Electronic Supplementary Information

for

Direct Characterization of Polymer Network through Its Retainable Units

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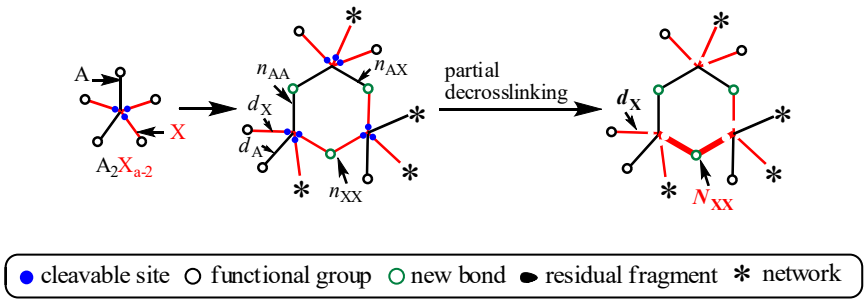
Outline

1. Theoretical analysis of network generated by A_a with cleavable groups

For a monomer containing *a* functional groups with equal reactivity shown in Scheme S1, in which two groups are uncleavable (noted as A) and a-2 groups are cleavable (noted as X), is denoted as $A_2X_{a\text{-}2}$.

1.1. *Calculation of extent of the inter- and intramolecular reactions (p_{inter} and p_{intra})*



Scheme S1 Formation of various network chains by intermolecular reaction between functional groups of $A_2X_{a\text{-}2}$ in PDN.

The intermolecular reaction of $A_2X_{a\text{-}2}$ results in three kinds of network chains, which are composed of segments AA, AX and XX as shown in **Scheme S1**. The ratios between different network chains are given by

$$n_{AA}:n_{AX}:n_{XX}= (C_2^1)^2:2C_2^1C_{a-2}^1:(C_{a-2}^1)^2=4:4(a\text{-}2):(a\text{-}2)^2 \quad (1)$$

where n_{AA}, n_{AX} and n_{XX} are the numbers of corresponding network chains.

The fraction of network chains XX (F_{XX}) is given by

$$F_{XX} \equiv \frac{n_{XX}}{n_{AA}+n_{AX}+n_{XX}} = \frac{(a-2)^2}{a^2} \quad (2)$$

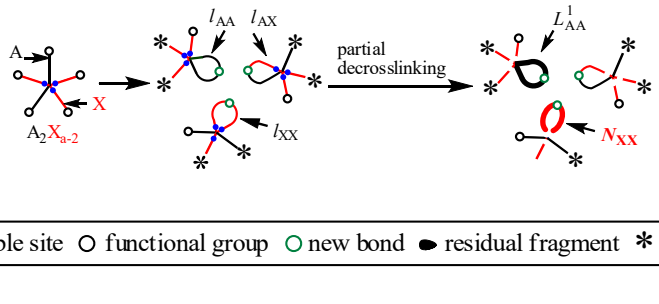
The total number of network chains (n_{net}) can be estimated from n_{XX} and F_{XX} that is given by

$$n_{net} \equiv n_{AA} + n_{AX} + n_{XX} = n_{XX}/F_{XX} = \frac{a^2}{(a-2)^2}\, n_{XX} \quad (3)$$

The extent of intermolecular reaction (p_{inter}) defined as **the reaction between two groups of two different monomers/oligomers** can be given by

$$p_{inter} = \frac{2n_{net}}{an_M} = \frac{2a}{(a-2)^2}\frac{n_{XX}}{n_M} \quad (4)$$

where n_M is the initial number of the monomer $A_2X_{a\text{-}2}$. The network chain XX can be "cut off" from the network after decrosslinking and the number of XX (n_{XX}) can be measured by normal methods. So, p_{inter} can be obtained according to n_{XX} and n_M.



Scheme S2 Formation of various primary loops by intramolecular reaction between functional groups of A_2X_{a-2} in PDN.

If intramolecular reactions occur, primary loops composed of AA , AX and XX are formed， which are shown in **Scheme S2**. The ratios between different primary loops are given by

$$l_{AA}:l_{AX}:l_{XX}=1:C_2^1C_{a-2}^1:C_{a-2}^2=1:2(a-2):0.5(a-2)(a-3) \tag{5}$$

where l_{AA}, l_{AX} and l_{XX} are the numbers of primary loops composed of corresponding segments.

The fraction of primary loop AA ($F_{l_{AA}}$) is given by

$$F_{l_{AA}} \equiv \frac{l_{AA}}{l_{AA}+l_{AC}+l_{CC}} = \frac{2}{a(a-1)} \tag{6}$$

The total number of primary loops (L^1) can be estimated from l_{AA} and $F_{l_{AA}}$ that is given by

$$L^1 \equiv l_{AA} + l_{AX} + l_{XX} = \frac{l_{AA}}{F_{l_{AA}}} = 0.5a(a-1)l_{AA} \tag{7}$$

The extent of intramolecular reaction (p_{intra}) defined as **the reaction between two different groups of the same monomer** is given by equation 8.

$$p_{intra} = \frac{2L^1}{an_M} = (a-1)\frac{l_{AA}}{n_M} \tag{8}$$

Since only loops AA preserve after decrosslinking that can be detected by normal methods p_{intra} can be obtained according to l_{AA} and n_M.

It can be seen from **Schemes S1** and **S2**, both inter- and intra-molecular reactions generate segments XX after cleavage except for A_2X_1 system, in which no loop composed of segment XX is formed (see Scheme S5). Therefore, the number of segments XX after decrosslinking includes contribution from both intermolecular reaction (n_{XX}) and intramolecular reactions (l_{XX}). The number of XX after decrosslinking (N_{XX}) is given by

$$N_{XX} = n_{XX} + l_{XX} \tag{9}$$

From equation 5, it is deduced that

$l_{XX}=0.5(a-2)(a-3)l_{AA}$ (10)

So $n_{XX} = N_{XX} - l_{XX} = N_{XX} - 0.5(a-2)(a-3)l_{AA}$ (11)

Based on equation 4, p_{inter} is given by

$$p_{inter} = \frac{2a}{(a-2)^2}\frac{N_{XX}-0.5(a-2)(a-3)l_{AA}}{n_M} \quad (12)$$

Furthermore, the ratio of p_{intra} to p_{inter}, can be given by:

$$\frac{p_{intra}}{p_{inter}} = \frac{(a-1)(a-2)^2 l_{AA}}{2a(N_{XX}-0.5(a-2)(a-3)l_{AA})} \quad (13)$$

As shown in **Scheme S1**, two kinds of dangling chains, cleavable (d_X) and uncleavable dangling chains (d_A) can be found. According to the assumption of equal activity of groups, the ratio of these two kinds of unreacted groups is given by

$d_A:d_X$ =2:(a-2) (14)

The total number of unreacted groups (d) is given by

$d = d_A+d_X$ = a/(a-2)d_X (15)

Because group X is cleavable, d_X can be measured after decrosslinking and d can be obtained as well.

The total number of functional groups (f) of the monomer A_2X_{a-2} also equals to the sum of all network chains, dangling chains and primary loops that is

$f = 2n_{net} + 2L^l + d$ (16)

According to equations 3, 7 and 15, we get

$$f = \frac{2a^2}{(a-2)^2}n_{XX} + a(a-1)l_{AA} + \frac{a}{a-2}d_X \quad (17)$$

Since the number of functional groups (f) is equal to an_M, equations 8 and 12 yield

$$p_{intra} = \frac{(a-1)(a-2)^2 L^1_{AA}}{2a(N_{XX}-0.5(a-2)(a-3)L^1_{AA})+(a-1)(a-2)^2 L^1_{AA}+(a-2)d_X} = \frac{(a-1)(a-2)^2 L^1_{AA}}{2aN_{XX}+2(a-2)L^1_{AA}+(a-2)d_X} \quad (18)$$

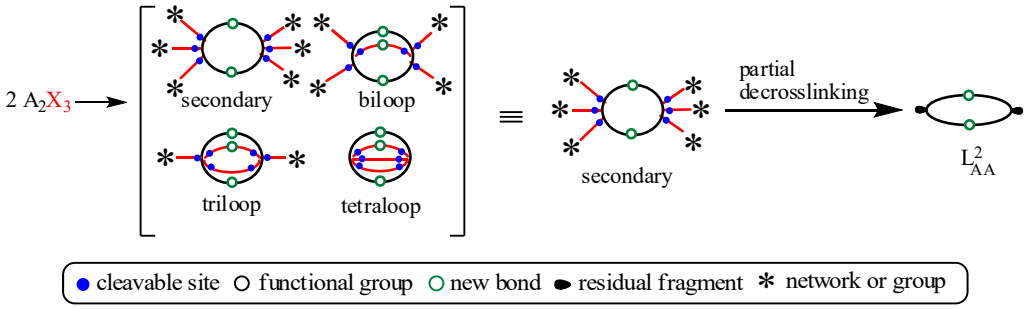
$$p_{inter} = \frac{2a(N_{XX}-0.5(a-2)(a-3)L^1_{AA})}{2a(N_{XX}-0.5(a-2)(a-3)L^1_{AA})+(a-1)(a-2)^2 L^1_{AA}+(a-2)d_X} = \frac{2a(N_{XX}-0.5(a-2)(a-3)L^1_{AA})}{2aN_{XX}+2(a-2)L^1_{AA}+(a-2)d_X} \quad (19)$$

l_{AA} is replaced by L^1_{AA} in equations 18 and 19 for convenience in the following discussion of higher-order loops.

In the network formed by A_2X_{a-2} monomer, cleavable dangling chains X, network chains XX and

primary loops AA are three kinds of small molecules can be collected after decrosslinking. The qualitative and quantitative measurement of three molecules can be achieved by general methods. If $N_{XX}: L_{AA}^{1}: d_X$ is known, the extent of reaction, both intra- and inter-molecular reactions, can be calculated by equations 18 and 19.

1.2 *Measurement of various monoloop-based structures*



Scheme S3 Formation of various monoloops in PDN.

Besides the primary loop, monoloops can be also generated by A_a. The monoloop is a macrocyclic unit composed of multiple segments. When A_2X_3 is used, various loops including secondary loop, biloop, triloop and tetraloop shown in **Scheme S3** are perhaps formed. All loops are changed to secondary loop composed of two AA segments (L_{AA}^{2}) after decrosslinking. Because the secondary loop L_{AA}^{2} can be measured, it is possible to estimate the number of all secondary loops (L^2) from the number of L_{AA}^{2}. The secondary loop is formed by reactions of two pairs of groups of two monomers, the relationship between L^2 and L_{AA}^{2} is given by

$$\frac{L_{AA}^{2}}{L^2} = \frac{1}{(C_5^2)^n} \tag{20}$$

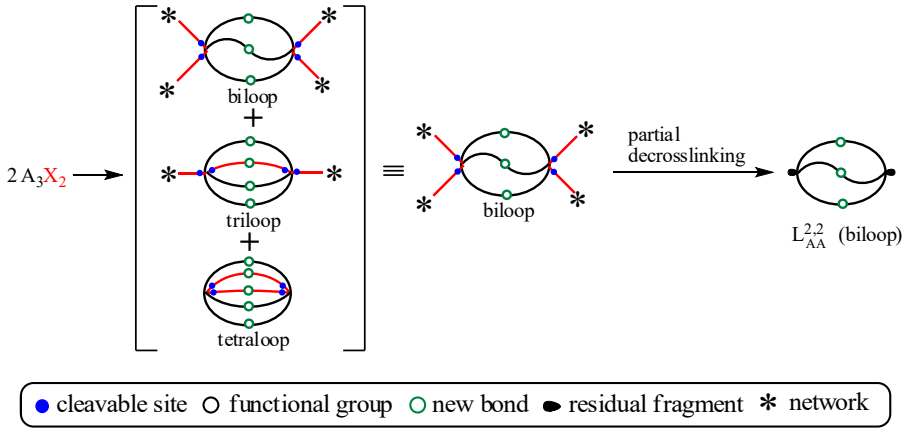
Generally, n-order monoloop (L^n) is formed by the reaction of n pairs of groups of n monomers. When $A_2X_{a\text{-}2}$ is used as monomer, the ratio of n-order monoloops composed of $(AA)_n$ (L_{AA}^{n}) to L^n is given by

$$\frac{L_{AA}^{n}}{L^n} = \frac{1}{(C_a^2)^n} = \frac{1}{(0.5a(a-1))^n} \tag{21}$$

The total number of n-order monoloops (L^n) is given by

$$L^n = (0.5a(a-1))^n L_{AA}^{n} \tag{22}$$

1.3 *Measurement of various polyloop-based structures*



Scheme S4 Formation of various polyloops in PDN.

The polyloop-based structures within the network can be explored using PDN. Here, a polyloop is one unit composed of more than one loop that has two non-adjacent bridged sites. The polyloop can be formed by reaction of more than two pairs of functional groups from two monomers that has more than two uncleavable groups. As shown in **Scheme S4**, different polyloops, such as biloop, triloop and tetraloop, can be formed by two A_3X_2. All polyloops are changed to the same biloop composed of AA segments ($L_{AA}^{2,2}$, the first superscript "2" is the order of the loop and the second "2" is the number of the loop, the subscript AA indicates the type of the segment) after decrosslinking. Because the biloop $L_{AA}^{2,2}$ can be measured, it is possible to estimate the number of all biloops ($L^{2,2}$) from the number of $L_{AA}^{2,2}$. The biloop is formed by reaction of three pairs of groups of two monomers, the relationship between $L^{2,2}$ and $L_{AA}^{2,2}$ is given by

$$\frac{L_{AA}^{2,2}}{L^{2,2}} = \frac{1}{(C_5^3)^2} \tag{23}$$

Generally, the polyloop containing n secondary loops ($L^{2,n}$) can be formed by reactions of $n+1$ pairs of groups of two $A_{n+1}X_{a\text{-}n\text{-}1}$, among which $L_{AA}^{2,n}$ is the cleavable polyloop. The relationship between $L^{2,n}$ and $L_{AA}^{2,n}$ is given by

$$\frac{L_{AA}^{2,n}}{L^{2,n}} = \frac{1}{(C_a^{n+1})^2} \tag{24}$$

So, we get

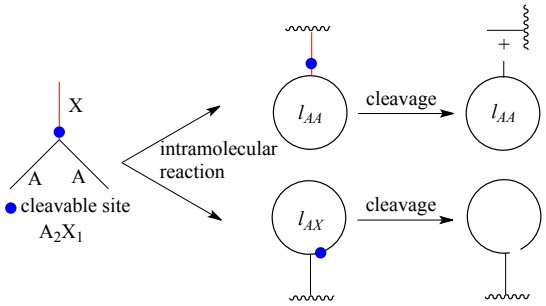
$$L^{2,n} = (C_a^{n+1})^2 L_{AA}^{2,n} \tag{25}$$

If $L_{AA}^{2,x}$ can be measured by current methods, the total numbers of polyloops can be obtained.

1. 4 Mixed monomers

If both A_2X_1 and A_3X_1 are used, monoloops with different orders and the polyloop can be simultaneously studied. The monoloops and polyloops with the same number of the segment can be discriminated by different residual fragments. For example, both $L_{AA}^{2,2}$ and L^3 have three AA segments, while the former one has two residual cores and the latter one has three cores. This difference in molar mass can be measured by mass spectrum.

1.5 A_2X_1 system



Scheme S5 Intramolecular reactions between functional groups of A_2X_1

If a=3 (A_2X_1 system in **Scheme S5**), the case is simple since no loop containing segments XX is formed. Therefore, no segment XX is generated from cleavage of loops, which yields $N_{XX} = n_{XX}$. The equations 8, 12 and 13 yield

$$p_{intra} = 2\frac{L_{AA}^1}{n_M} \tag{26}$$

$$p_{inter} = 6\frac{N_{XX}}{n_M} \tag{27}$$

$$\frac{p_{intra}}{p_{inter}} = \frac{L_{AA}^1}{3N_{XX}} \tag{28}$$

The equations 18 and 19 yield

$$p_{intra} = \frac{2L_{AA}^1}{6N_{XX} + 2L_{AA}^1 + d_X} \tag{29}$$

$$p_{inter} = \frac{6N_{XX}}{6N_{XX} + 2L_{AA}^1 + d_X} \tag{30}$$

Let $r_1 = L_{AA}^1/d_X$ and $r_2 = N_{XX}/d_X$, then

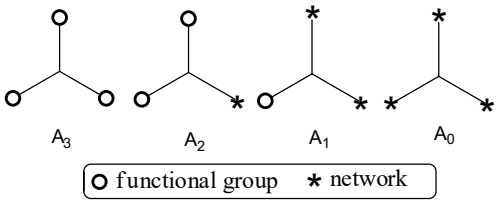
$$p_{intra} = \frac{2r_1}{6r_2 + 2r_1 + 1} \tag{31}$$

$$p_{inter} = \frac{6r_2}{6r_2 + 2r_1 + 1} \tag{32}$$

$$\frac{p_{intra}}{p_{inter}} = \frac{r_1}{3r_2} \tag{33}$$

For A_2X_1 system, equations 31-33 can be used to calculate the extent of reaction, both intra- and inter-molecular reactions.

1.6 Theoretical ratio of p_{intra}/p_{inter}



Scheme S6 Different oligomers formed in the polymerization of A_3

The intramolecular reaction is a unimolecular reaction that is determined by the concentration of oligomers might undergo such reaction. In A_3 system, primary loops are only formed via intramolecular reactions of oligomers having at least two unreacted groups, such as A_3 and A_2 shown in Scheme S6, while A_1 and A_0 do not result in primary loops. The concentration of A_3 and A_2 are $[M]_0(1-p)^3$ and $C_3^2[M]_0p(1-p)^2$, where $[M]_0$ and p are initial concentration of monomer and the extent of reaction. Since A_3 has three ways to form the primary loop and A_2 has one, the formation rate of primary loop (R_{intra}) is given by

$$R_{intra} = k_{intra}(3[M]_0(1-p)^3 + C_3^2[M]_0p(1-p)^2) = 3k_{intra}[M]_0(1-p)^2 = k_{intra}[A]_0(1-p)^2 \quad (34)$$

where k_{intra} is the rate parameter of cyclization reaction, $[A]_0$ is the initial concentration of functional groups.

On the other hand, if the intermolecular reaction is the second order reaction of functional groups, the rate of intermolecular reaction (R_{inter}) is given by

$$R_{inter} = k_{inter}[A]^2 = k_{inter}[A]_0^2(1-p)^2 \quad (35)$$

where k_{inter} is the rate parameter of intermolecular reactions.

$$\frac{R_{intra}}{R_{inter}} = \frac{k_{intra}}{k_{inter}[A]_0} \quad (36)$$

The ratio of intra- and intermolecular reaction rate is given by equation 36, which suggests that the ratio keeps constant and is independent of the extent of reaction. It can be deduced that the ratio p_{intra}/p_{inter} given by equation 37 keeps constant and is independent of the extent of reaction.

$$\frac{p_{intra}}{p_{inter}} = \frac{\int R_{intra}}{\int R_{inter}} = \frac{k_{intra}}{k_{inter}[A]_0} \quad (37)$$

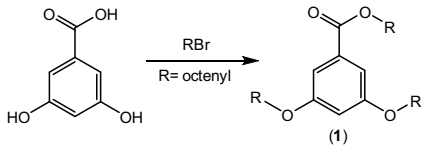
2. Experimental section

2.1 Materials and methods

Tetrahydrofuran (THF) was distilled from sodium. Dichloromethane (DCM) was distilled from calcium hydride. 8-bromo-1-octene (TCI, 98.0%), 3,5-dihydroxybenzoic acid (TCI, 98%), 7-octenyl acetate (TCI, 98.0%), methyl 3,5-dihydroxybenzoate (J&K, 96.0%), Grubbs 1st Generation catalyst $(PCy_3)_2Cl_2$-RuCHPh (Sigma-Aldrich, 96.0%) (Sigma-Aldrich, 96.0%) were used as received. NMR spectra were collected with a Bruker 400 MHz or 500 MHz NMR using $CDCl_3$ as a solvent. Elemental analyses were performed on a Flash EA1112 (Thermo Finnigan). GC-MS (m/z) spectra were performed on a GCMS-QP2010. High resolution mass spectra (HRMS) were performed on a GCT Premier GC-TOFMA mass spectrometer. MALDI-TOF MS was performed on a Bruker Ultraflex. 2,5-Dihydroxylbenzoic (20 mg/mL) solution in THF was used as matrix. Samples were dissolved in THF and mixed with NaTFA (5 mg/mL) in 1:1 ratio, then the mixture was mixed with the matrix solution in 1:1 ratio.

2.2 Synthesis of organic compounds

2.2.1 Synthesis of A_2X_1 monomer 7-octenyl-3,5-di-(7-octenyl-1-oxy)-benzoate (1)

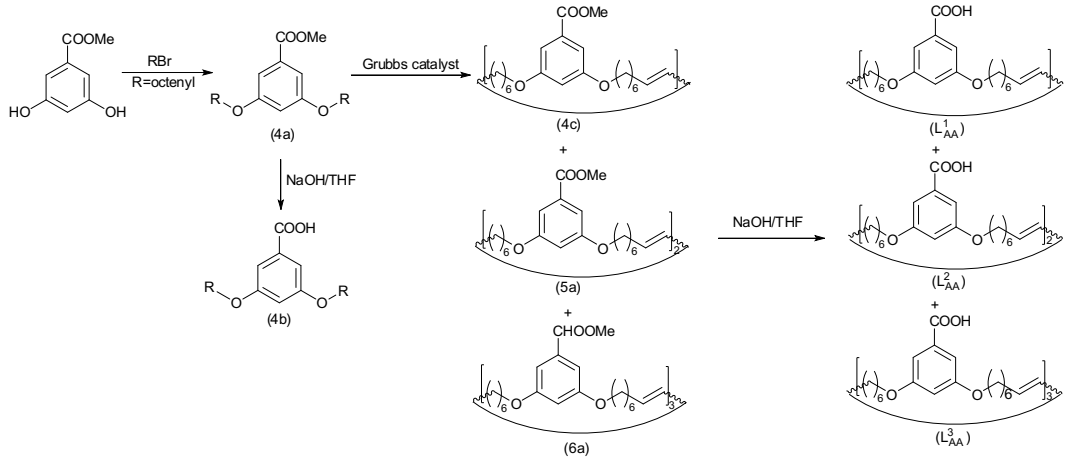


Scheme S7 Synthesis of A_2X_1 monomer (**1**)

3.82 g of 8-bromo-1-octene (20 mmol), 0.77 g of 3,5-dihydroxybenzoic acid (5 mmol), 5.52 g of potassium carbonate (40 mmol), 0.05 g of 18-crown-6 and 30 mL of DMF were placed in 100 mL Schlenk flask. The solution was bubbled with N_2 for 15 minutes then the mixture was stirred at 65 °C was stirred at 65 °C for 24 hours. After reaction the suspension was filtered and obtained solution was evaporated under vacuum to afford crude product. The crude product was dissolved in 40 mL of DCM and washed by 30 mL of brine for 3 times. The oil phase was then dried over magnesium sulfate. After the solvent was evaporated, the product was purified by flash chromatography on silica-gel (300-400 mesh) with petroleum ether/ethyl acetate (from 100/1 to 10/1 by volume) to give compound 7-octenyl 3,5-bis(7-octenyl-1-oxy)benzoate (**1**) in 80% yield (1.94 g) as light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.14 (d, 2H), 6.64-6.61 (t, 1H),

5.88-5.74 (m, 3H), 5.08-4.86 (m, 6H), 4.32-4.26 (t, 2H), 4.01-3.93 (t, 4H), 2.12-1.99 (m, 6H), 1.85-1.70 (m, 6H), 1.52-1.31 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.79, 160.34, 139.23, 132.45, 114.57, 107.88, 106.45, 77.30, 68.47, 65.45, 33.97, 29.39, 29.07, 26.13. GC-MS (EI, m/z): 484.4 $[M]^+$, 154.0 $[M-330.4]^+$, 137.0 $[M-347.4]^+$, 69.1 $[M-415.3]^+$. HRMS (ESI) m/z calculated for $C_{31}H_{48}O_4$ $[M]^+$: 484.3553. Found: 484.3550.

2.2.2 Synthesis of cleavable primary, secondary, tertiary loops, and related compounds



Scheme S8 Preparation of primary ($\mathbf{L^1_{AA}}$), secondary ($\mathbf{L^2_{AA}}$) and tertiary ($\mathbf{L^3_{AA}}$) loops

*Synthesis of methyl 3,5-bis(7-octenyloxy)benzoate (**4a**)*

Methyl 3,5-bis(7-oct-1-enyloxy)benzoate (**4a**) was prepared from methyl 3,5-dihydroxybenzoate and 8-bromo-1-octene following the procedure described in the synthesis of **1**. The product was purified by flash chromatography on silica-gel (300-400 mesh) with petroleum ether/ethyl acetate (from 100/1 to 10/1 by volume) to give compound **4a** in 83% yield (1.65 g) as light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.14 (d, 2H), 6.65-6.61 (t, 1H), 5.87-5.75 (m, 2H), 5.06-4.89 (m, 4H), 4.01-3.92 (t, 4H), 3.92-3.86 (s, 3H), 2.20-1.95 (m, 4H), 1.85-1.68 (m, 4H), 1.55-1.30 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.18, 160.35, 139.20, 132.03, 114.55, 107.82, 106.76, 68.45, 52.40, 33.94, 29.36, 29.05, 26.11. GC-MS (EI, m/z): 388.3 $[M]^+$, 279.2 $[M-109.1]^+$, 168.1 $[M-220.2]^+$, 69.1 $[M-319.2]^+$. HRMS (ESI) m/z calculated for $C_{24}H_{36}O_4$ $[M]^+$: 388.2614. Found: 388.2614.

*Synthesis of **4b** by hydrolysis of **4a***

The 3,5-bis(7-octenyloxy)benzoic acid (**4b**) was prepared by hydrolysis of methyl 3,5-bis(7-oct-1-enyloxy)benzoate (**4a**) in 97% yield (139.7mg) as light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (d, 2H), 6.70-6.67 (t, 1H), 5.92-5.73 (m, 2H), 5.08-4.90 (m, 4H), 4.05-3.92 (t, 4H), 2.14-2.00 (m, 4H), 1.88-1.70 (m, 4H), 1.56-1.31 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.21, 160.20, 139.00, 130.95, 114.34, 108.16, 107.50, 68.31, 33.72, 29.12, 28.84, 25.88. GC-MS (EI, m/z, %): 374.4 $[M]^+$, 154.1 $[M-220.3]^+$, 110.2 $[M-264.2]^+$, 69.2 $[M-305.2]^+$. HRMS (ESI) m/z calculated for $C_{23}H_{36}O_3$ $[M]^+$: 374.2457. Found: 374.2455.

*Synthesis of metacyclophanes (**4c, 5a** and **6a**)*

The mixture of **4c 5a** and **6a** were prepared from **4a** by reported method[2] and the three metacyclophances were obtained by flash chromatography on silica-gel (300-400 mesh) with petroleum ether/ethyl acetate (from 100/1 to 10/1 by volume)

Fraction 1 is compound **4c**, as a colorless solid in 45.2% yield (40.7mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.14 (m, 2H), 6.67-6.61 (m, 1H), 5.37-5.28 (m, 2H), 4.15-3.99 (m, 4H), 3.92-3.84 (d, 3H), 2.09-1.89 (m, 4H), 1.84-1.69 (m, 4H), 1.55-1.26 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.89, 159.83, 132.06, 130.53, 109.69, 105.74, 68.37, 52.18, 31.92, 28.86, 27.70, 27.30, 25.11. GC-MS (EI, m/z, %): 360.3 $[M]^+$, 329.3 $[M-31.0]^+$, 168.1 $[M-192.2]^+$, 137.1 $[M-223.2]^+$. HRMS (ESI) m/z calculated for $C_{22}H_{32}O_4$ $[M]^+$: 360.2301. Found: 360.2300.

Fraction 2 is compound **5a**, as a colorless solid in 39.8% yield (39.5mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.12 (m, 4H), 6.65-6.69(m, 2H), 5.43-5.30 (m, 4H), 4.01-3.91 (t, 8H), 3.91-3.86 (s, 6H), 2.11-1.91 (m, 8H), 1.82-1.69 (m, 8H), 1.55-1.27 (m, 24H).

Fraction 3 is compound **6a**, as a colorless solid in 11.4% yield (10.3mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.12 (m, 6H), 6.65-6.69(m, 3H), 5.43-5.30 (m, 6H), 4.01-3.91 (t, 12H), 3.91-3.86 (s, 9H), 2.11-1.91 (m, 12H), 1.82-1.69 (m, 12H), 1.55-1.27 (m, 36H).

Synthesis of various loops L^1_{AA}, L^2_{AA} *and* L^3_{AA}

30.7mg of 4c (0.70mmol), and 10 mL of THF were added into a round flask. After the solid was

dissolved completely, 5 mL of 1M NaOH solution in methanol was added. The mixture was stirred under 40 ℃ for 12 hours. Then Excessive amounts of dilute aqueous solution of HCl was added and stirred for an hour. The product was extracted from the mixture with DCM, then dried with $MgSO_4$. After the solvent was evaporated, pure product of L^1_{AA} was obtained. (yield 29.2mg, 98%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 6.72-6.65 (m, 1H), 5.38-5.27 (m, 2H), 4.16-4.01 (m, 4H), 2.10-1.91 (m, 4H), 1.84-1.69 (m, 4H), 1.55-1.28 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.76, 159.90, 130.54, 110.21, 68.44, 31.93, 28.87, 27.69, 27.32, 25.13. GC-MS (EI, m/z, %): 346.3 $[M]^+$, 154.1 $[M-192.2]^+$, 81.2 $[M-265.1]^+$. HRMS (ESI) m/z calculated for $C_{21}H_{32}O_3$ $[M]^+$: 346.2144. Found: 346.2145.

Loop L^2_{AA} was synthesized by the same method for loop L^1_{AA} (yield 24.5mg, 86%). ^{1}H NMR (400 MHz, THF-d^8) δ 7.06-6.97 (m, 4H), 6.57-6.49 (m, 2H), 5.35-5.19 (m, 4H), 3.92-3.78 (t, 8H), 2.02-1.81 (m, 8H), 1.74-1.55 (m, 8H), 1.47-1.20 (m, 24H). ^{13}C NMR (101 MHz, THF-d^8) δ 166.50, 160.19, 132.64, 130.25, 107.43, 105.69, 67.68, 32.26, 29.37, 29.08, 28.50, 25.7. HRMS (ESI) m/z calculated for $C_{42}H_{60}O_8$ $[M]^+$:692.4288. Found: 692.4289.

Loop, L^3_{AA} was synthesized by the same method for loop L^1_{AA} (yield 8.1mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 6H), 6.70-6.62 (m, 3H), 5.45-5.31 (m, 6H), 4.04-3.86 (t, 12H), 2.14-1.87 (m, 12H), 1.86-1.66 (m, 12H), 1.56-1.27 (m, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.66, 160.14, 130.40, 108.11, 107.59, 68.25, 32.37, 30.33, 29.37, 28.57, 25.75. HRMS (ESI) m/z calculated for $C_{63}H_{90}O_{12}$ $[M]^+$:1038.6432. Found: 1038.6432.

2.3 Polymerization of A_2X and decrosslinking process

2.3.1 General Procedure for Polymerization

0.2904 g of monomer **1** (0.6 mmol) was dissolved in 2 mL of DCM in a 10 mL Schlenk flask and degassed with Freeze-Pump-Thaw cycling 3 times. 0.0074 g of Grubbs 1st Generation catalyst (0.009 mmol) was dissolved in 1.5 mL of DCM. After being degassed with Freeze-Pump-Thaw cycling 3 times, 1 mL of the catalyst solution was added into the Schlenk flask using a syringe under nitrogen. The solution was stirred under 40 ºC for a given time and quenched by stirred with 2 mL of vinyl ethyl ether for an hour. Then the mixture was poured into 100 mL of 1,2-dichloroethane

and heated to 75 ºC for another hour to deactivate the catalyst. After filtration, the gel part was further extracted with 100 mL of DCM for three times. The combined soluble fractions were evaporated to provide the sol part. The yields of sol and gel parts were determined by gravimetry.

2.3.2 General procedure for decrosslinking

The 150-200 mg of polymer sample and 25 mL of THF were added into a round flask. When the sample was gel, it was fully swelled before further treatment. 5 mL of 1 M NaOH solution in methanol was added and the mixture was stirred under 40 °C for 12 hours. Then excessive amount of dilute aqueous solution of HCl was added and stirred for an hour. The product was extracted from the mixture with DCM, then dried with $MgSO_4$. After the solvent was evaporated, a decrosslinked product was obtained.

2.4 Quantitative measurement of the extent of reaction

2.4.1 Measurement of the extent of reaction (*p*)

Since terminal and internal C=C bonds can be detected by ^{1}H NMR, the extent of reaction can be estimated from the peak area of corresponding proton. The peak areas of H_a (S_a) and H_b (S_b) in Figure 1 represent the amount of internal and terminal C=C bonds respectively, which is related to the total free end group of monomer and the total formed bond within the polymer (both linear and cyclic bonds). The following quantitative relationships are obtained.

$$0.5S_a = n_{net} + L^1 \quad ; \quad 0.5S_b = d \tag{38}$$

According to equation 3, 7 and 15,

$$0.5S_a = n_{net} + L^1 = \frac{a^2}{(a-2)^2}\, n_{XX} + 0.5a(a-1)l_{AA} \tag{39}$$

$$0.5S_b = d = a/(a\text{-}2)d_X \tag{40}$$

When a=3, according to equation 11, $n_{xx}=N_{xx}$.. Equations 39 and 40 leads to

$$0.5S_a = 9N_{XX} + 3L^1_{AA} = 3(3N_{XX} + L^1_{AA}) \tag{41}$$

$$0.5S_b = 3d_X \tag{42}$$

In equation 41, l_{AA} is replaced by L^1_{AA} as previous mentioned.

For A_2X_1 system , from equations 29 and 30, we get

$$p_{total} = p_{intra} + p_{intel} = \frac{6N_{XX}+2L^1_{AA}}{6N_{XX}+2L^1_{AA}+d_X} \tag{43}$$

Combination of equations 41-43 results

$$p_{total} = \frac{S_a}{S_a + S_b/2} \tag{44}$$

On the other side, according to the definition of the extent of reaction, the total extent of reaction (p_{total}) of soluble products, before and after decrosslinking, can be calculated as

$$p_{total} = \frac{2[C=C]_{internal}}{2[C=C]_{internal} + [C=C]_{terminal}} = \frac{S_a}{S_a + S_b/2} \tag{45}$$

The equation 45 is the same as equation 44. where S_a and S_b are peak areas of H_a and H_b in ^{1}H NMR spectra.

2.4.2 Calculation of extent of reaction contributed from primary loop (p_{intra})

In A_2X_{a-2} system, only loops composed of AA segments can be detected as cyclic structure after decrosslinking. The peak area of H_f (S_f) of cleaved product in Figure 1 represent the amount of primary loops composed of AA (L^1_{AA}); the sum peak area of H_e (S_e) and H_f (S_f) of cleaved product in Figure 1 correspond to the total amount of group A, which is related to the amount of monomer (n_M). The following quantitative relationships are obtained.

$$S_f = 4L^1_{AA}; \qquad S_e + S_f = 2[A] = 4n_M \tag{46}$$

According to equation 26, we get

$$p_{intra} = \frac{2L^1_{AA}}{n_M} = \frac{S_f/2}{(S_f + S_e)/4} = \frac{2S_f}{S_f + S_e} \tag{47}$$

2.4.3 Calibration method for peak intensities of different loops

The mixture of n_1 mol of L^1, n_2 mol of L^2 and n_3 mol of L^3 was measured by MALDI-TOF MS by the same test condition as polymer samples and three peaks' intensities (M+Na) were I_1, I_2, and I_3. The calibration factors (F_i) of three loops are defined as

$F_1 = n_1/I_1$, $F_2 = n_2/I_2$, $F_3 = n_3/I_3$ (48)

According to equation 22, for A_2B_1 (n=3), the number of the primary (L^1), secondary (L^2) and tertiary (L^3) loops in polymer is given by following equations,

$[L^1] = 3L^1_{AA}$; $[L^2] = 9L^2_{AA}$; $[L^3] = 27L^3_{AA}$

The intensities of above three loops composed of AA of each sample, T_1, T_2 and T_3, were obtained from its MALDI-TOF-MS. The molar ratio of different loops of the test sample is calculated by

equation 49.

$$[L^1]:[L^2]:[L^3]=T_1*F_1:3T_2*F_2:9T_3*F_3 \quad (49)$$

3. Tables

Table S1. Characterization of polymer prepared by A_2X_1 monomers

Run	Time (min)	M_n/Đ[b]	p_{total} [c] p_{sol}[f]/p_{sol}^c[g]/p_{gel}^c[h]	p_{intra}*100[d]	p_{intra}/p_{inter}[e] *100	$[L^2]/[L^1]$[k] *100	$[L^3]/[L^1]$[k] *100
1	20	1600/2.76	0.51/0.51/-	2.53[i]/-[j]	5.2[i]/-[j]	0.86[i]/-[j]	0.64[i]/-[j]
2	40	1760/17.3	0.66/0.64/-	3.50/-	5.8/-	9.2/-	7.7/-
3	60	2180/50.3	0.75/0.74/-	4.00/-	5.7/-	15/-	9.3/-
4	86	1780/10.3	0.73/0.75/0.79	5.50/3.51	7.9/4.6	27/40	25/23
5	96	3109/14.1	0.73/0.71/0.81	6.00/2.51	9.2/3.2	11/38	8.9/28

a) polymerization conditions: [1] = 0.2 M, [Ru]= 0.002 M, 40 ºC, CH_2Cl_2. b) number-average molar mass (in Da) and its distribution index of soluble part of product; c) the total extent of reaction estimated by $S_a/(S_a + 0.5S_b)$, where S_a and S_b are peak areas of H_a and H_b in ^{1}H NMR spectra; d) extent of reaction contributed from all primary loops (p_{L^1}), estimated by $2S_f/(S_f + S_e)$; e) calculated by $p_{L^1}/(p_{sol}^c - p_{L^1})$ or $p_{L^1}/(p_{gel}^c - p_{L^1})$; f) soluble polymer; g) cleaved soluble polymer; h) cleaved gel; i) cleaved soluble polymer; j) cleaved gel. k) molar ratio of primary, secondary and tertiary loops estimated by MALDI-TOF MS

Table S2 The peaks intensities of primary, secondary and tertiary loops measured by MALDI-TOF MS[a]

Polymerization time (min)	L^1	L^2	L^3	Noise	Error (%)[b]
20	37556	4078	1384	100	0.3-7.2
40	2448	2829	1082	80	2.8-7.4
60	1535	2841	828	100	3.5-12
86(sol)	848	2902	1236	100	3.5-12
86(gel)	574	2876	756	100	3.5-17
96(sol)	7330	10344	3763	200	1.9-5.3
96(gel)	2419	11573	3878	400	3.5-17

a) The data are collected from Figure S13-S19; b) error % = noise/max(L^1, L^2, L^3)*100 - noise/min(L^1, L^2, L^3)*100

4. Collections of spectra data

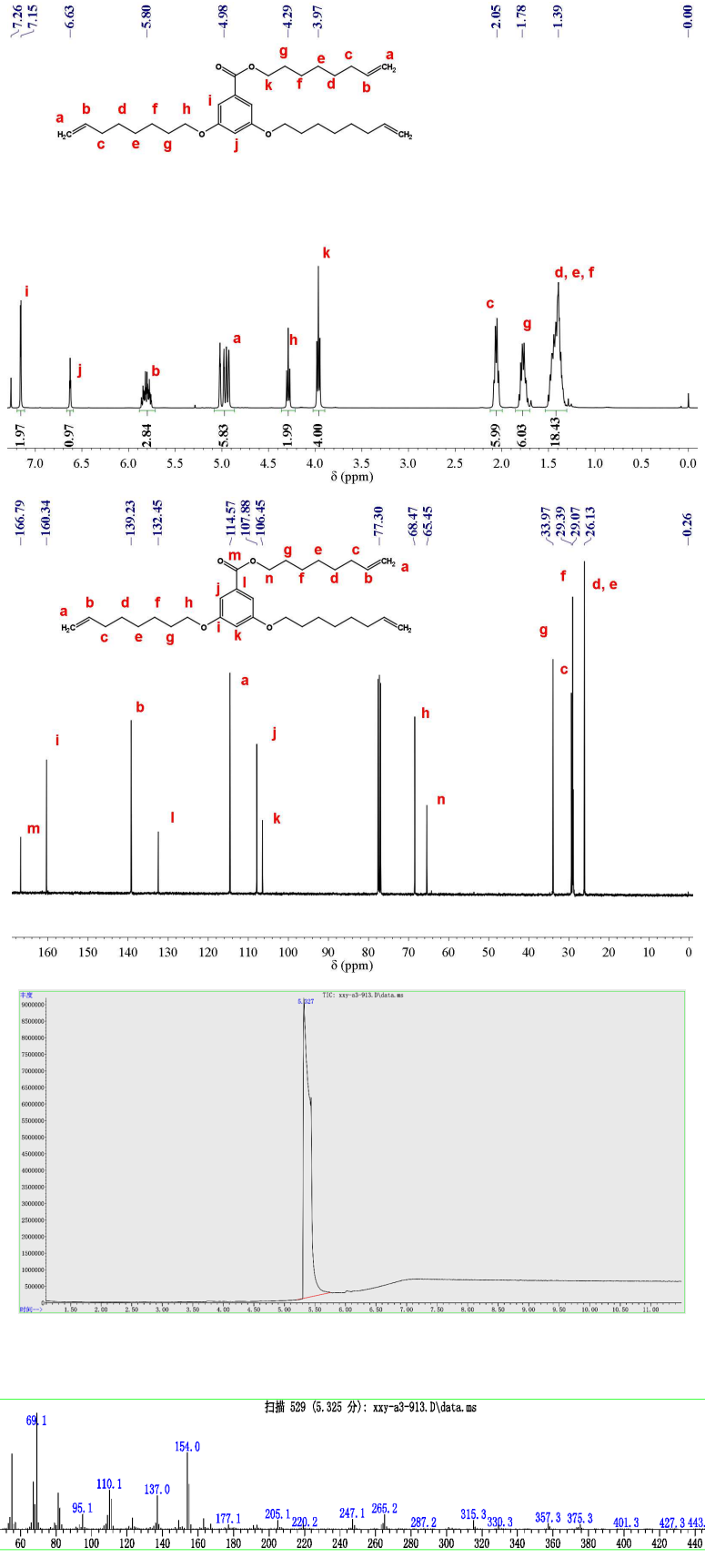


Figure S1 ^{1}H and ^{13}C NMR, GC-MS spectra of monomer A_2X (**1**)

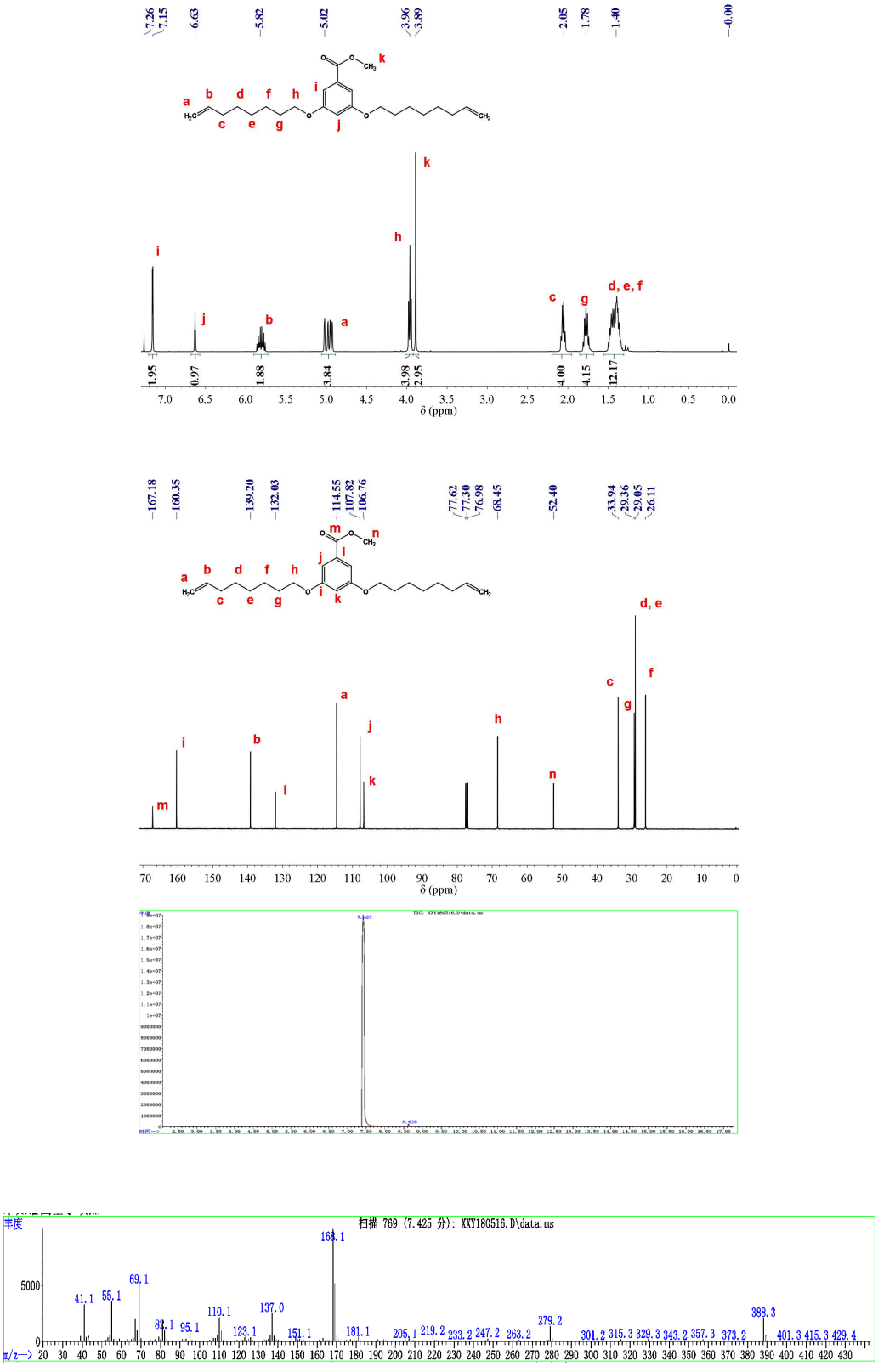


Figure S2 ^{1}H and ^{13}C NMR, GC-MS spectra of methyl 3,5-bis(oct-5-enyloxy)benzoate (**4a**)

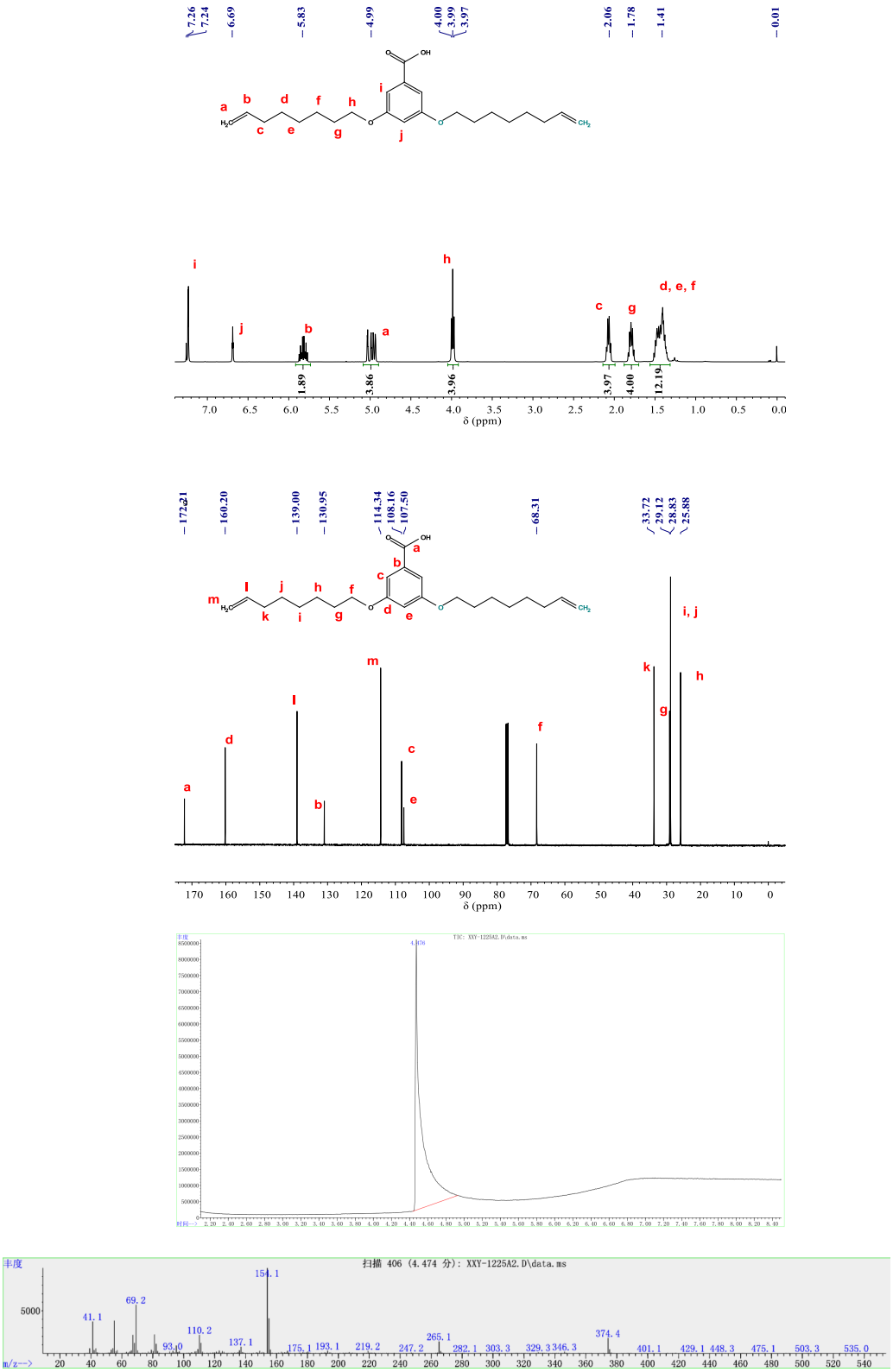


Figure S3 ^{1}H and ^{13}C NMR, GC-MS spectra of 3,5-di-(7-octenyloxy)-benzoic acid (**4b**)

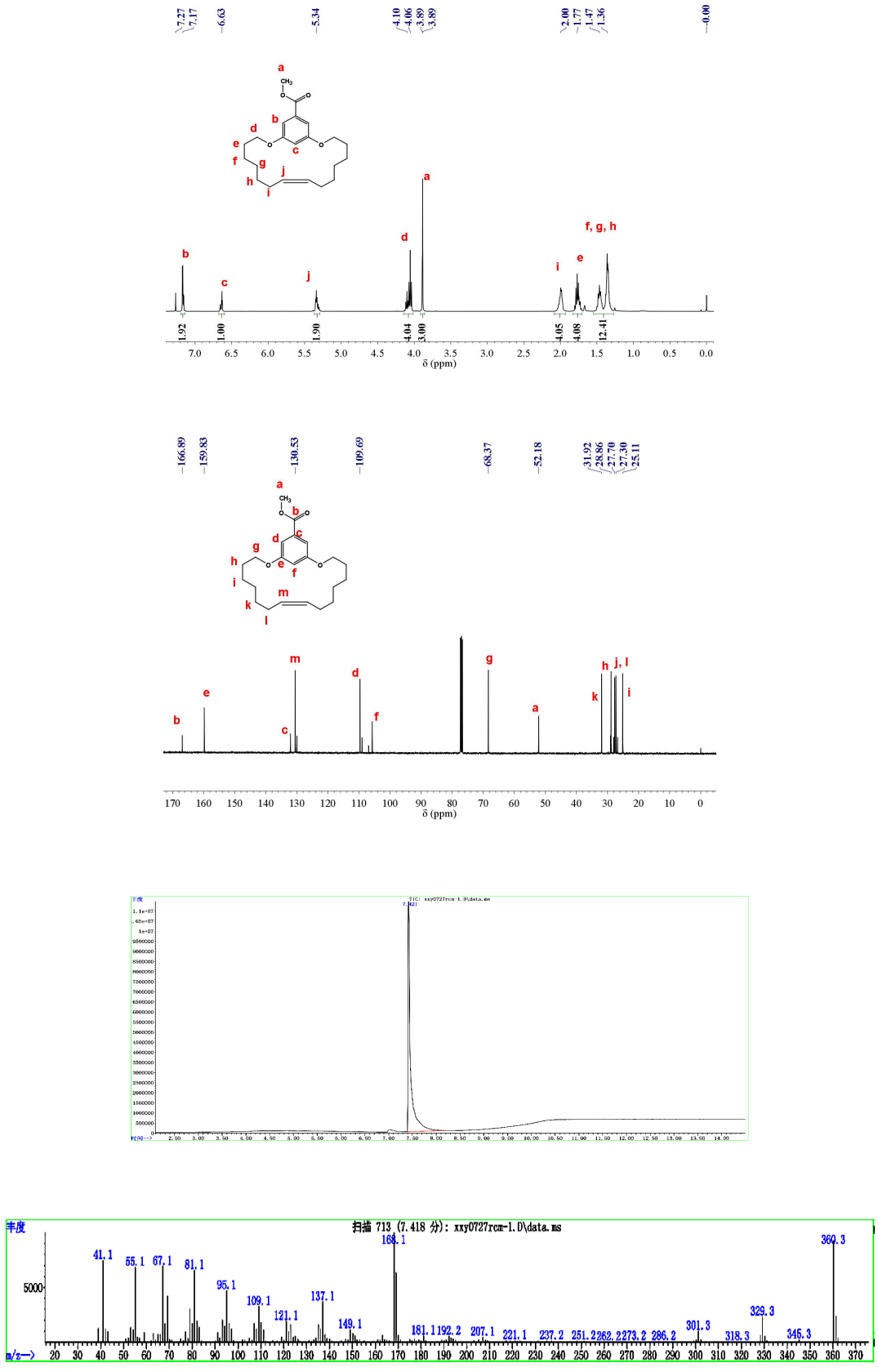


Figure S4 ^{1}H and ^{13}C NMR, GC-MS spectra of *metacyclophane* (**4c**)

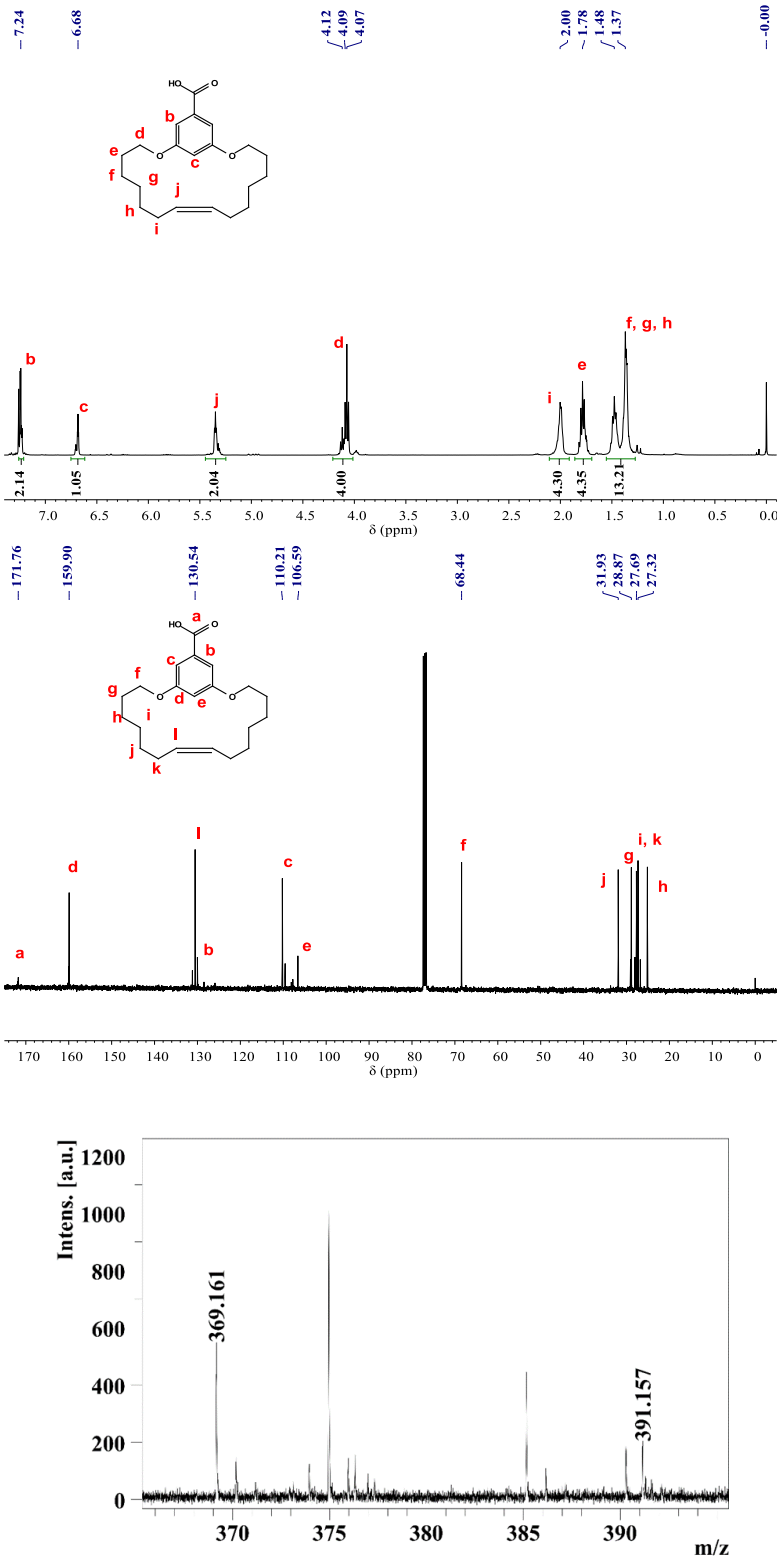


Figure S5 ^{1}H-NMR, ^{13}C NMR and MALDI-TOF MS spectra of hydroxymethyl 3,5-(7-tetradecenyl-1,14-dioxy)-benzoic acid ($\boldsymbol{L_{AA}^{1}}$, cleaved primary loop)

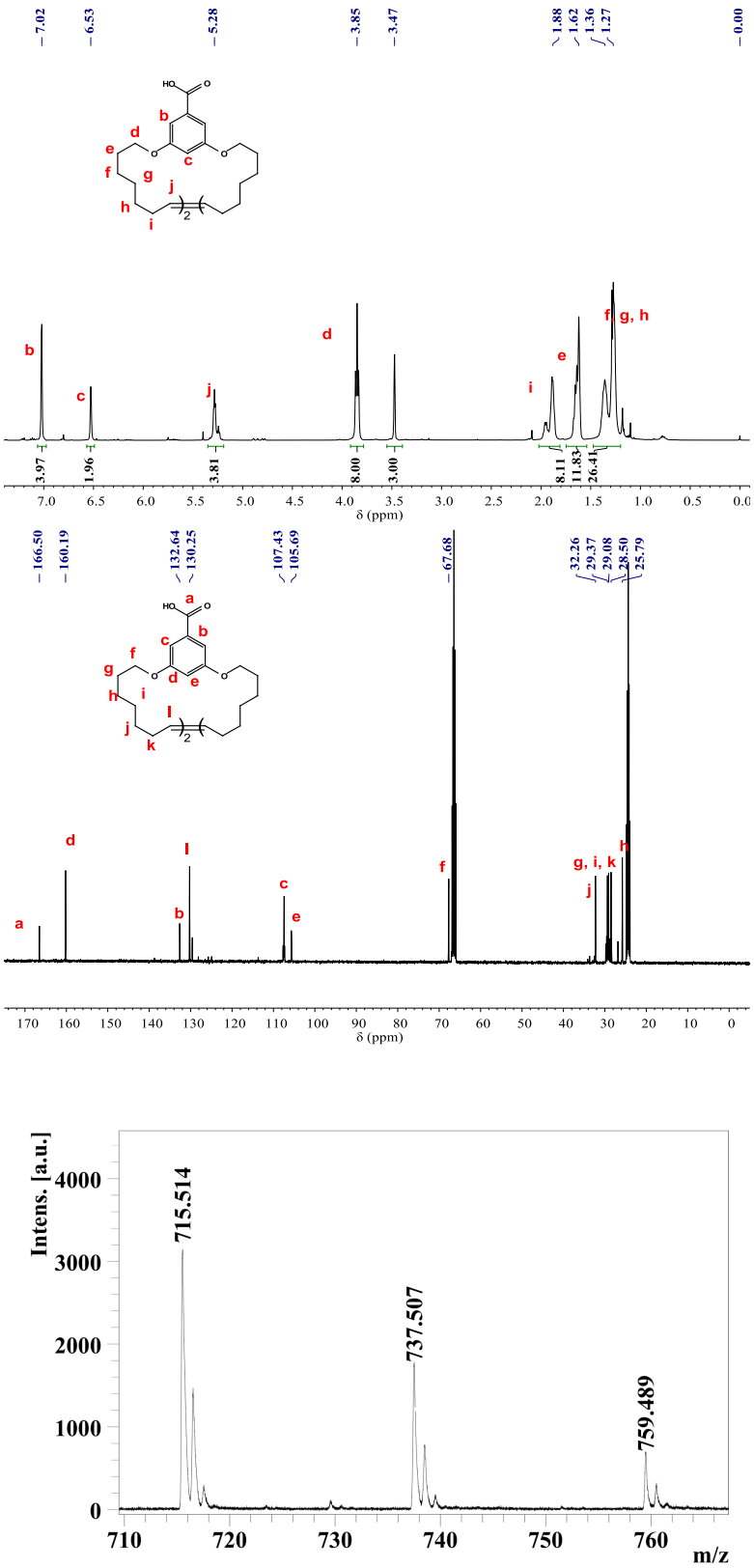


Figure S6 ^{1}H NMR, ^{13}C NMR (in THF-d_8), and MALDI-TOF MS spectra of secondary loop ($\boldsymbol{L^2_{AA}}$)

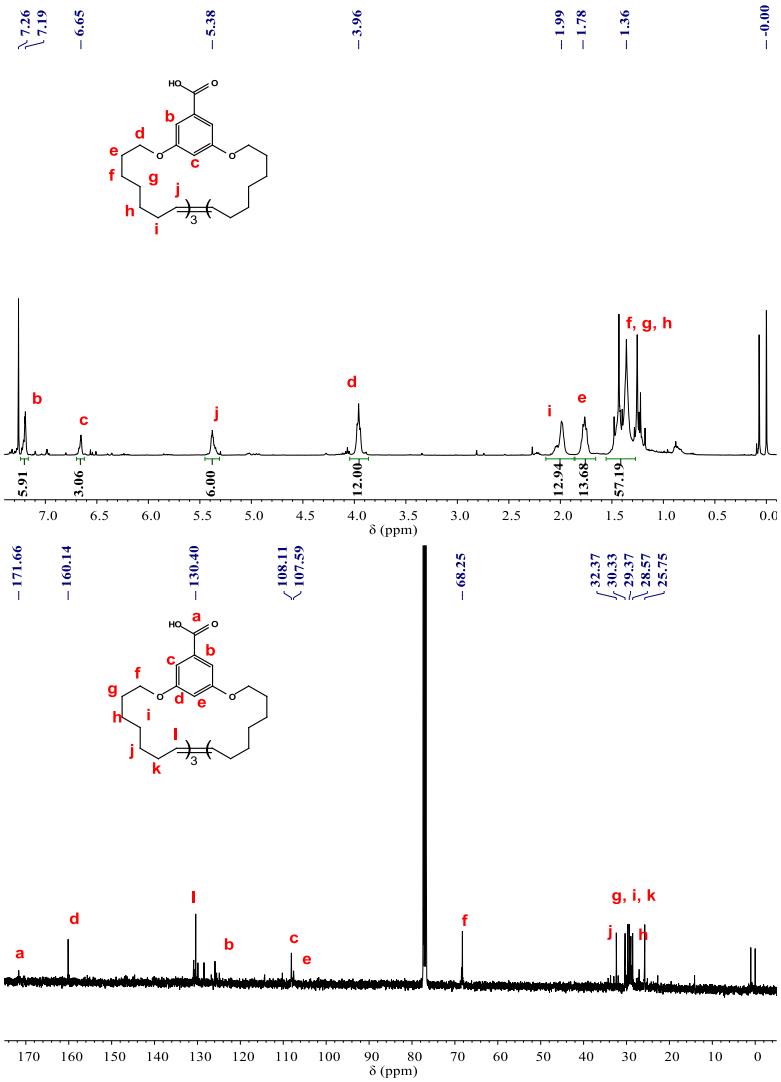


Figure S7 ^{1}H NMR and ^{13}C NMR of tertiary loop ($\boldsymbol{L^{3}_{AA}}$)

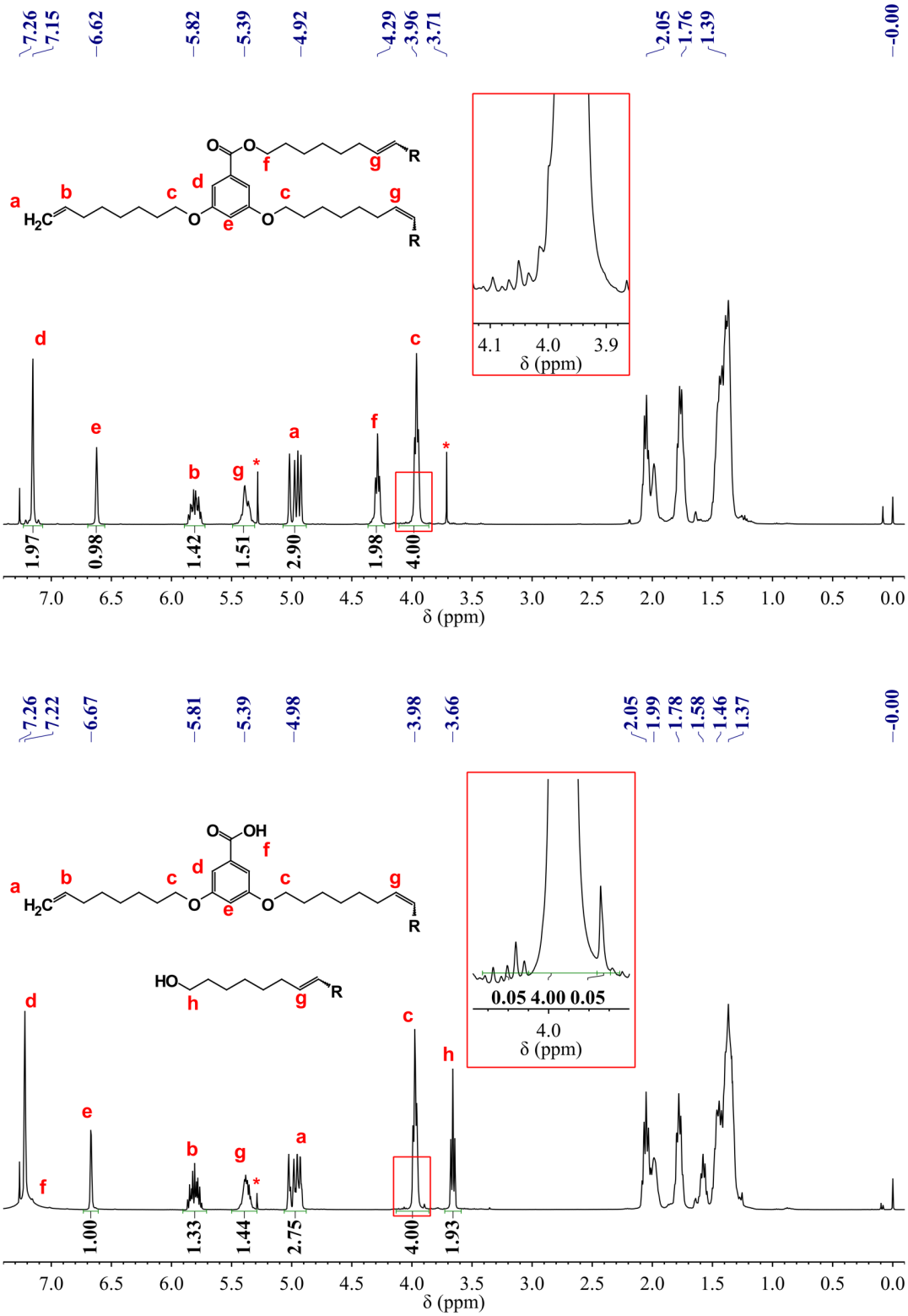


Figure S8 ^{1}H NMR spectra of polymer obtained at 20 minutes (top) and its decrosslinked product (bottom)

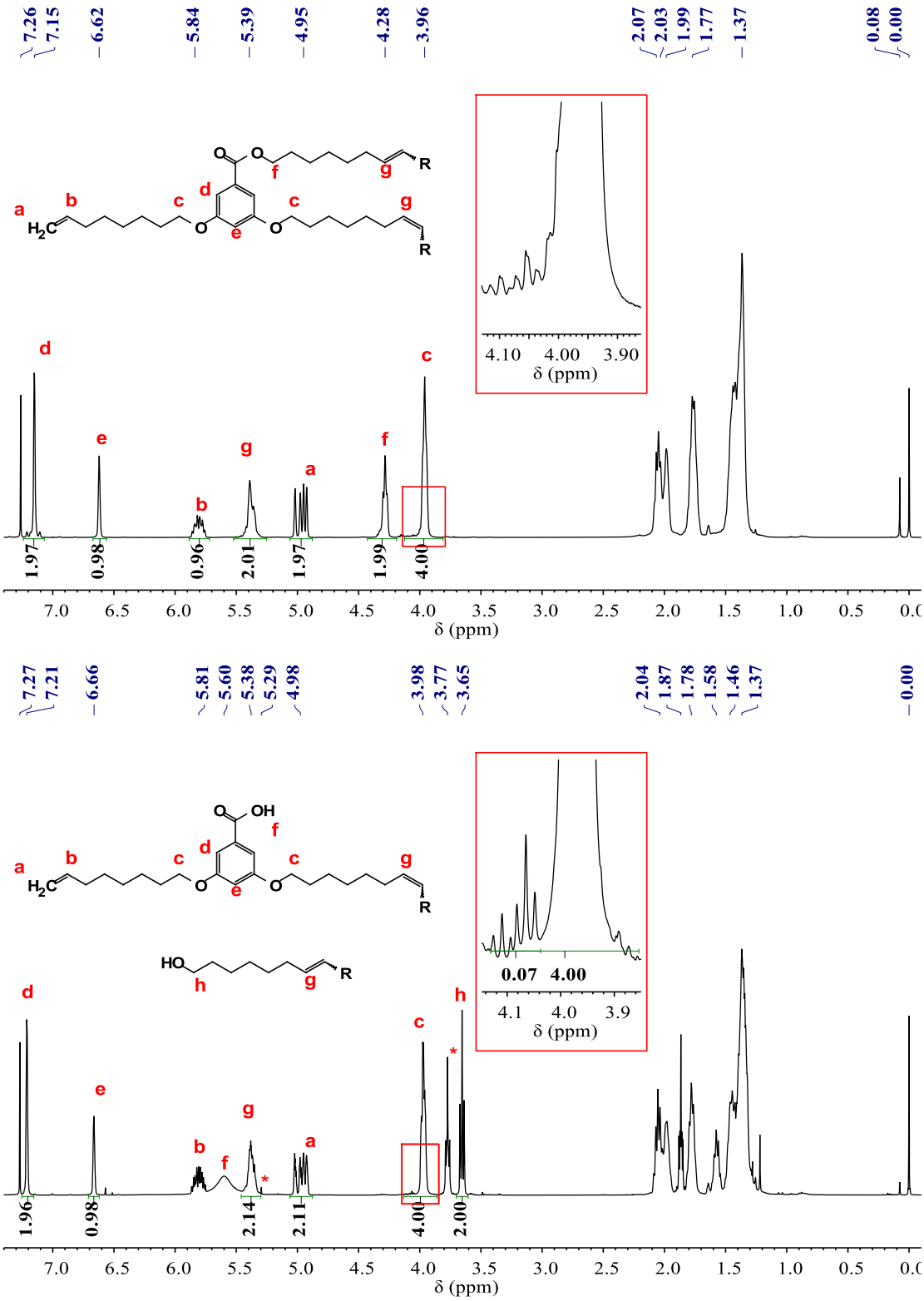


Figure S9 ^{1}H NMR spectra of polymer obtained at 40 minutes (top) and its decrosslinked product (bottom)

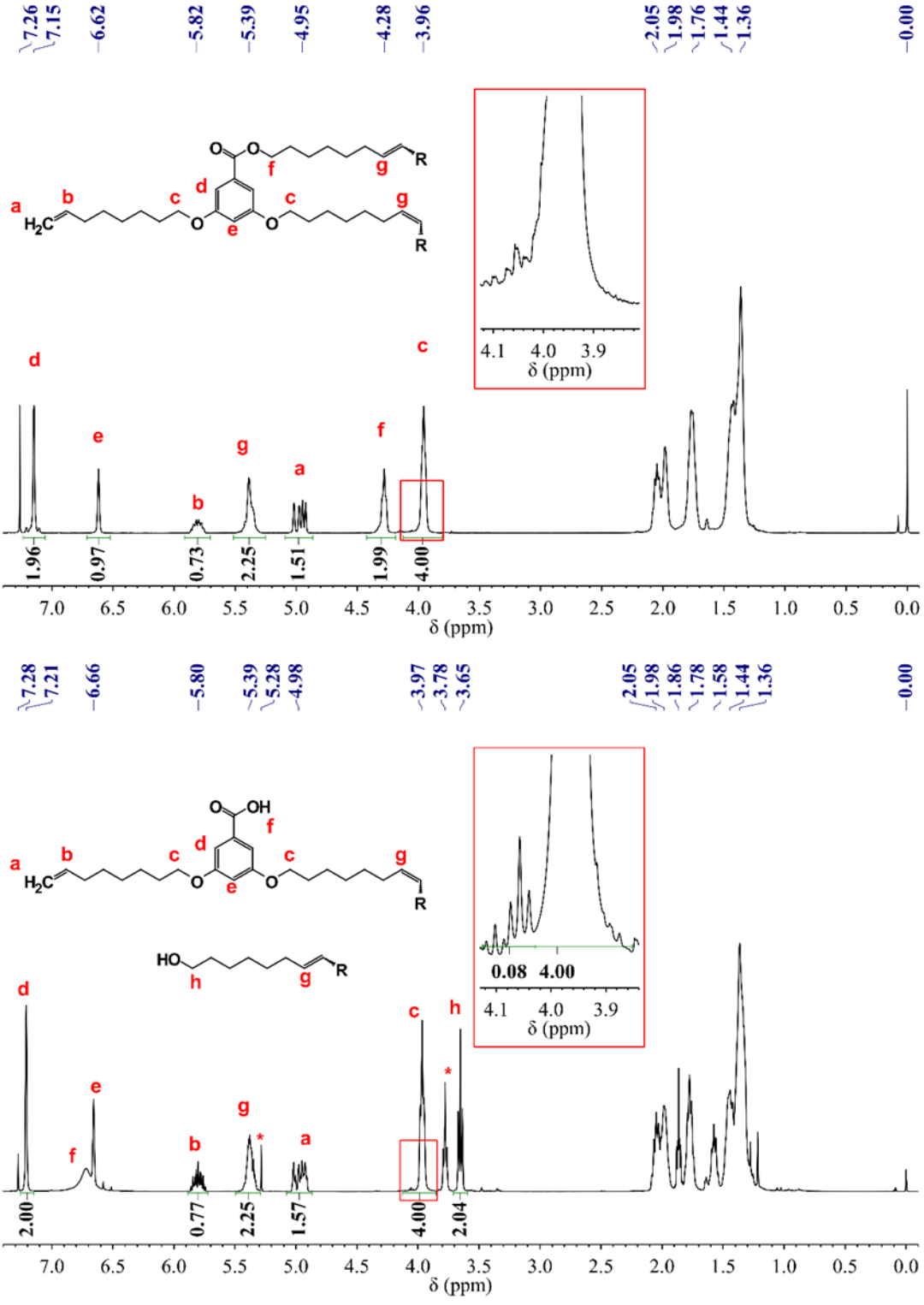


Figure S10 ^{1}H NMR spectra of polymer obtained at 60 minutes (top) and its decrosslinked product (bottom)

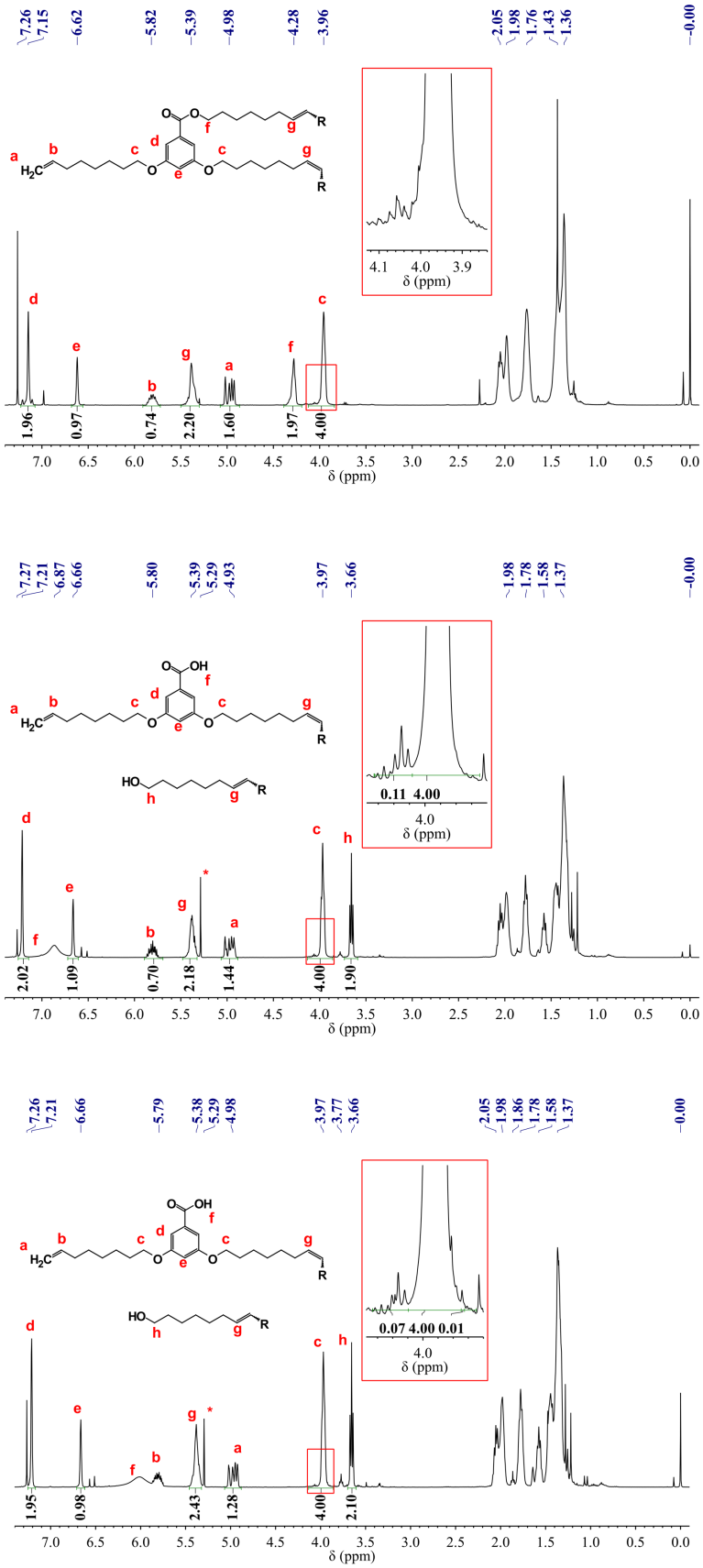


Figure S11 ^{1}H NMR spectra of sol fraction(top) and its decrosslinked product (middle) obtained at 86 minutes and decrosslinked gel fraction (bottom)

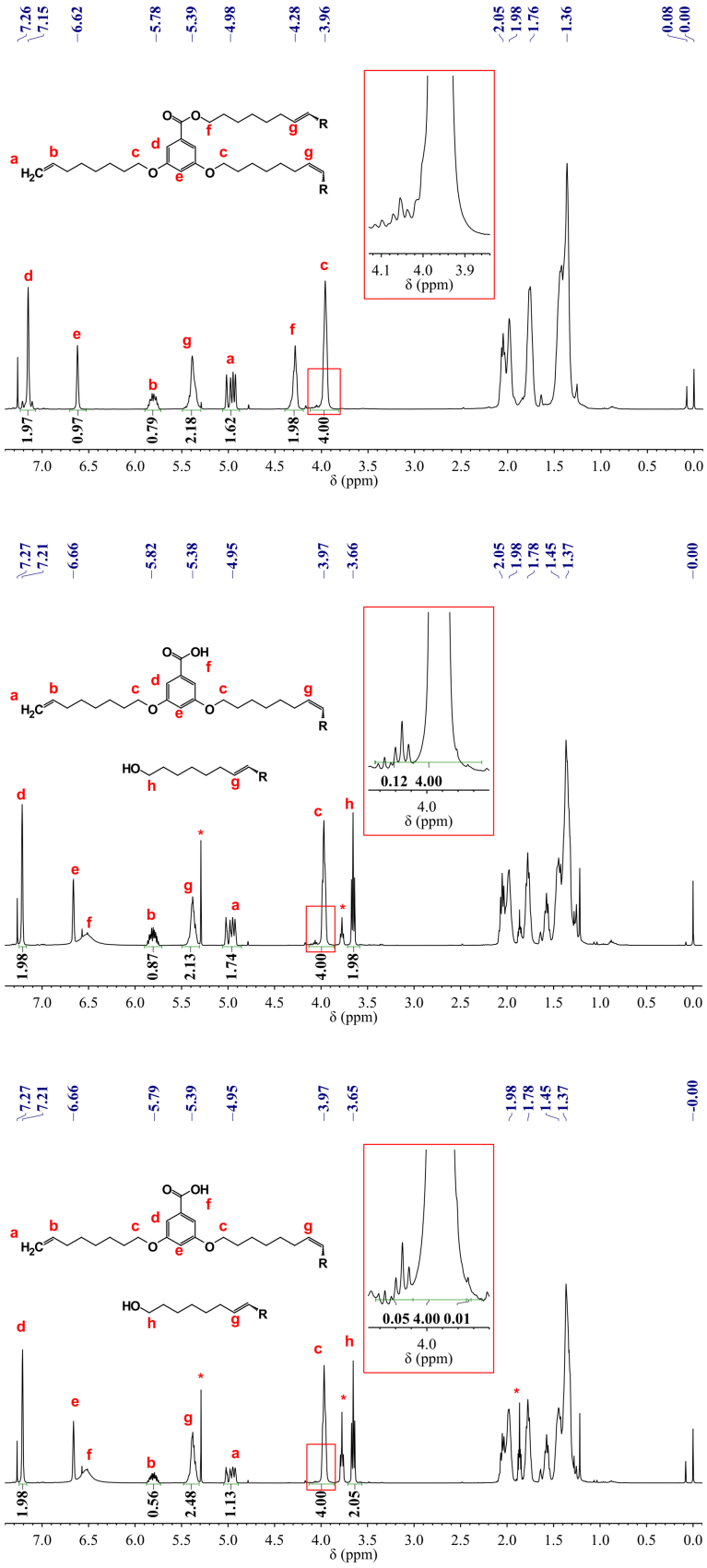
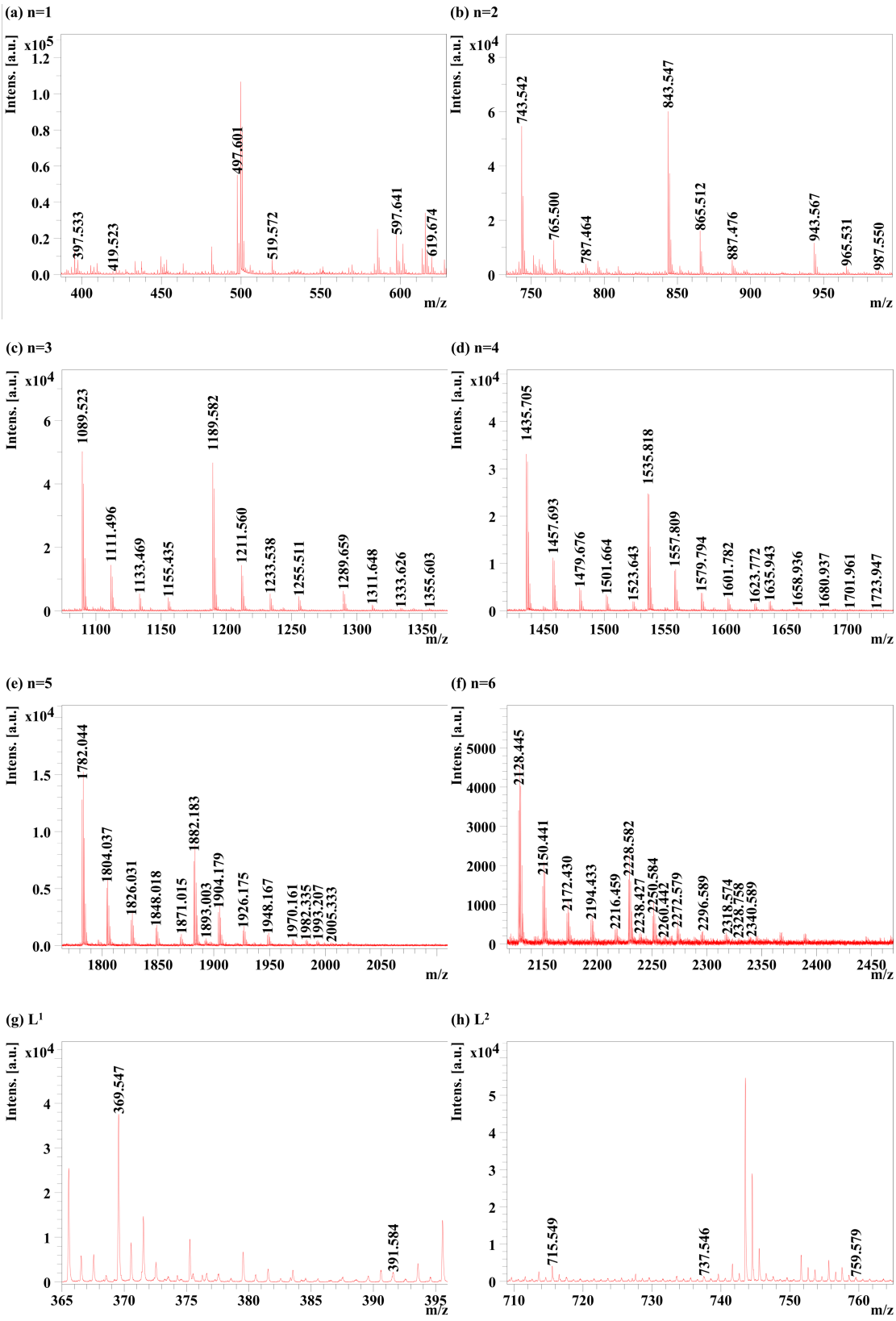


Figure S12 ^{1}H NMR spectra of sol fraction(top) and its decrosslinked product (middle) obtained at 96 minutes and decrosslinked gel fraction (bottom)


(a) n=1
Intens. [a.u.]
x10^5
1.2
1.0
0.8
0.6
0.4
0.2
0.0
397.533
419.523
497.601
519.572
597.641
619.674
400
450
500
550
600
m/z
(b) n=2
Intens. [a.u.]
x10^4
8
6
4
2
0
743.542
765.500
787.464
843.547
865.512
887.476
943.567
965.531
987.550
750
800
850
900
950
m/z
(c) n=3
Intens. [a.u.]
x10^4
6
4
2
0
1089.523
1111.496
1133.469
1155.435
1189.582
1211.560
1233.538
1255.511
1289.659
1311.648
1333.626
1355.603
1100
1150
1200
1250
1300
1350
m/z
(d) n=4
Intens. [a.u.]
x10^4
4
3
2
1
0
1435.705
1457.693
1479.676
1501.664
1523.643
1535.818
1557.809
1579.794
1601.782
1623.772
1635.943
1658.936
1680.937
1701.961
1723.947
1450
1500
1550
1600
1650
1700
m/z
(e) n=5
Intens. [a.u.]
x10^4
1.5
1.0
0.5
0.0
1782.044
1804.037
1826.031
1848.018
1871.015
1882.183
1893.003
1904.179
1926.175
1948.167
1970.161
1982.335
1993.207
2005.333
1800
1850
1900
1950
2000
2050
m/z
(f) n=6
Intens. [a.u.]
5000
4000
3000
2000
1000
0
2128.445
2150.441
2172.430
2194.433
2216.459
2228.582
2238.427
2250.584
2260.442
2272.579
2296.589
2318.574
2328.758
2340.589
2150
2200
2250
2300
2350
2400
2450
m/z
(g) L1
Intens. [a.u.]
x10^4
4
3
2
1
0
369.547
391.584
365
370
375
380
385
390
395
m/z
(h) L2
Intens. [a.u.]
x10^4
5
4
3
2
1
0
715.549
737.546
759.579
710
720
730
740
750
760
m/z

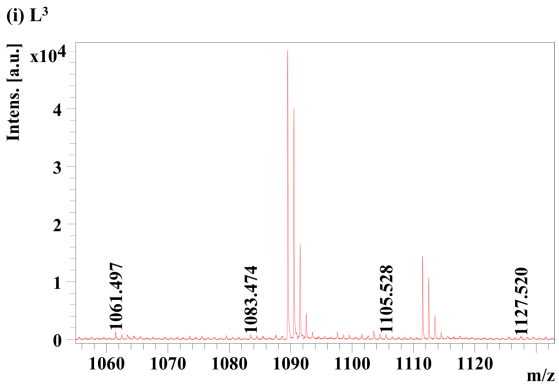
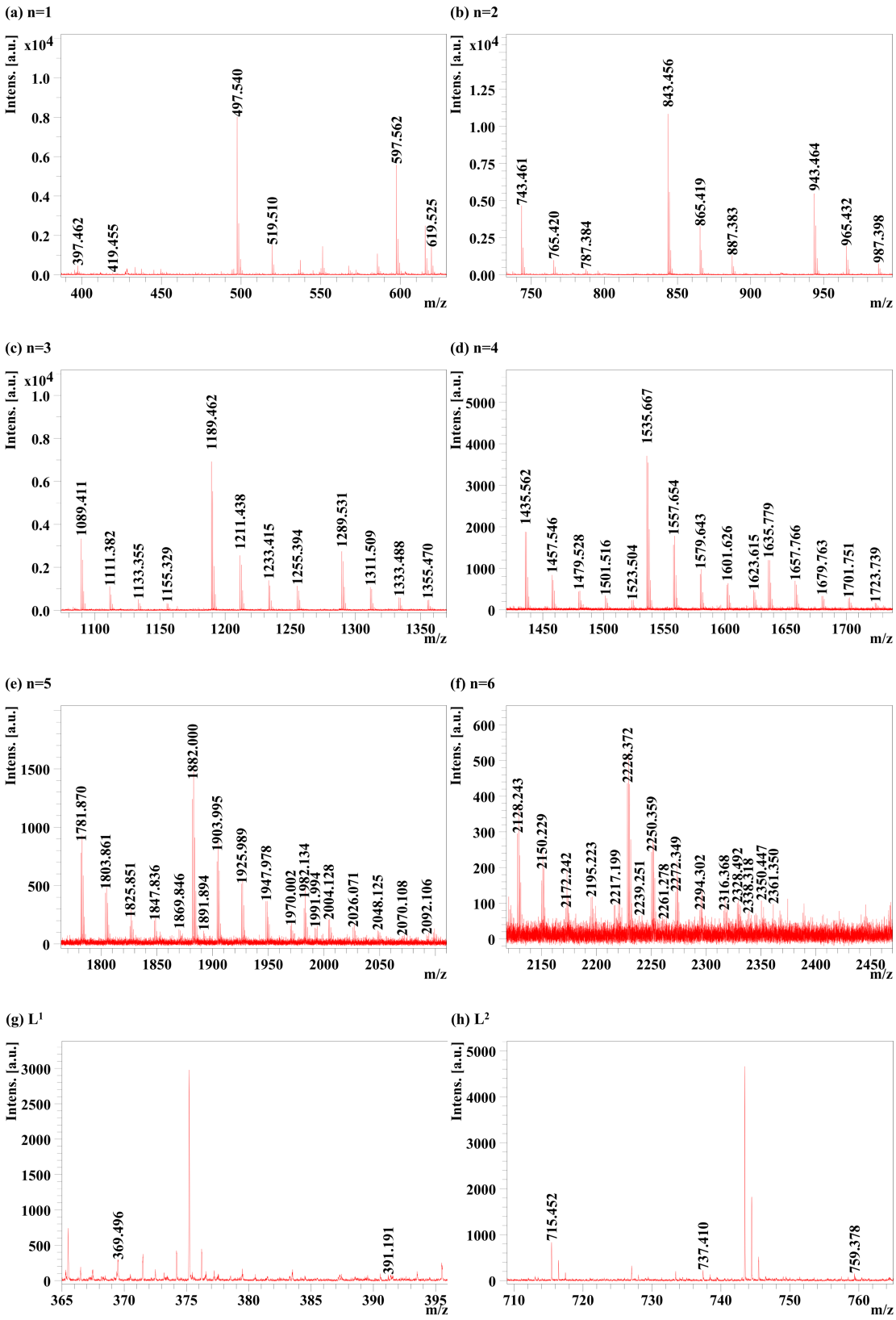


Figure S13 MALDI-TOF MS spectra of decrosslinked polymer obtained at 20 minutes


(a) n=1
Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
397.462
419.455
497.540
519.510
597.562
619.525
400
450
500
550
600
m/z
(b) n=2
Intens. [a.u.]
x10^4
1.25
1.00
0.75
0.50
0.25
0.00
743.461
765.420
787.384
843.456
865.419
887.383
943.464
965.432
987.398
750
800
850
900
950
m/z
(c) n=3
Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
1089.411
1111.382
1133.355
1155.329
1189.462
1211.438
1233.415
1255.394
1289.531
1311.509
1333.488
1355.470
1100
1150
1200
1250
1300
1350
m/z
(d) n=4
Intens. [a.u.]
5000
4000
3000
2000
1000
0
1435.562
1457.546
1479.528
1501.516
1523.504
1535.667
1557.654
1579.643
1601.626
1623.615
1635.779
1657.766
1679.763
1701.751
1723.739
1450
1500
1550
1600
1650
1700
m/z
(e) n=5
Intens. [a.u.]
1500
1000
500
0
1781.870
1803.861
1825.851
1847.836
1869.846
1882.000
1891.894
1903.995
1925.989
1947.978
1970.002
1982.134
1991.994
2004.128
2026.071
2048.125
2070.108
2092.106
1800
1850
1900
1950
2000
2050
m/z
(f) n=6
Intens. [a.u.]
600
500
400
300
200
100
0
2128.243
2150.229
2172.242
2195.223
2217.199
2228.372
2239.251
2250.359
2261.278
2272.349
2294.302
2316.368
2328.492
2338.318
2350.447
2361.350
2150
2200
2250
2300
2350
2400
2450
m/z
(g) L1
Intens. [a.u.]
3000
2500
2000
1500
1000
500
0
369.496
391.191
365
370
375
380
385
390
395
m/z
(h) L2
Intens. [a.u.]
5000
4000
3000
2000
1000
0
715.452
737.410
759.378
710
720
730
740
750
760
m/z

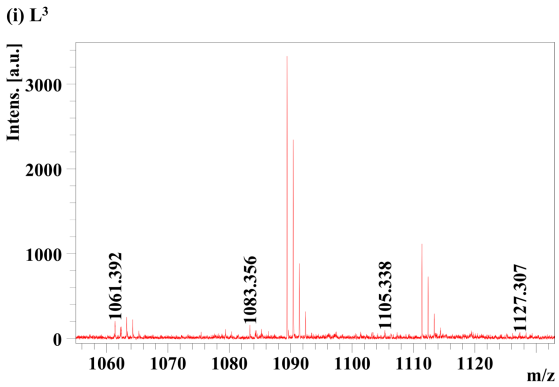
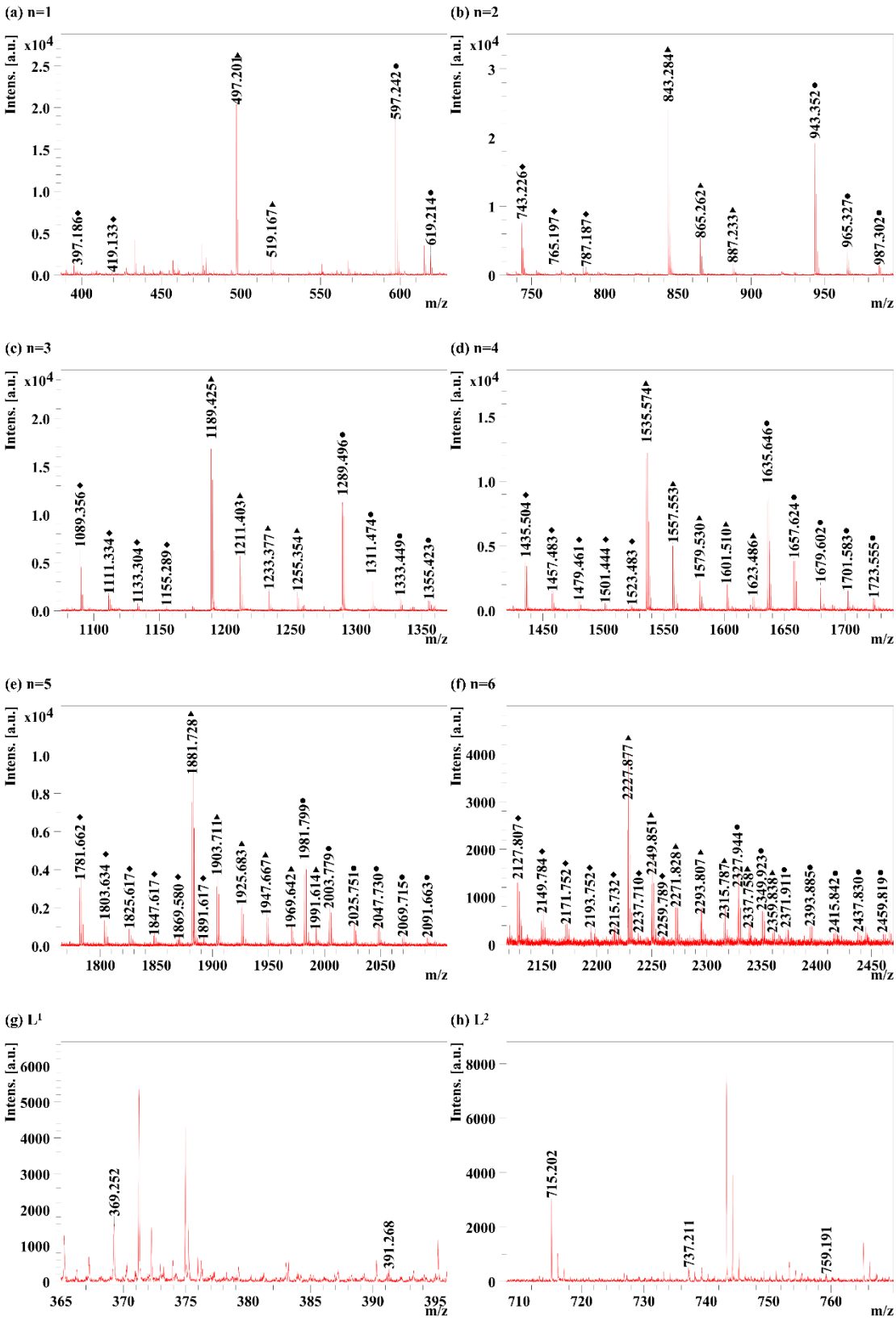


Figure S14 MALDI-TOF MS spectra of decrosslinked polymer obtained at 40 minutes


(a) n=1
Intens. [a.u.]
x10^4
397.186
419.133
497.201
519.167
597.242
619.214
m/z
(b) n=2
743.226
765.197
787.187
843.284
865.262
887.233
943.352
965.327
987.302
(c) n=3
1089.356
1111.334
1133.304
1155.289
1189.425
1211.403
1233.377
1255.354
1289.496
1311.474
1333.449
1355.423
(d) n=4
1435.504
1457.483
1479.461
1501.444
1523.483
1535.574
1557.553
1579.530
1601.510
1623.486
1635.646
1657.624
1679.602
1701.583
1723.555
(e) n=5
1781.662
1803.634
1825.617
1847.617
1869.580
1881.728
1891.617
1903.711
1925.683
1947.667
1969.642
1981.799
1991.614
2003.779
2025.751
2047.730
2069.715
2091.663
(f) n=6
2127.807
2149.784
2171.752
2193.752
2215.732
2227.877
2237.710
2249.851
2259.789
2271.828
2293.807
2315.787
2327.944
2337.758
2349.923
2359.838
2371.911
2393.885
2415.842
2437.830
2459.819
(g) L1
369.252
391.268
(h) L2
715.202
737.211
759.191

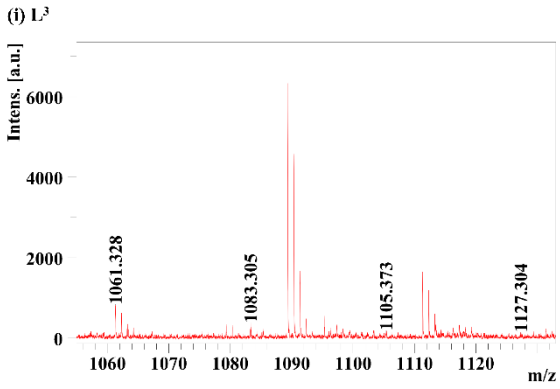
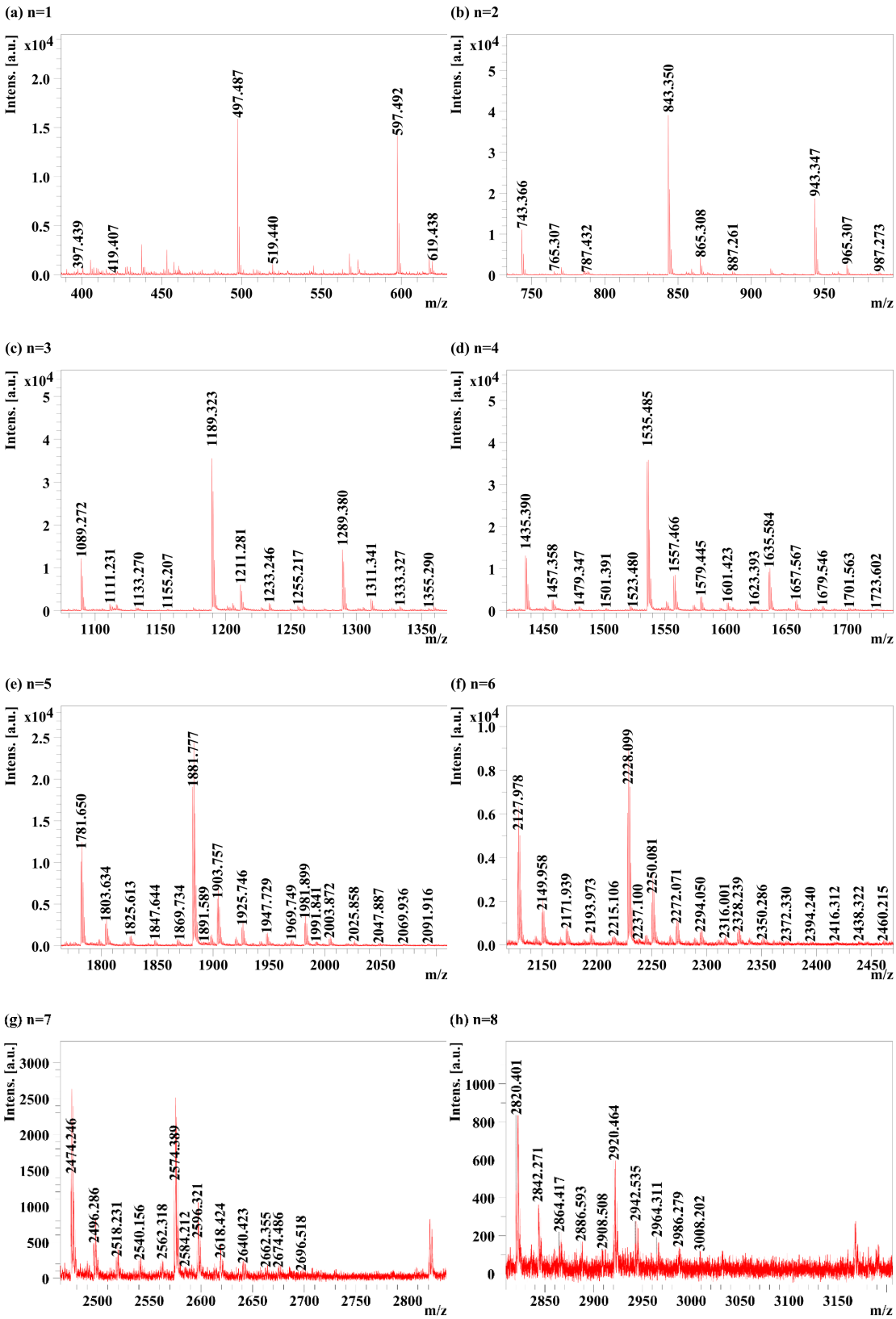
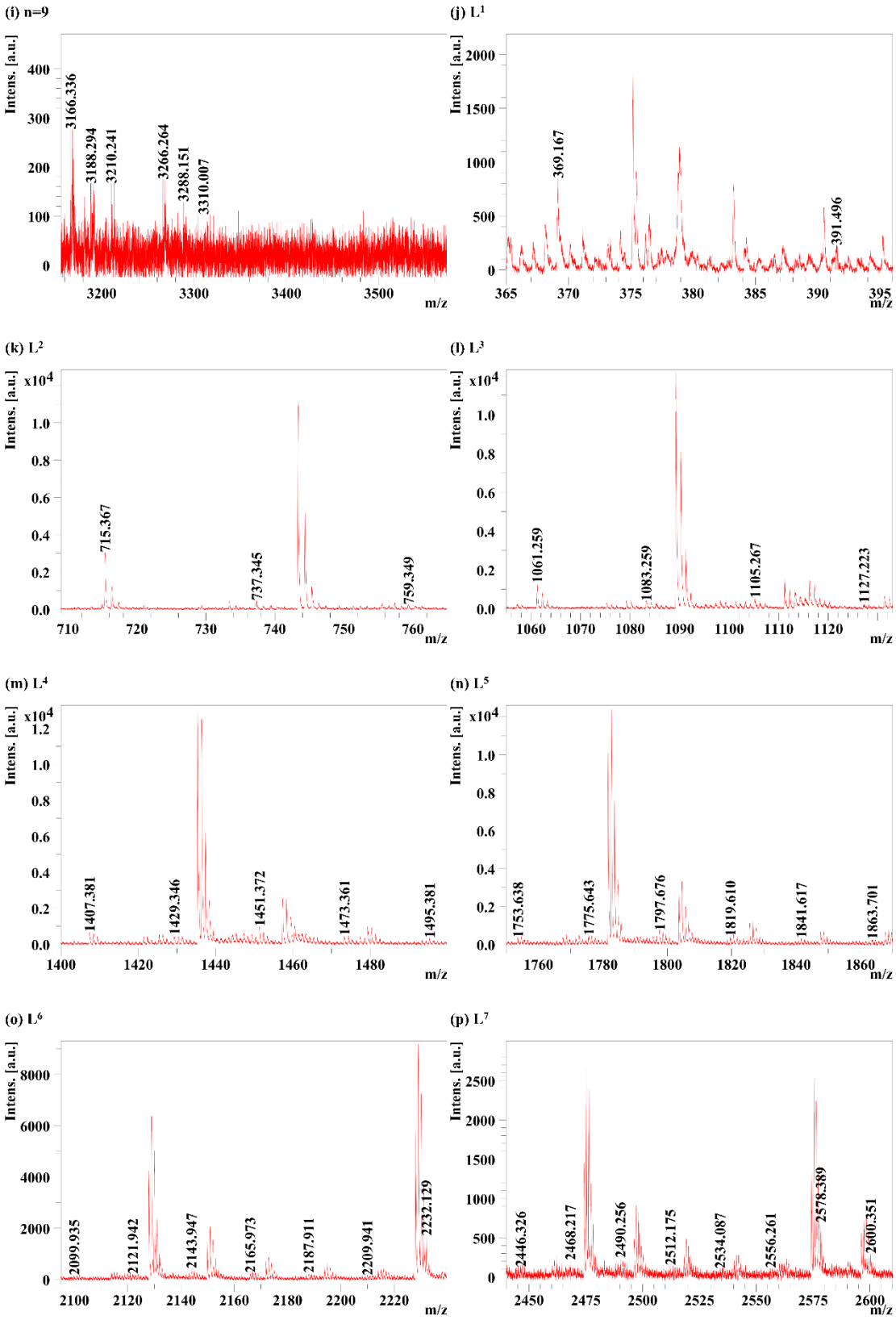


Figure S15 MALDI-TOF MS spectra of decrosslinked polymer obtained at 60 minutes


(a) n=1
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
397.439
419.407
497.487
519.440
597.492
619.438
400
450
500
550
600
m/z
(b) n=2
Intens. [a.u.]
x10^4
5
4
3
2
1
0
743.366
765.307
787.432
843.350
865.308
887.261
943.347
965.307
987.273
750
800
850
900
950
m/z
(c) n=3
Intens. [a.u.]
x10^4
5
4
3
2
1
0
1089.272
1111.231
1133.270
1155.207
1189.323
1211.281
1233.246
1255.217
1289.380
1311.341
1333.327
1355.290
1100
1150
1200
1250
1300
1350
m/z
(d) n=4
Intens. [a.u.]
x10^4
5
4
3
2
1
0
1435.390
1457.358
1479.347
1501.391
1523.480
1535.485
1557.466
1579.445
1601.423
1623.393
1635.584
1657.567
1679.546
1701.563
1723.602
1450
1500
1550
1600
1650
1700
m/z
(e) n=5
Intens. [a.u.]
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
1781.650
1803.634
1825.613
1847.644
1869.734
1881.777
1891.589
1903.757
1925.746
1947.729
1969.749
1981.899
1991.841
2003.872
2025.858
2047.887
2069.936
2091.916
1800
1850
1900
1950
2000
2050
m/z
(f) n=6
Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
2127.978
2149.958
2171.939
2193.973
2215.106
2228.099
2237.100
2250.081
2272.071
2294.050
2316.001
2328.239
2350.286
2372.330
2394.240
2416.312
2438.322
2460.215
2150
2200
2250
2300
2350
2400
2450
m/z
(g) n=7
Intens. [a.u.]
3000
2500
2000
1500
1000
500
0
2474.246
2496.286
2518.231
2540.156
2562.318
2574.389
2584.212
2596.321
2618.424
2640.423
2662.355
2674.486
2696.518
2500
2550
2600
2650
2700
2750
2800
m/z
(h) n=8
Intens. [a.u.]
1000
800
600
400
200
0
2820.401
2842.271
2864.417
2886.593
2908.508
2920.464
2942.535
2964.311
2986.279
3008.202
2850
2900
2950
3000
3050
3100
3150
m/z


(i) n=9
Intens. [a.u.]
3166.336
3188.294
3210.241
3266.264
3288.151
3310.007
m/z
(j) L1
Intens. [a.u.]
369.167
391.496
m/z
(k) L2
Intens. [a.u.]
x10^4
715.367
737.345
759.349
m/z
(l) L3
Intens. [a.u.]
x10^4
1061.259
1083.259
1105.267
1127.223
m/z
(m) L4
Intens. [a.u.]
x10^4
1407.381
1429.346
1451.372
1473.361
1495.381
m/z
(n) L5
Intens. [a.u.]
x10^4
1753.638
1775.643
1797.676
1819.610
1841.617
1863.701
m/z
(o) L6
Intens. [a.u.]
2099.935
2121.942
2143.947
2165.973
2187.911
2209.941
2232.129
m/z
(p) L7
Intens. [a.u.]
2446.326
2468.217
2490.256
2512.175
2534.087
2556.261
2578.389
2600.351
m/z

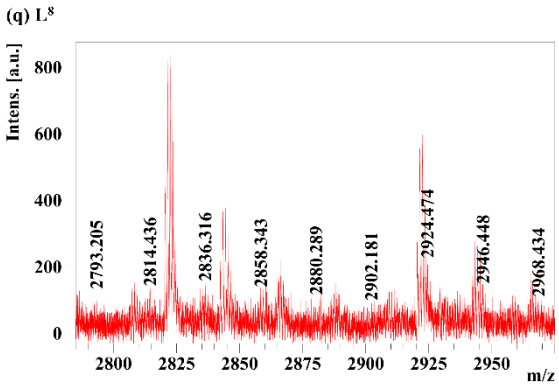
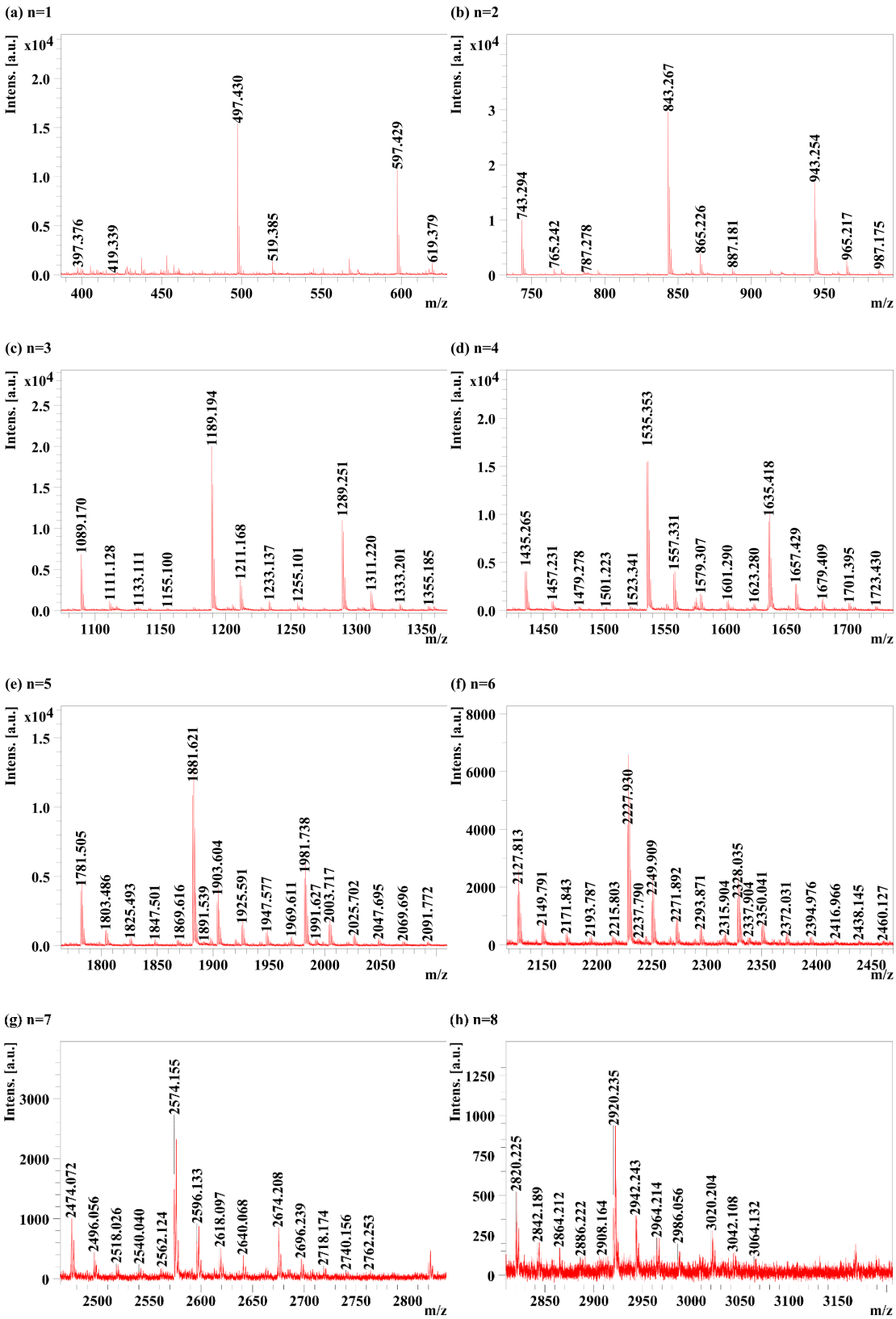


Figure S16 MALDI-TOF MS spectra of decrosslinked polymer (sol part) obtained at 86 minutes


(a) n=1
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
397.376
419.339
497.430
519.385
597.429
619.379
400
450
500
550
600
m/z
(b) n=2
Intens. [a.u.]
x10^4
3
2
1
0
743.294
765.242
787.278
843.267
865.226
887.181
943.254
965.217
987.175
750
800
850
900
950
m/z
(c) n=3
Intens. [a.u.]
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
1089.170
1111.128
1133.111
1155.100
1189.194
1211.168
1233.137
1255.101
1289.251
1311.220
1333.201
1355.185
1100
1150
1200
1250
1300
1350
m/z
(d) n=4
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
1435.265
1457.231
1479.278
1501.223
1523.341
1535.353
1557.331
1579.307
1601.290
1623.280
1635.418
1657.429
1679.409
1701.395
1723.430
1450
1500
1550
1600
1650
1700
m/z
(e) n=5
Intens. [a.u.]
x10^4
1.5
1.0
0.5
0.0
1781.505
1803.486
1825.493
1847.501
1869.616
1881.621
1891.539
1903.604
1925.591
1947.577
1969.611
1981.738
1991.627
2003.717
2025.702
2047.695
2069.696
2091.772
1800
1850
1900
1950
2000
2050
m/z
(f) n=6
Intens. [a.u.]
8000
6000
4000
2000
0
2127.813
2149.791
2171.843
2193.787
2215.803
2227.930
2237.790
2249.909
2271.892
2293.871
2315.904
2328.035
2337.904
2350.041
2372.031
2394.976
2416.966
2438.145
2460.127
2150
2200
2250
2300
2350
2400
2450
m/z
(g) n=7
Intens. [a.u.]
3000
2000
1000
0
2474.072
2496.056
2518.026
2540.040
2562.124
2574.155
2596.133
2618.097
2640.068
2674.208
2696.239
2718.174
2740.156
2762.253
2500
2550
2600
2650
2700
2750
2800
m/z
(h) n=8
Intens. [a.u.]
1250
1000
750
500
250
0
2820.225
2842.189
2864.212
2886.222
2908.164
2920.235
2942.243
2964.214
2986.056
3020.204
3042.108
3064.132
2850
2900
2950
3000
3050
3100
3150
m/z

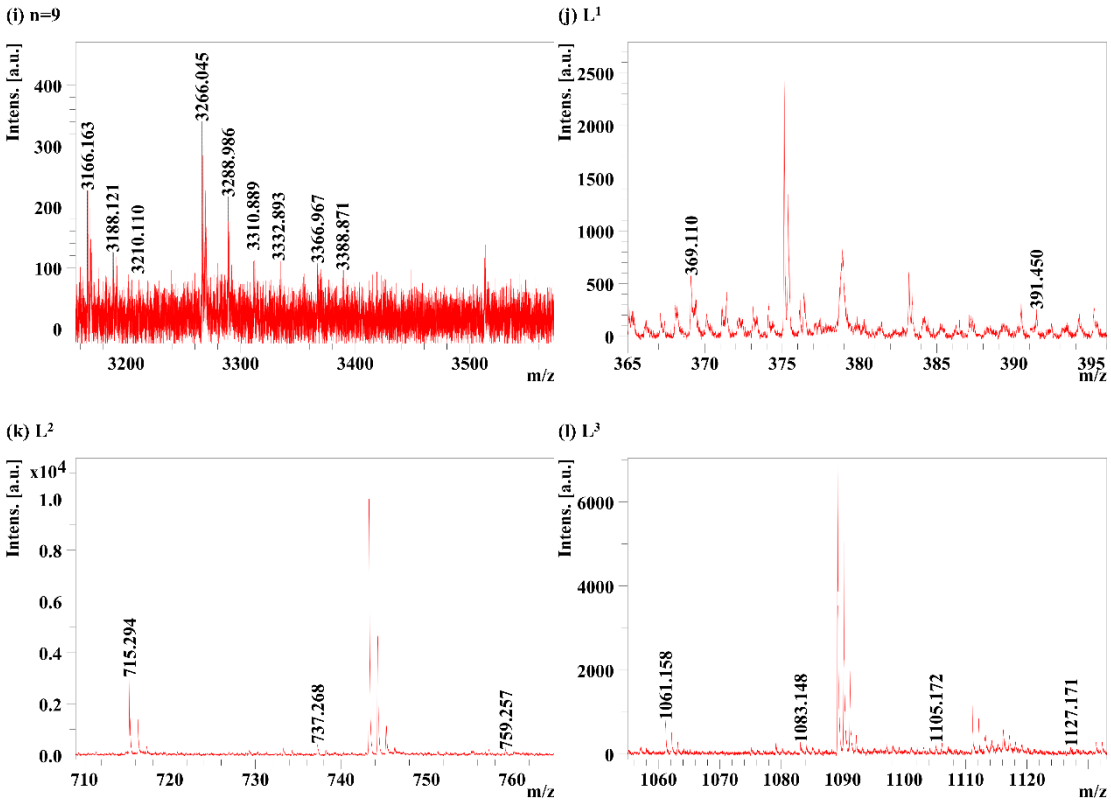
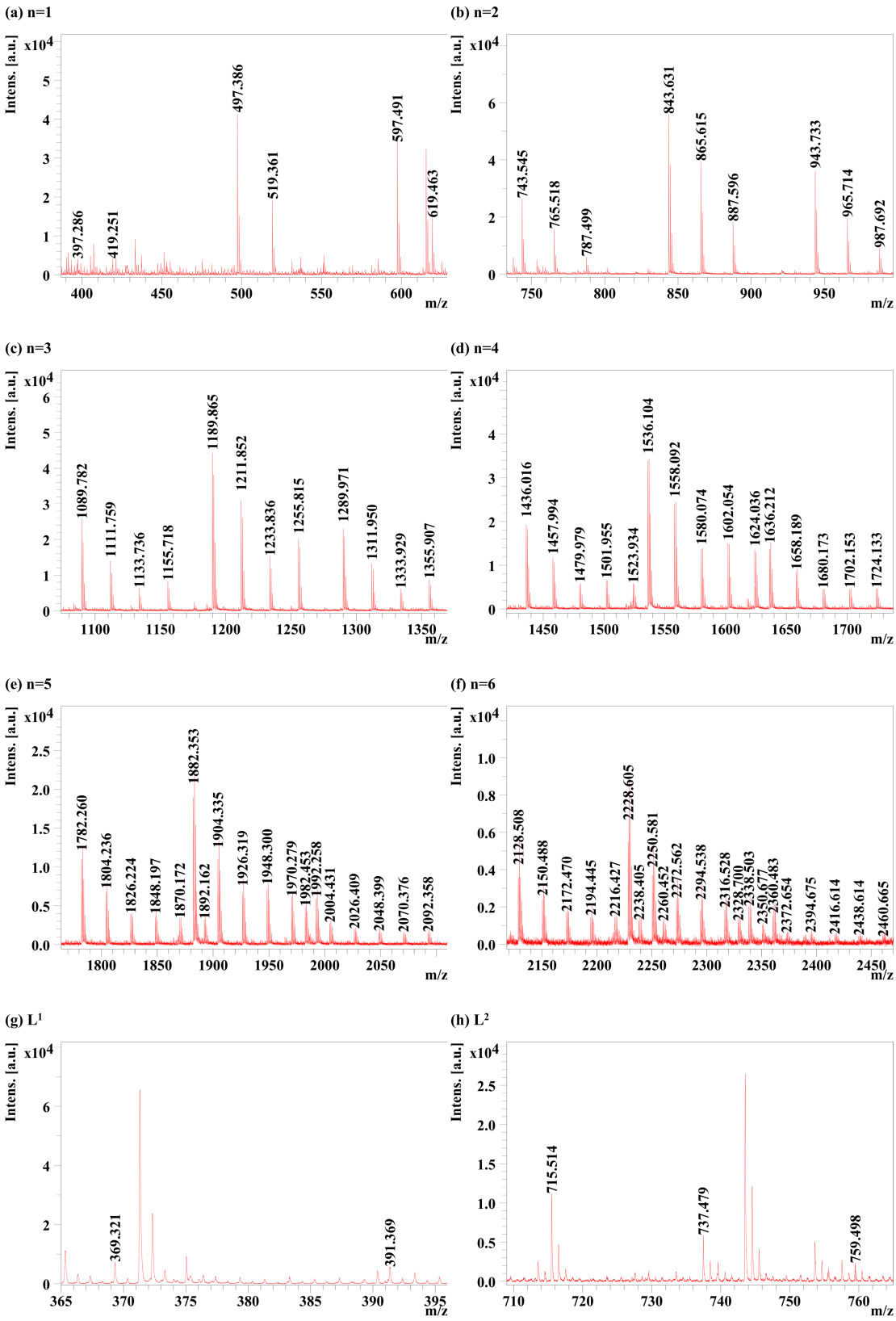


Figure S17 MALDI-TOF MS spectra of decrosslinked polymer (gel part) obtained at 86 minutes


(a) n=1
Intens. [a.u.]
x10^4
397.286
419.251
497.386
519.361
597.491
619.463
m/z
(b) n=2
743.545
765.518
787.499
843.631
865.615
887.596
943.733
965.714
987.692
(c) n=3
1089.782
1111.759
1133.736
1155.718
1189.865
1211.852
1233.836
1255.815
1289.971
1311.950
1333.929
1355.907
(d) n=4
1436.016
1457.994
1479.979
1501.955
1523.934
1536.104
1558.092
1580.074
1602.054
1624.036
1636.212
1658.189
1680.173
1702.153
1724.133
(e) n=5
1782.260
1804.236
1826.224
1848.197
1870.172
1882.353
1892.162
1904.335
1926.319
1948.300
1970.279
1982.453
1992.258
2004.431
2026.409
2048.399
2070.376
2092.358
(f) n=6
2128.508
2150.488
2172.470
2194.445
2216.427
2228.605
2238.405
2250.581
2260.452
2272.562
2294.538
2316.528
2328.700
2338.503
2350.677
2360.483
2372.654
2394.675
2416.614
2438.614
2460.665
(g) L¹
369.321
391.369
(h) L²
715.514
737.479
759.498

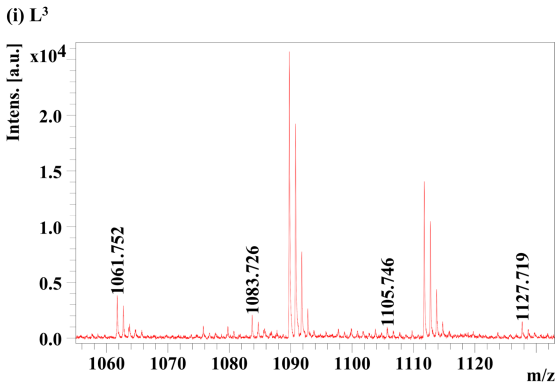
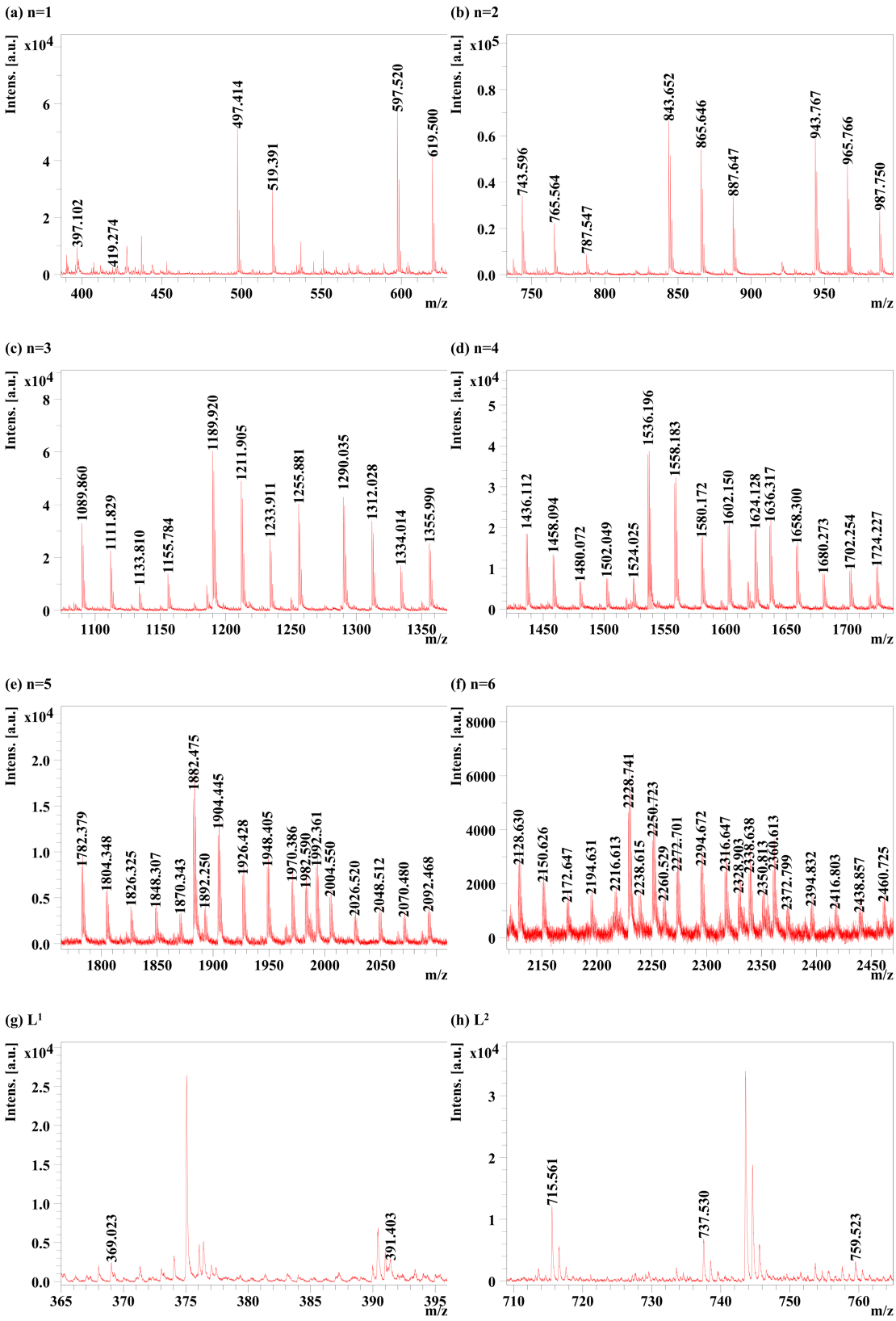


Figure S18 MALDI-TOF MS spectra of decrosslinked polymer (sol part) obtained at 96 minutes


(a) n=1
Intens. [a.u.]
x10^4
397.102
419.274
497.414
519.391
597.520
619.500
m/z
(b) n=2
Intens. [a.u.]
x10^5
743.596
765.564
787.547
843.652
865.646
887.647
943.767
965.766
987.750
m/z
(c) n=3
Intens. [a.u.]
x10^4
1089.860
1111.829
1133.810
1155.784
1189.920
1211.905
1233.911
1255.881
1290.035
1312.028
1334.014
1355.990
m/z
(d) n=4
Intens. [a.u.]
x10^4
1436.112
1458.094
1480.072
1502.049
1524.025
1536.196
1558.183
1580.172
1602.150
1624.128
1636.317
1658.300
1680.273
1702.254
1724.227
m/z
(e) n=5
Intens. [a.u.]
x10^4
1782.379
1804.348
1826.325
1848.307
1870.343
1882.475
1892.250
1904.445
1926.428
1948.405
1970.386
1982.590
1992.361
2004.550
2026.520
2048.512
2070.480
2092.468
m/z
(f) n=6
Intens. [a.u.]
2128.630
2150.626
2172.647
2194.631
2216.613
2228.741
2238.615
2250.723
2260.529
2272.701
2294.672
2316.647
2328.903
2338.638
2350.813
2360.613
2372.799
2394.832
2416.803
2438.857
2460.725
m/z
(g) L1
Intens. [a.u.]
x10^4
369.023
391.403
m/z
(h) L2
Intens. [a.u.]
x10^4
715.561
737.530
759.523
m/z

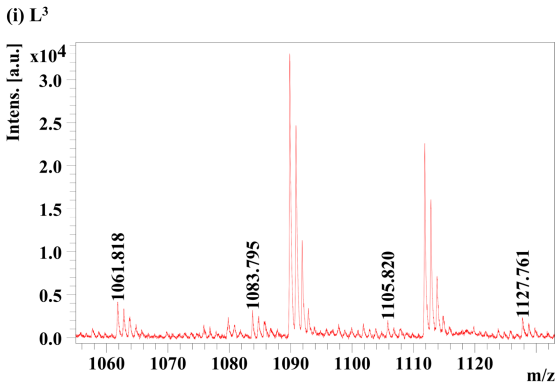


Figure S19 MALDI-TOF MS spectra of decrosslinked polymer (gel part) obtained at 96 minutes