Electronic Supplementary Information

for

Direct Characterization of Polymer Network through Its Retainable Units

Xiaoyan Xu, Qi Wang*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou, 310027, P. R. China.

* Corresponding author, wangq@zju.edu.cn
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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 $A_2X_{a-2}$.

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

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

The intermolecular reaction of $A_2X_{a-2}$ 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

$$n_{AA} : n_{AX} : n_{XX} = (C_1^2)^2 : 2C_2^1 C_{a-2}^1 : (C_{a-2}^1)^2 = 4:4(a-2):(a-2)^2 \quad (1)$$

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 ($n_{\text{net}}$) can be estimated from $n_{XX}$ and $F_{XX}$ that is given by

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

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

$$p_{\text{inter}} = \frac{2n_{\text{net}}}{an_{M}} = \frac{2a}{(a-2)^2} \frac{n_{XX}}{n_{M}} \quad (4)$$

where $n_{M}$ is the initial number of the monomer $A_2X_{a-2}$. 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, $p_{\text{inter}}$ can be obtained according to $n_{XX}$ and $n_{M}$.
Scheme S2 Formation of various primary loops by intramolecular reaction between functional groups of A₂Xₐ 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

$$l_{AA}:l_{AX}:l_{XX} = 1:2(a-2):0.5(a-2)(a-3)$$  \hspace{1cm} (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 ($F_{AA}$) is given by

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

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

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

$$p_{intra} = \frac{2L^1}{a_m} = (a - 1) \frac{l_{AA}}{n_m}$$  \hspace{1cm} (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 A₂X₁ 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

$$N_{XX} = n_{XX} + l_{XX}$$  \hspace{1cm} (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, \( p_{\text{inter}} \) is given by

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

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

\[ \frac{p_{\text{intra}}}{p_{\text{inter}}} = \frac{(a-1)(a-2)^2l_{AA}}{2a(N_{XX} - 0.5(a-2)(a-3)l_{AA})} \] (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 \( \Lambda_2X_{a-2} \) also equals to the sum of all network chains, dangling chains and primary loops that is

\[ f = 2n_{\text{net}} + 2L^I + d \] (16)

According to equations 3, 7 and 15, we get

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

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

\[ p_{\text{intra}} = \frac{2a(N_{XX} - 0.5(a-2)(a-3)l_{AA})}{2a(N_{XX} + 2(a-2)l_{AA}^1 + (a-2)d_X)} \] (18)

\[ p_{\text{inter}} = \frac{2a(N_{XX} - 0.5(a-2)(a-3)l_{AA})}{2a(N_{XX} + 2(a-2)l_{AA}^1 + (a-2)d_X)} \] (19)

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

In the network formed by \( \Lambda_2X_{a-2} \) 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 \( N_{XX}: L_{AA}^d : d_X \) 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

![Diagram](attachment:image.png)

**Scheme S3** Formation of various monoloops in PDN.

Besides the primary loop, monoloops can be also generated by \( \text{A}_n \). The monoloop is a macrocyclic unit composed of multiple segments. When \( \text{A}_2X_3 \) 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

\[
\frac{L_{AA}^2}{L^2} = \frac{1}{(c_2)^n} \tag{20}
\]

Generally, \( n \)-order monoloop (\( L^n \)) is formed by the reaction of \( n \) pairs of groups of \( n \) monomers. When \( \text{A}_2X_{a+2} \) is used as monomer, the ratio of \( n \)-order monoloops composed of \( (\text{AA})_n \) (\( L_{AA}^n \)) to \( L^n \) is given by

\[
\frac{L_{AA}^n}{L^n} = \frac{1}{(c_2)^n} = \frac{1}{(0.5a(a-1))^n} \tag{21}
\]

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

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 A₃X₂. All polyloops are changed to the same biloop composed of AA segments (L₅₅, 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 L²,2 can be measured, it is possible to estimate the number of all biloops (L²,2) from the number of L²,2. The biloop is formed by reaction of three pairs of groups of two monomers, the relationship between L²,2 and L²,2 is given by

$$\frac{L_{AA}^{2,2}}{L_{AA}^{2,2}} = \frac{1}{(C_d^2)^2}$$  \hspace{1cm} (23)

Generally, the polyloop containing n secondary loops (L²,n) can be formed by reactions of n + 1 pairs of groups of two Aₙ₋₁Xₙ₋₉₋₁, among which L²,n is the cleavable polyloop. The relationship between L²,n and L²,2 is given by

$$\frac{L_{AA}^{2,n}}{L_{AA}^{2,2}} = \frac{1}{(C_d^{n+1})^2}$$  \hspace{1cm} (24)

So, we get

$$L_{AA}^{2,n} = (C_d^{n+1})^2 L_{AA}^{2,2}$$  \hspace{1cm} (25)

If L²,n 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

![Diagram of intramolecular reactions between functional groups of $A_2X_1$]

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

$$p_{\text{intra}} = 2 \frac{L_{AA}^1}{n_{M}}$$ (26)

$$p_{\text{inter}} = 6 \frac{N_{XX}}{n_{M}}$$ (27)

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

The equations 18 and 19 yield

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

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

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

$$p_{\text{intra}} = \frac{2r_1}{6r_2 + 2r_1 + 1}$$ (31)

$$p_{\text{inter}} = \frac{6r_2}{6r_2 + 2r_1 + 1}$$ (32)

$$\frac{p_{\text{intra}}}{p_{\text{inter}}} = \frac{r_1}{3r_2}$$ (33)
For A₂X₁ system, equations 31-33 can be used to calculate the extent of reaction, both intra- and inter-molecular reactions.

### 1.6 Theoretical ratio of $p_{\text{intra}}/p_{\text{inter}}$

**Scheme S6** Different oligomers formed in the polymerization of A₃

The intramolecular reaction is a unimolecular reaction that is determined by the concentration of oligomers might undergo such reaction. In A₃ system, primary loops are only formed via intramolecular reactions of oligomers having at least two unreacted groups, such as A₃ and A₂ shown in Scheme S6, while A₁ and A₀ do not result in primary loops. The concentration of A₃ and A₂ are $[M]₀(1 – p)^3$ and $C_{2}^{3}[M]₀p(1 – p)^2$, where $[M]₀$ and $p$ are initial concentration of monomer and the extent of reaction. Since A₃ has three ways to form the primary loop and A₂ has one, the formation rate of primary loop ($R_{\text{intra}}$) is given by

$$R_{\text{intra}} = k_{\text{intra}}(3[M]₀(1 – p)^3 + C_{2}^{3}[M]₀p(1 – p)^2) = 3k_{\text{intra}}[M]₀(1 – p)^2 = k_{\text{intra}}[A]₀(1 – p)^2$$  \hspace{1cm} (34)

where $k_{\text{intra}}$ 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 ($R_{\text{inter}}$) is given by

$$R_{\text{inter}} = k_{\text{inter}}[A]^2 = k_{\text{inter}}[A]₀^2(1 – p)^2$$  \hspace{1cm} (35)

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

$$\frac{R_{\text{intra}}}{R_{\text{inter}}} = \frac{k_{\text{intra}}}{k_{\text{inter}}[A]₀}$$  \hspace{1cm} (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 $p_{\text{intra}}/p_{\text{inter}}$ given by equation 37 keeps constant and is independent of the extent of reaction.

$$\frac{p_{\text{intra}}}{p_{\text{inter}}} = \frac{R_{\text{intra}}}{R_{\text{inter}}} = \frac{k_{\text{intra}}}{k_{\text{inter}}[A]₀}$$  \hspace{1cm} (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$_3$)$_2$Cl$_2$-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-Dihydroxybenzoic (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)](image)

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 for 2 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 1/10 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 ($L^1_{AA}$), secondary ($L^2_{AA}$) and tertiary ($L^3_{AA}$) loops](image)

**Synthesis of methyl 3,5-bis(7-octenlyoxy)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**

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The 3,5-bis(7-octenloyloxy)benzoic acid (4b) was prepared by hydrolysis of methyl 3,5-bis(7-oct-1-enloyloxy)benzoate (4a) in 97% yield (139.7mg) as light-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.25-7.21 (d, 2H), 6.70-6.67 (t, 1H), 5.92-5.73 (m, 2H), 5.08-4.90 (m, 4H), 4.05-3.92 (t, 4H), 2.14-2.00 (m, 4H), 1.88-1.70 (m, 4H), 1.56-1.31 (m, 12H).\]
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)):
\[\delta 172.21, 160.20, 139.00, 130.95, 114.34, 108.16, 107.50, 68.31, 33.72, 29.12, 28.84, 25.88.\]

**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 metacyclophanes 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\(_3\)):
\[\delta 7.19-7.14 (m, 2H), 6.67-6.61 (m, 1H), 5.37-5.28 (m, 2H), 4.15-3.99 (m, 4H), 3.92-3.84 (s, 3H), 2.09-1.89 (m, 4H), 1.84-1.69 (m, 4H), 1.55-1.26 (m, 12H).\]
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)):
\[\delta 166.89, 159.83, 132.06, 130.53, 109.69, 105.74, 68.37, 52.18, 31.92, 28.86, 27.70, 27.30, 25.11.\]

Fraction 2 is compound 5a, as a colorless solid in 39.8% yield (39.5mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.18-7.12 (m, 4H), 6.65-6.69 (m, 2H), 5.43-5.30 (m, 4H), 4.01-3.91 (t, 8H), 3.91-3.86 (s, 3H), 2.11-1.91 (m, 12H), 1.82-1.69 (m, 8H), 1.55-1.27 (m, 24H).\]

Fraction 3 is compound 6a, as a colorless solid in 11.4% yield (10.3mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.18-7.12 (m, 6H), 6.65-6.69 (m, 3H), 5.43-5.30 (m, 6H), 4.01-3.91 (t, 12H), 3.91-3.86 (s, 9H), 2.11-1.91 (m, 12H), 1.82-1.69 (m, 12H), 1.55-1.27 (m, 36H).\]

**Synthesis of various loops** \(L_{1AA}^1, L_{2AA}^2\) and \(L_{3AA}^3\)

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 °C 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 MgSO₄. After the solvent was evaporated, pure product of Loop L₃ was obtained. (yield 29.2mg, 98%) ⁱH NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 L₃ was synthesized by the same method for loop L₂ (yield 24.5mg, 86%). ⁱH NMR (400 MHz, THF-d₈) 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). ¹³C NMR (101 MHz, THF-d₈) 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, L₄ was synthesized by the same method for loop L₃ (yield 8.1mg, 82%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 A₂X 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 °C 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 °C 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 MgSO₄. 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 ¹H NMR, the extent of reaction can be estimated from the peak area of corresponding proton. The peak areas of Hₐ (Sₐ) and Hₐ (Sₐ) 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.

\[ 0.5S_a = n_{net} + L^1 ; \quad 0.5S_b = d \]  

According to equation 3, 7 and 15,

\[ 0.5S_a = n_{net} + L^1 = \frac{a^2}{(a-2)^2} n_{XX} + 0.5a(a - 1)L_{AA} \]  

\[ 0.5S_b = d = a/(a-2)d_X \]

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

\[ 0.5S_a = 9N_{XX} + 3L_{AA}^1 = 3(3N_{XX} + L_{AA}^1) \]  

\[ 0.5S_b = 3d_X \]

In equation 41, \( l_{xx} \) is replaced by \( L_{AA}^1 \) as previous mentioned.

For A₂X₁ system, from equations 29 and 30, we get

\[ p_{total} = p_{intra} + p_{intet} = \frac{6N_{XX} + 2L_{AA}^1}{6N_{XX} + 2L_{AA}^1 + d_X} \]

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Combination of equations 41-43 results

\[ p_{\text{total}} = \frac{S_a}{S_a + S_b/2} \]  

(44)

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

\[ p_{\text{total}} = \frac{2[C=\text{c}]_{\text{internal}}}{2[C=\text{c}]_{\text{internal}} + [C=\text{c}]_{\text{terminal}}} = \frac{S_a}{S_a + S_b/2} \]  

(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 \(^1\text{H} \) NMR spectra.

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

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.

\[ S_f = 4L^1_{AA}; \quad S_e + S_f = 2[A] = 4n_M \]  

(46)

According to equation 26, we get

\[ p_{\text{intra}} = \frac{2L^1_{AA}}{n_M} = \frac{S_f/2}{(S_f + S_e)/4} = \frac{2S_f}{S_f + S_e} \]  

(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

\[ F_1 = n_1/I_1, \quad F_2 = n_2/I_2, \quad F_3 = n_3/I_3 \]  

(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,

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

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.

\[ [L^1]:[L^2]:[L^3] = T_1 \cdot F_1: 3T_2 \cdot F_2: 9T_3 \cdot F_3 \]  

(49)
### 3. Tables

**Table S1.** Characterization of polymer prepared by A<sub>2</sub>X<sub>1</sub> monomers

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;/D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>M&lt;sub&gt;total&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>P&lt;sub&gt;intr&lt;/sub&gt;&lt;sup&gt;*100&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
<th>P&lt;sub&gt;intr&lt;/sub&gt;/P&lt;sub&gt;inter&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</th>
<th>[L&lt;sup&gt;2&lt;/sup&gt;]/[L&lt;sup&gt;1&lt;/sup&gt;]&lt;sup&gt;k&lt;/sup&gt;</th>
<th>[L&lt;sup&gt;3&lt;/sup&gt;]/[L&lt;sup&gt;1&lt;/sup&gt;]&lt;sup&gt;k&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>1600/2.76</td>
<td>0.51/0.51</td>
<td>2.53&lt;sup&gt;i&lt;/sup&gt;/&lt;sup&gt;j&lt;/sup&gt;</td>
<td>5.2&lt;sup&gt;i&lt;/sup&gt;/&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.86&lt;sup&gt;i&lt;/sup&gt;/&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.64&lt;sup&gt;i&lt;/sup&gt;/&lt;sup&gt;j&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>1760/17.3</td>
<td>0.66/0.64</td>
<td>3.50&lt;sup&gt;/&lt;/sup&gt;</td>
<td>5.8&lt;sup&gt;/&lt;/sup&gt;</td>
<td>9.2&lt;sup&gt;/&lt;/sup&gt;</td>
<td>7.7&lt;sup&gt;/&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>2180/50.3</td>
<td>0.75/0.74</td>
<td>4.00&lt;sup&gt;/&lt;/sup&gt;</td>
<td>5.7&lt;sup&gt;/&lt;/sup&gt;</td>
<td>15&lt;sup&gt;/&lt;/sup&gt;</td>
<td>9.3&lt;sup&gt;/&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>86</td>
<td>1780/10.3</td>
<td>0.73/0.75</td>
<td>5.50/3.51</td>
<td>7.9/4.6</td>
<td>27/40</td>
<td>25/23</td>
</tr>
<tr>
<td>5</td>
<td>96</td>
<td>3109/14.1</td>
<td>0.73/0.71</td>
<td>6.00/2.51</td>
<td>9.2/3.2</td>
<td>11/38</td>
<td>8.9/28</td>
</tr>
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</table>

a) polymerization conditions: [1] = 0.2 M, [Ru]= 0.002 M, 40 °C, CH<sub>2</sub>Cl<sub>2</sub>. 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<sub>a</sub>/(S<sub>a</sub> + 0.5S<sub>b</sub>), where S<sub>a</sub> and S<sub>b</sub> are peak areas of H<sub>a</sub> and H<sub>b</sub> in 1H NMR spectra; d) extent of reaction contributed from all primary loops (p<sub>L1</sub>), estimated by 2S<sub>α</sub>/(S<sub>α</sub>+S<sub>β</sub>); e) calculated by p<sub>L1</sub>/(p<sub>sol</sub><sup>f</sup> − p<sub>L1</sub>) or p<sub>L1</sub>/(p<sub>gel</sub><sup>g</sup> − p<sub>L1</sub>); 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.

<table>
<thead>
<tr>
<th>Polymerization time (min)</th>
<th>L¹</th>
<th>L²</th>
<th>L³</th>
<th>Noise</th>
<th>Error (%)³</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>37556</td>
<td>4078</td>
<td>1384</td>
<td>100</td>
<td>0.3-7.2</td>
</tr>
<tr>
<td>40</td>
<td>2448</td>
<td>2829</td>
<td>1082</td>
<td>80</td>
<td>2.8-7.4</td>
</tr>
<tr>
<td>60</td>
<td>1535</td>
<td>2841</td>
<td>828</td>
<td>100</td>
<td>3.5-12</td>
</tr>
<tr>
<td>86(sol)</td>
<td>848</td>
<td>2902</td>
<td>1236</td>
<td>100</td>
<td>3.5-12</td>
</tr>
<tr>
<td>86(gel)</td>
<td>574</td>
<td>2876</td>
<td>756</td>
<td>100</td>
<td>3.5-17</td>
</tr>
<tr>
<td>96(sol)</td>
<td>7330</td>
<td>10344</td>
<td>3763</td>
<td>200</td>
<td>1.9-5.3</td>
</tr>
<tr>
<td>96(gel)</td>
<td>2419</td>
<td>11573</td>
<td>3878</td>
<td>400</td>
<td>3.5-17</td>
</tr>
</tbody>
</table>

a) The data are collected from Figure S13-S19; b) error % = noise/\text{max}(L¹, L², L³) * 100 - noise/\text{min}(L¹, L², L³) * 100
4. Collections of spectra data

Figure S1 $^1$H and $^{13}$C NMR, GC-MS spectra of monomer A$_2$X (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-octenylxyloxy)-benzoic acid (4b)
Figure S4 $^1$H and $^{13}$C NMR, GC-MS spectra of metacyclophane (4e)
Figure S5 $^1$H-NMR, $^{13}$C NMR and MALDI-TOF MS spectra of hydroxymethyl 3,5-(7-tetradecenyl-1,14-dioxy)-benzoic acid ($L_{AA}$, cleaved primary loop)
Figure S6 $^1$H NMR, $^{13}$C NMR (in THF-$d_8$), and MALDI-TOF MS spectra of secondary loop ($L_{AA}^2$)
Figure S7 $^1$H NMR and $^{13}$C NMR of tertiary loop ($L_{AA}^3$)
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)
Figure S13 MALDI-TOF MS spectra of decrosslinked polymer obtained at 20 minutes
Figure S14 MALDI-TOF MS spectra of decrosslinked polymer obtained at 40 minutes
Figure S15 MALDI-TOF MS spectra of decrosslinked polymer obtained at 60 minutes
Figure 9

A series of mass spectrometry graphs showing the intensity of various peaks at different masses. Each graph corresponds to a different series of data labeled as (i), (j), (k), (l), (m), (n), (o), (p) respectively. The x-axis represents the mass (m/z) and the y-axis shows the intensity in arbitrary units (a.u.). Specific mass values are highlighted on each graph, indicating the presence of particular substances or compounds in the samples tested.
Figure S16 MALDI-TOF MS spectra of decrosslinked polymer (sol part) obtained at 86 minutes
Figure S17 MALDI-TOF MS spectra of decrosslinked polymer (gel part) obtained at 86 minutes
Figure S18 MALDI-TOF MS spectra of decrosslinked polymer (sol part) obtained at 96 minutes
Figure S19 MALDI-TOF MS spectra of decrosslinked polymer (gel part) obtained at 96 minutes.