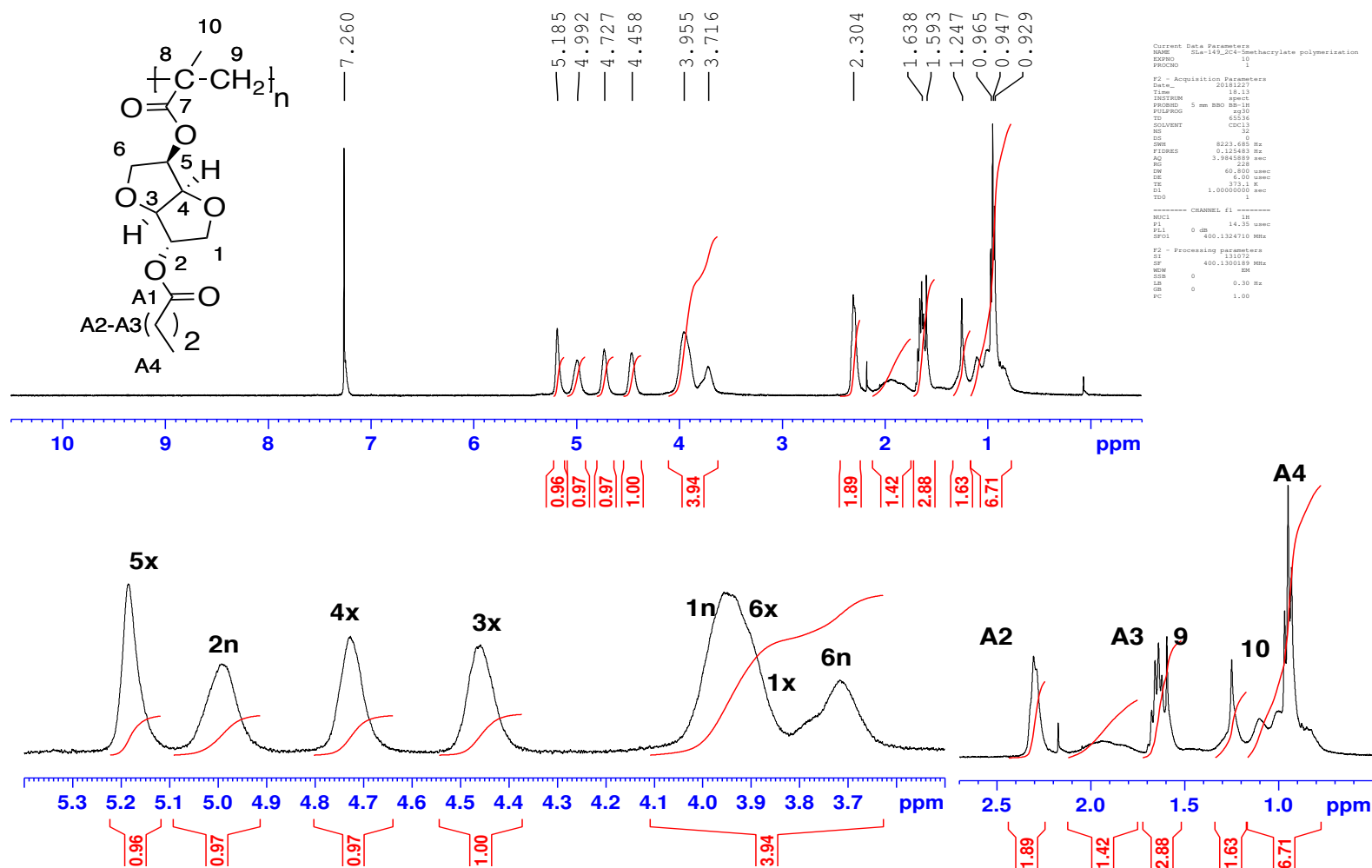
**Figure S25.**  $^1\text{H}\{^{13}\text{C}\}$  spectrum of D-isosorbide-2-eicosanoate-5-methacrylate AIMA20



**Figure S26.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of D-isosorbide-2-eicosanoate-5-methacrylate AIMA20

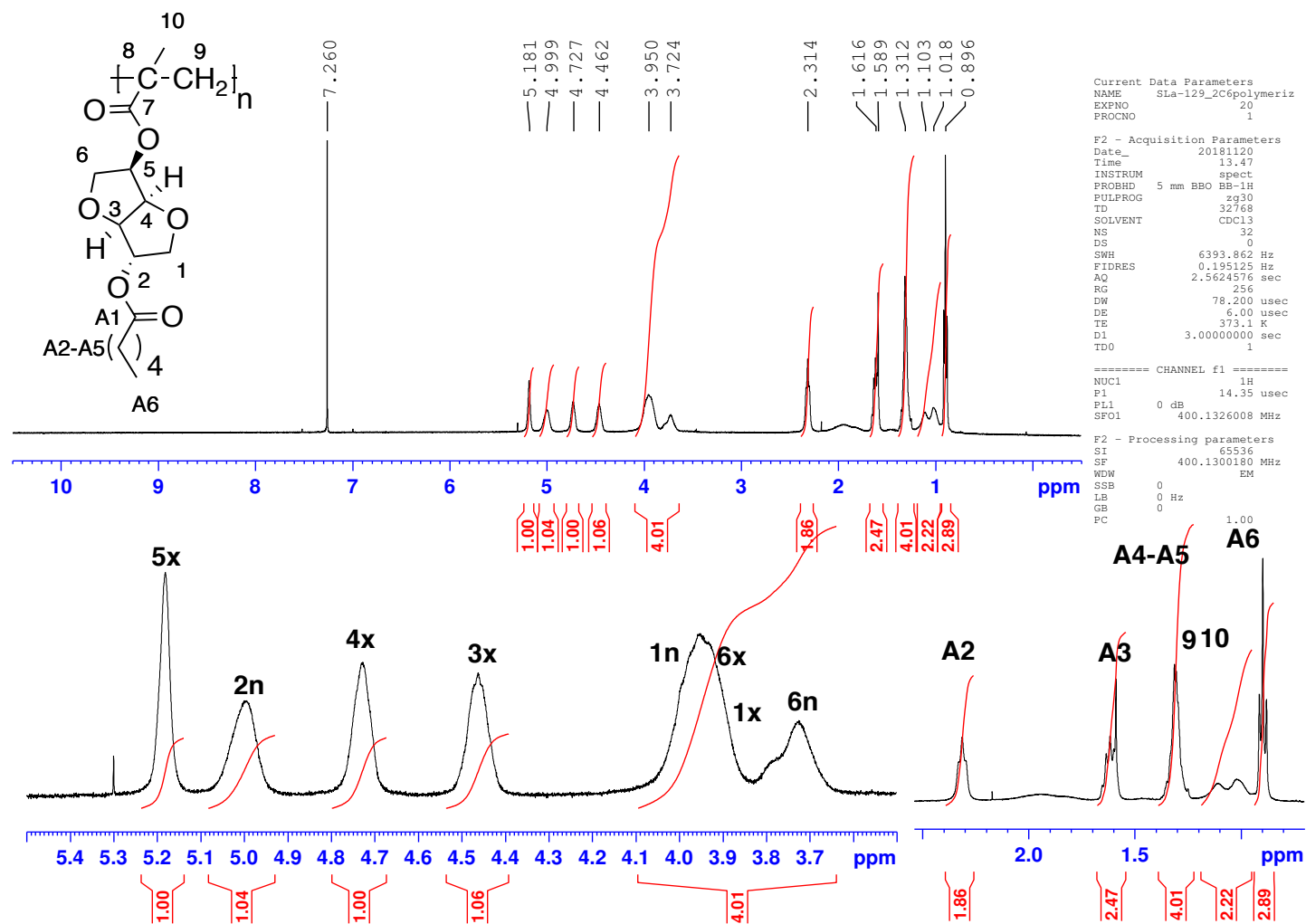


**Figure S27.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-acetate-5-methacrylate polymer **PAIMA2**

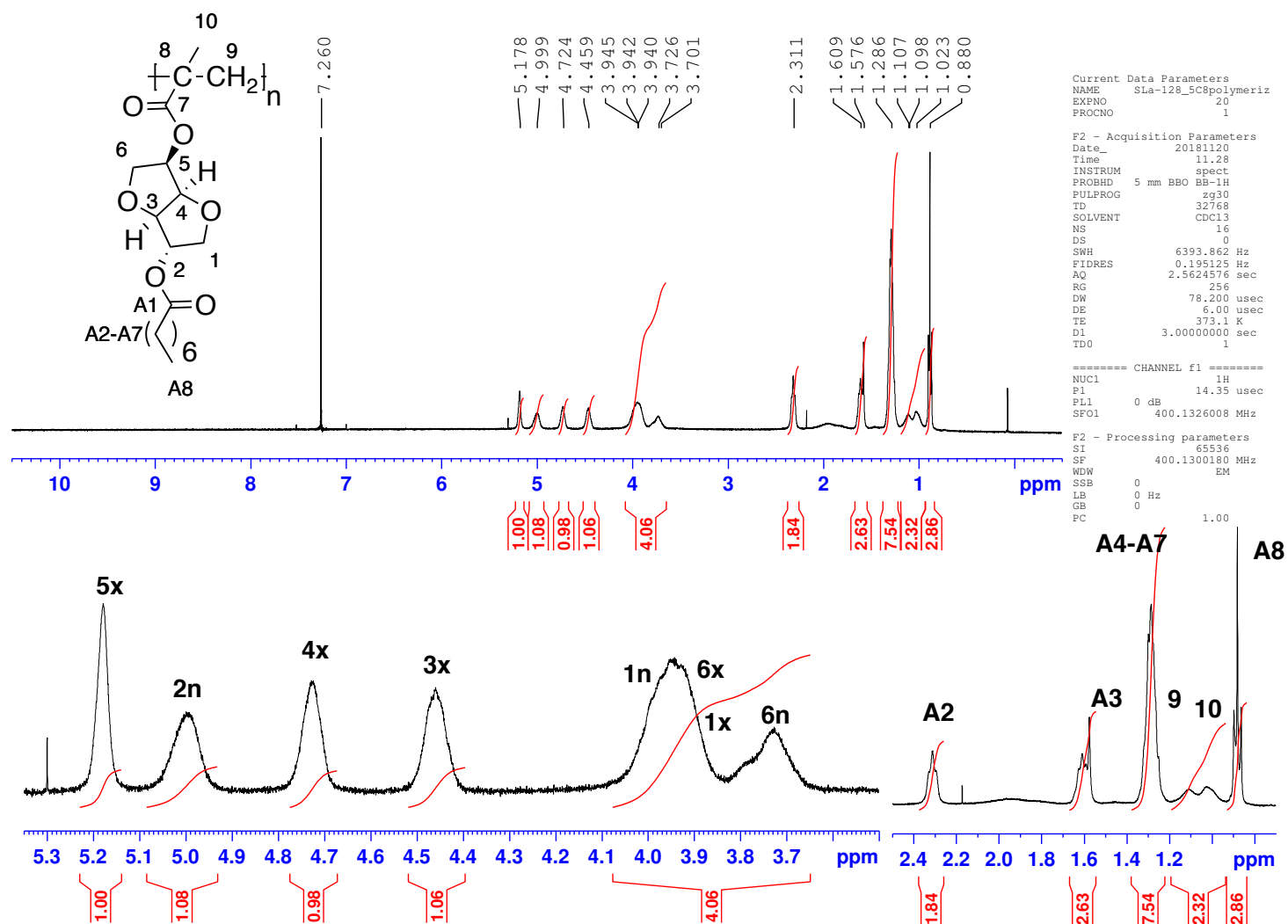


**Figure S28.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-butanoate-5-methacrylate polymer **PAIMA4**

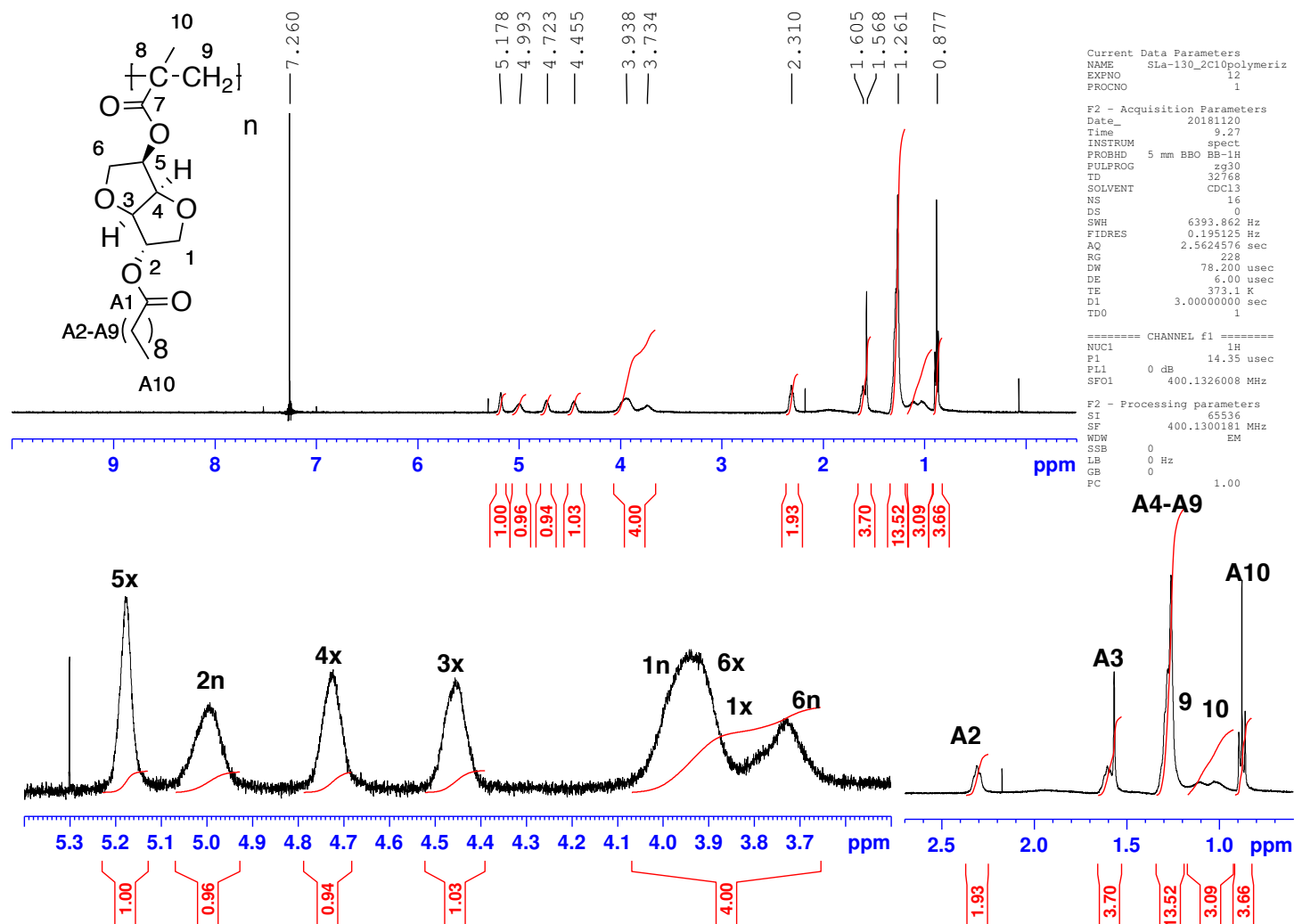




**Figure S29.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-hexanoate-5-methacrylate polymer **PAIMA6**



**Figure S30.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-octanoate-5-methacrylate polymer **PAIMA8**



**Figure S31.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-decanoate-5-methacrylate polymer **PAIMA10**

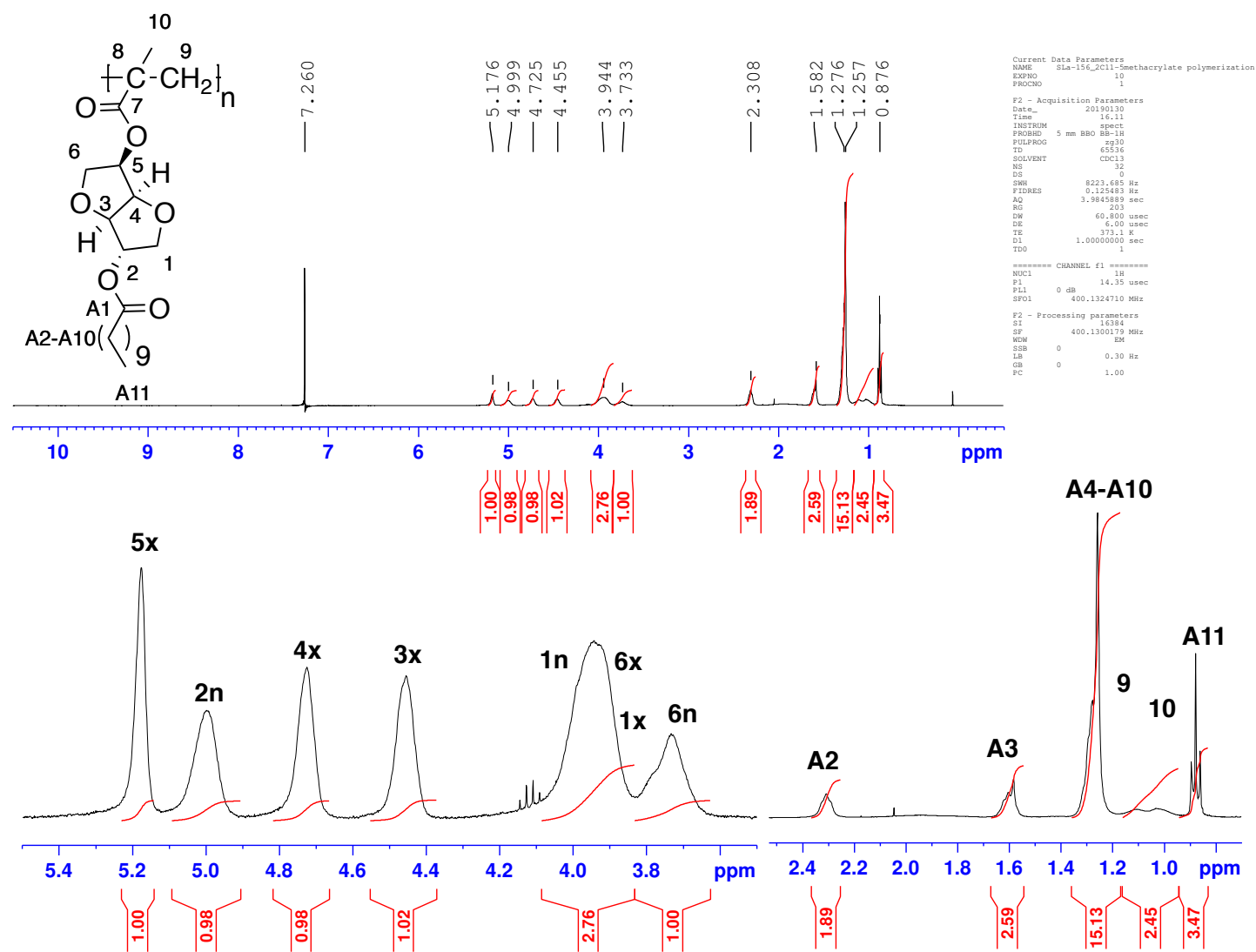


Figure S32. <sup>1</sup>H{<sup>13</sup>C} NMR spectrum of D-isosorbide-2-undecanoate-5-methacrylate polymer PAIMA11

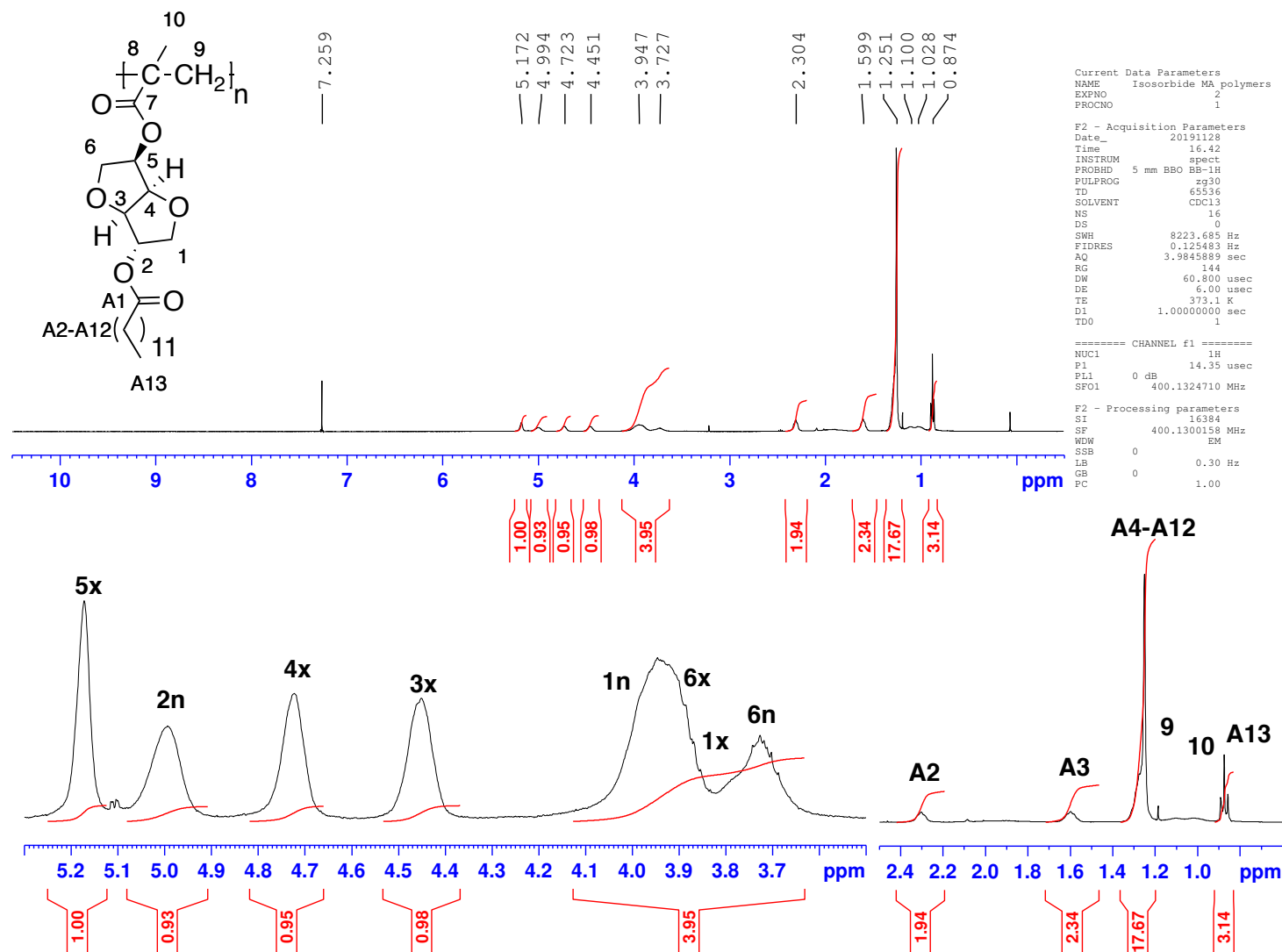
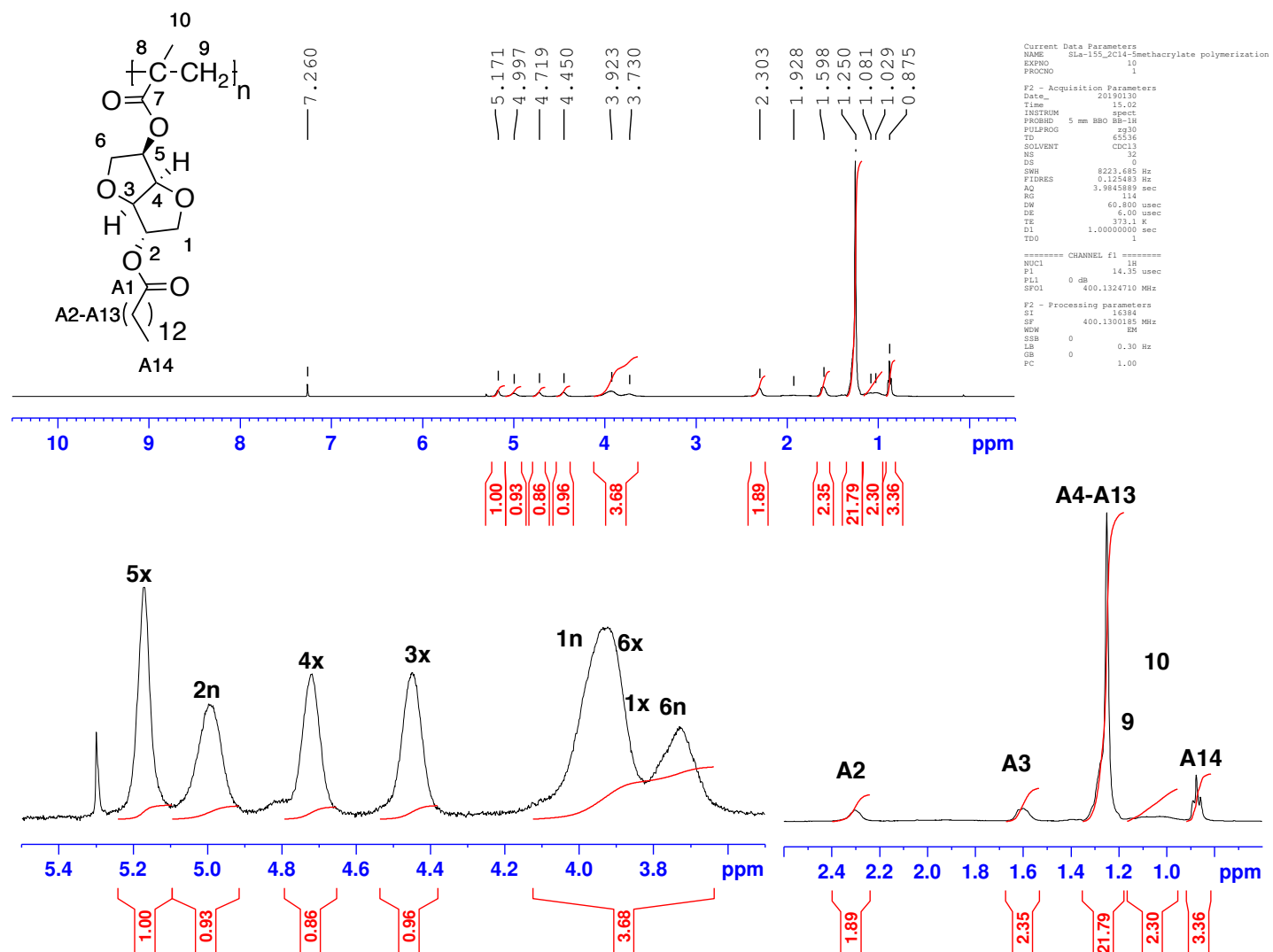
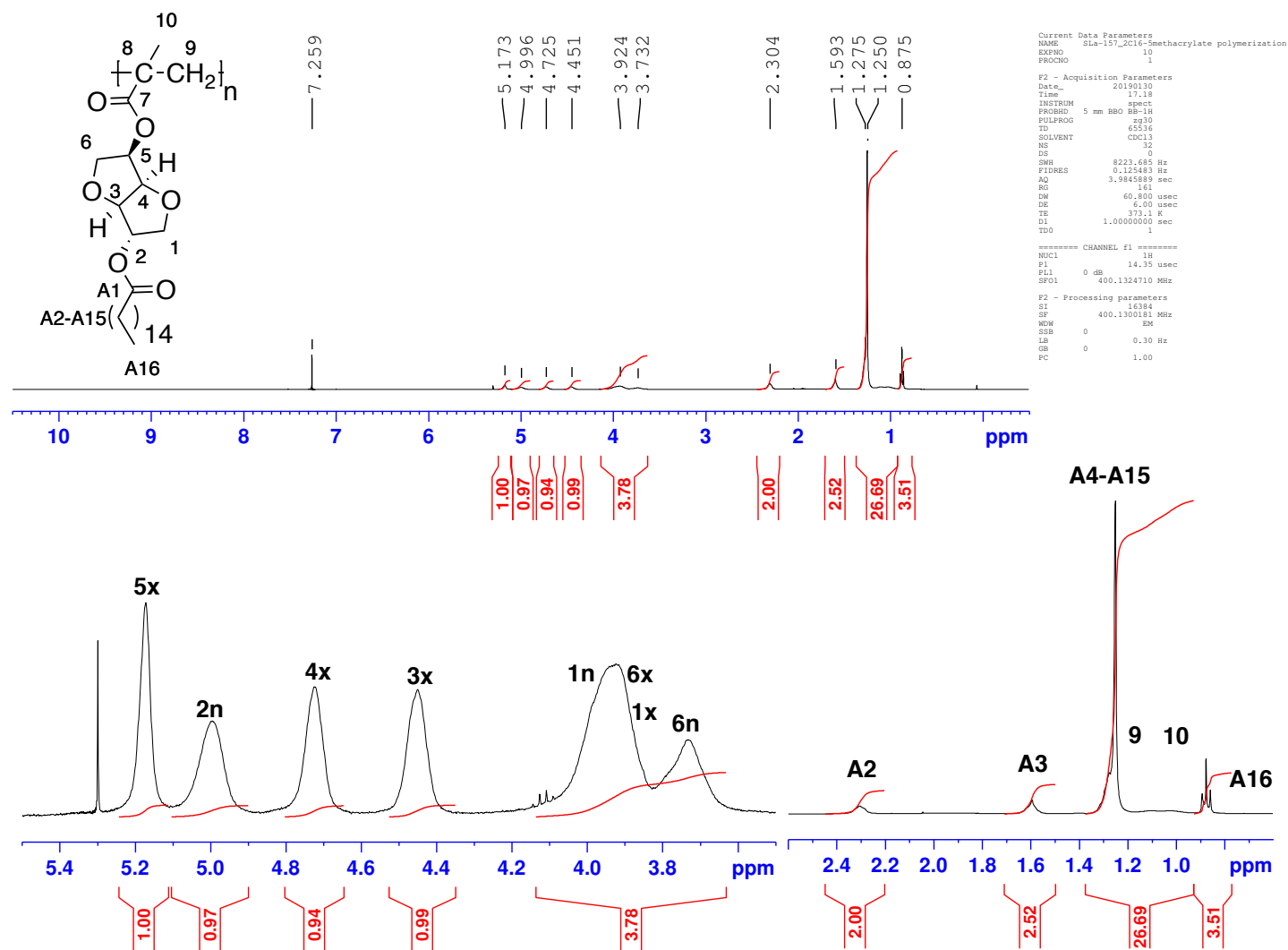


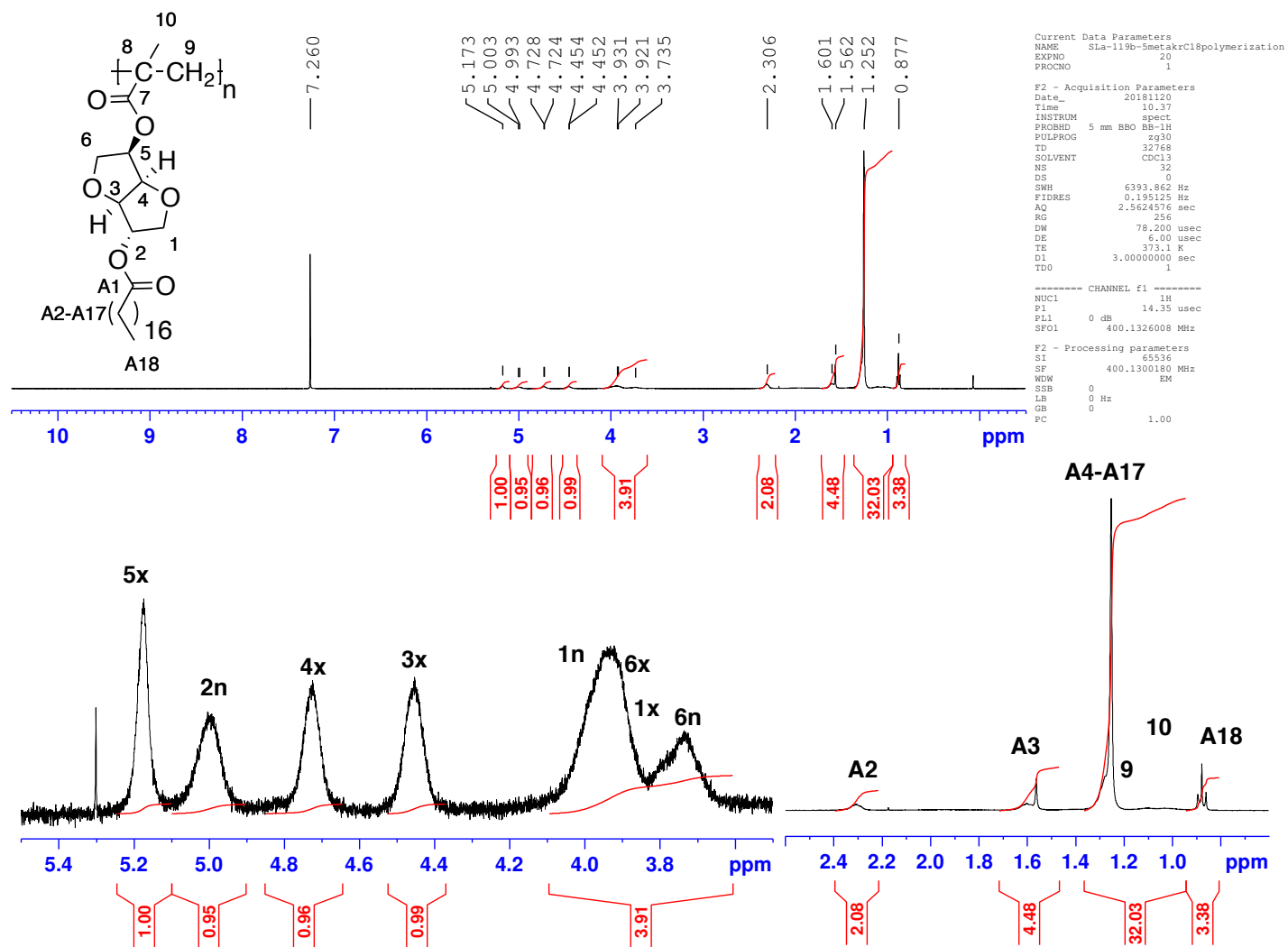
Figure S33. <sup>1</sup>H{<sup>13</sup>C} NMR spectrum of D-isosorbide-2-tridecanoate-5-methacrylate polymer PAIMA13



**Figure S34.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-tetradecanoate-5-methacrylate polymer **PAIMA14**



**Figure S35.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-hexadecanoate-5-methacrylate polymer **PAIMA16**



**Figure S36.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-octadecanoate-5-methacrylate polymer **PAIMA18**



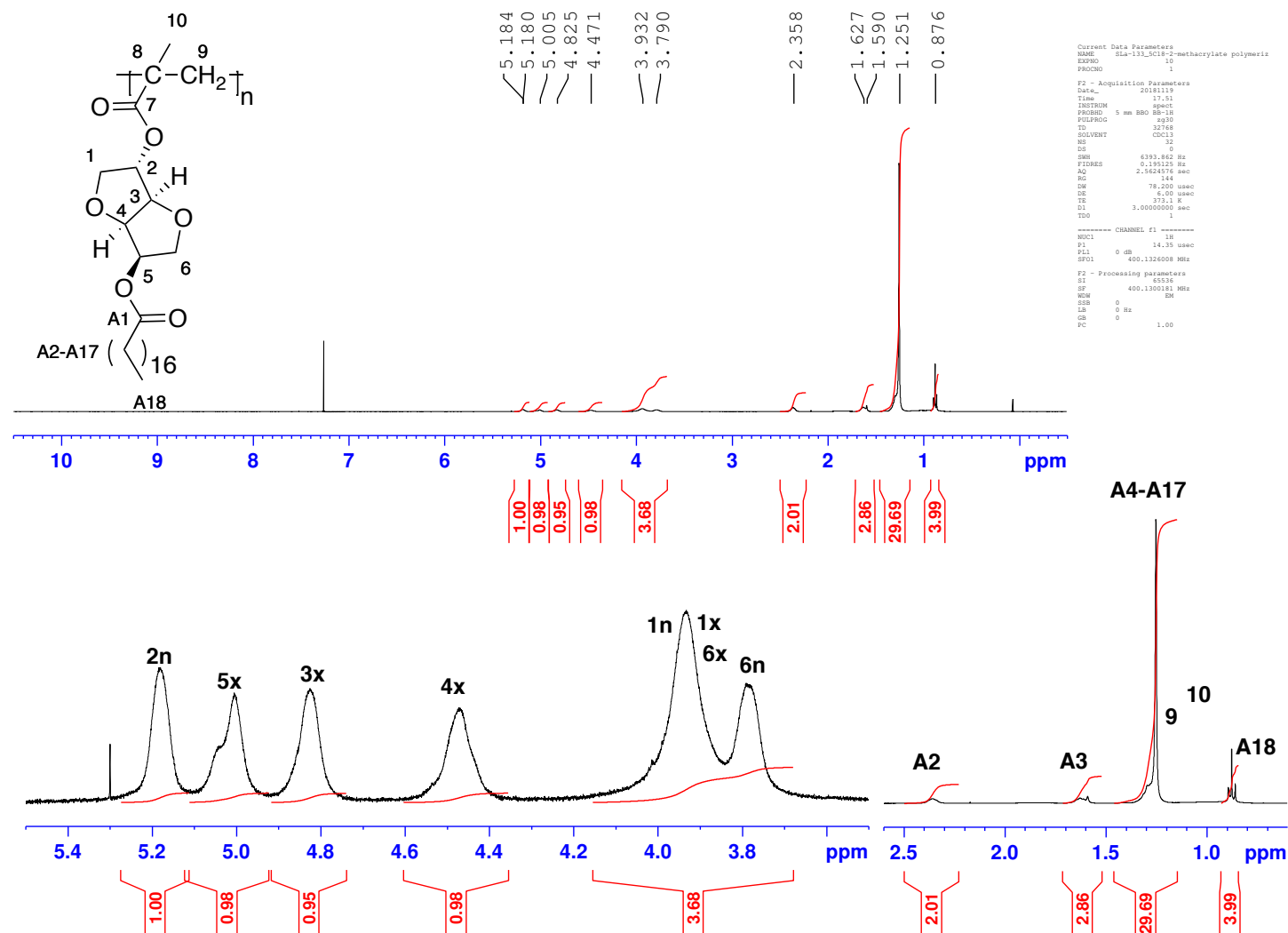
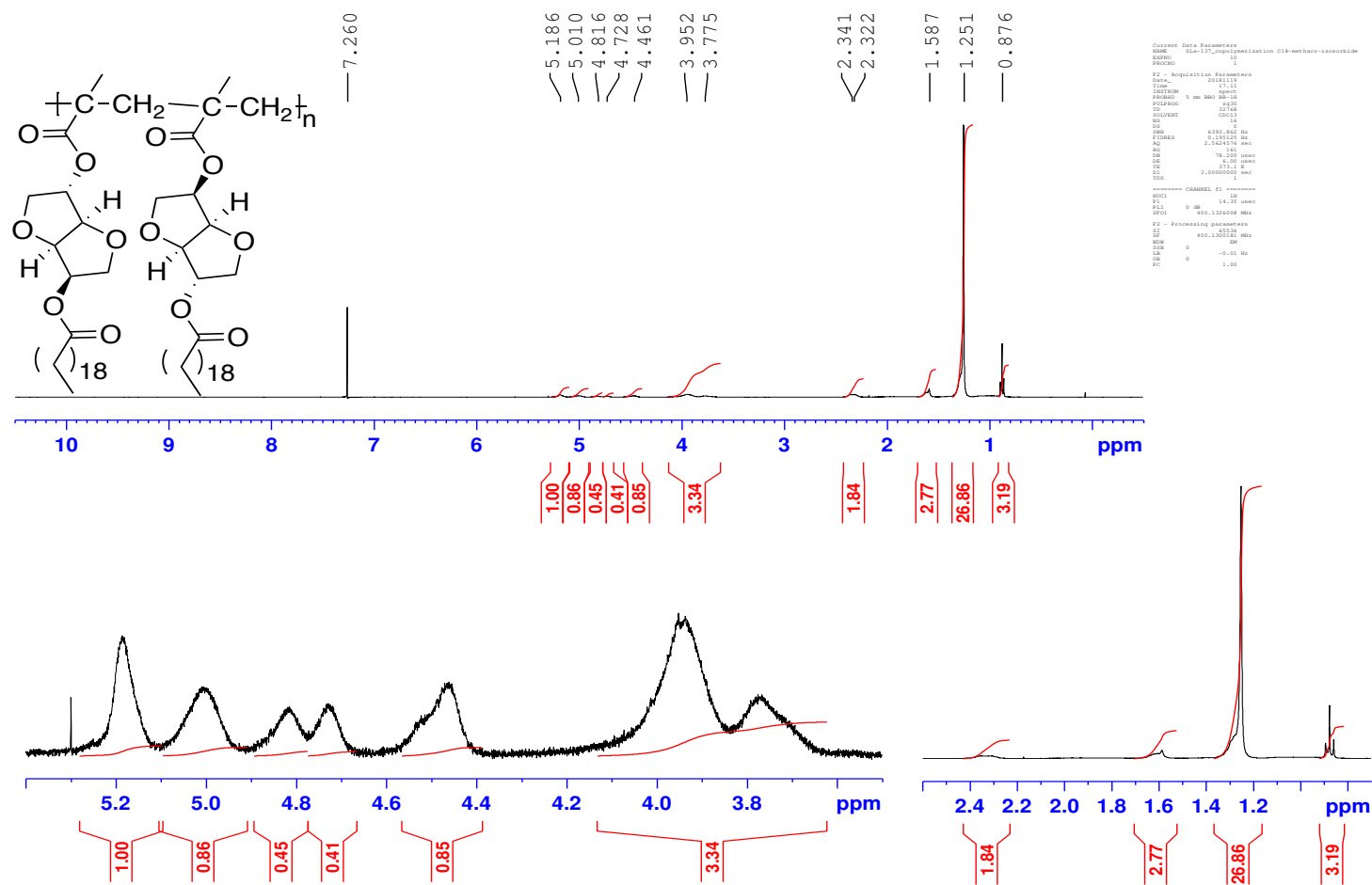
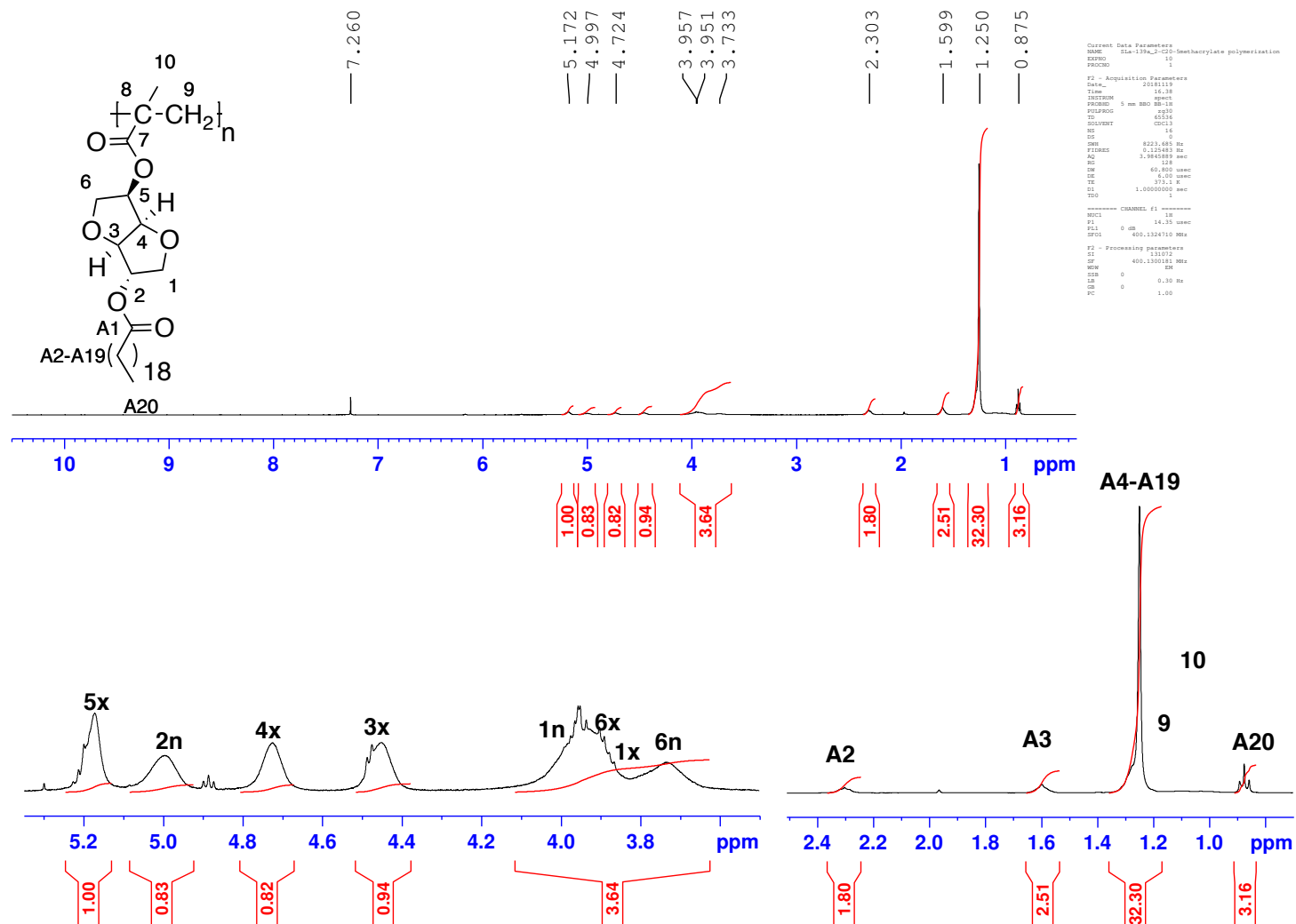


Figure S37. <sup>1</sup>H{<sup>13</sup>C} NMR spectrum of D-isosorbide-5-octadecanoate-2-methacrylate polymer *r*-PAIMA18



**Figure S38.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-5-octadecanoate-2-methacrylate and D-isosorbide-2-octadecanoate-5-methacrylate copolymer **P(AlMA18-co-*r*-AlMA18)**



**Figure S39.**  $^1\text{H}\{^{13}\text{C}\}$  NMR spectrum of D-isosorbide-2-eicosanoate-5-methacrylate polymer **PAIMA20**