

## **Original**

### **Synthesis and thermal properties of polyamic acids and its six-membered cyclic polyimides from ethylenediaminetetraacetic acid**

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#### **Synopsis:**

This article represents the synthesis and characterization of polyamic acids and polyimides derived from several bifunctional amines with ethylenediaminetetraacetic acid (EDTA) anhydride using polyaddition followed by chemical/thermal imidization methods. The structural and thermal properties of the obtained polyamic acids and their six-membered cyclic polyimides were determined in detail by using FT-IR, TGA, and DSC analysis. Additionally, this method was also extended to synthesis of networked polyamic acid and polyimide using trifunctional amine and EDTA anhydride.

#### **Key-words:**

ethylenediaminetetraacetic acid, polyamic acids, polyimides, thermal properties

## **Introduction:**

The ethylenediaminetetraacetic acid (EDTA) is biodegradable colorless water-soluble solid.<sup>[1]</sup> EDTA and its related compounds are widely used in the field of industrial, medical, cosmetics and laboratory applications.<sup>[2]</sup> Due to the presence of two amino and four carboxylates functionals within the structure of EDTA it acts as an excellent sequester for metal ions complexation.<sup>[3]</sup> EDTA-anhydride (EDTAA) is a dibasic dicarboxylic anhydride, and can be easily prepared from EDTA using condensation in a single step.<sup>[4]</sup> The EDTAA can replace other widely used bifunctional anhydrides such as, pyromellitic dianhydride, naphthalene dianhydride and other aliphatic derived bifunctional anhydrides for polyaddition reactions.<sup>[5]</sup> In a similar manner EDTAA is expected to react with various bifunctional nucleophiles such as amines, thiols, and alcohols to give corresponding polymers. On the other hand, polyamic acids and polyimides can be synthesized from variety of functional amines and anhydrides by employing polyaddition method.<sup>[6]</sup> Among the available materials, the polyimides offer unique advantages such as low density and low dielectric constant which makes them special interest in aerospace and automotive industries.<sup>[7]</sup> Polymers based on EDTA structural unit have attracted the much attention in terms of their structural and physical properties and development into a biocompatible material.<sup>[8]</sup> Therefore, synthesis of various polyamic acids and their polyimides containing EDTA structural unit using bifunctional amines under mild conditions is a challenging work in the field of academia and

industry. Whereas, linear macromolecules, such as poly amic acids and polyimides, have been playing important role in the development of organic materials, since they possess a vast list of potential applications due to their unique characteristics.<sup>[9]</sup> Polyamic acids based on aromatic bifunctional amino structural units provides high chemical and UV-irradiation resistance and non-inflammability properties, which render it attractive for aerospace and defence applications.<sup>[10]</sup> Recently, few studies in literature have reported the EDTA polydentate structural units for waste water purification,<sup>[11]</sup> removal of heavy metal ions,<sup>[12]</sup> adhesive<sup>[13]</sup> and gene transfections applications.<sup>[14]</sup> In spite of these attractive features of polyamic acids and polyimides as a potential high performance functional polymers. And there is a lack of structural diversity on polyamic acids having EDTA structural units in the area of synthetic polymer chemistry. Herein, we report the synthesis and characterization of new type of polyamic acids and polyimides from aromatic bifunctional amines with EDTA anhydride by polyaddition followed by chemical/thermal imidization methods.

## Results and Discussion

The polyaddition of EDTA-anhydride with bifunctional amines were carried out in 1,3-dimethyl-2-imidazolidinone (DMI) solvent at 100 °C for 12 hours. After, 12 h the reaction mixture was poured into the large amount of acetone solvent to precipitate **Poly-1** in moderate to good yields 70-54% (Scheme 1, top). Next, the obtained **Poly-1** were cyclized

using both chemical/thermal imidization methods. For chemical imidization was carried out using NaOAC/AC<sub>2</sub>O, 145 °C, for 2 h. Afterwards, the obtained polymers were annealed at 200 °C for 4 h to make it cyclization completely by thermal imidization, the resulting polyimides **Poly-2** were obtained as insoluble solids in any solvents (Scheme 1, bottom). The solubility of **Poly-1a** and **Poly-1b** were tested in various solvents and the results are summarized in Table 1. Both polymers showed good solubility in highly polar solvents like DMF, DMSO and NMP, but were not shown the solubility in THF and CHCl<sub>3</sub>. Interestingly, **Poly-1b** possessing with aliphatic hexanediamine moiety showed excellent solubility in water at room temperature, whereas **Poly-1a** prepared from aromatic diamines were hardly soluble in water. Although these polymers were significantly soluble in DMF, unfortunately, molecular weight of **Poly-1a** and **Poly-1b** could not be estimated strictly by GPC system in DMF solvent, because polyamic acid is an ionic polymer having both positive and negative charges.<sup>[15]</sup> On the other hand, **Poly-2** were never soluble in any organic solvents and water. Thus, the chemical structures of **Poly-1** and **Poly-2** were confirmed in detail by FT-IR measurement as shown in Figure 1. The FT-IR spectra of **Poly-1a** and **Poly-1b** showed characteristics absorption due to the stretching vibrations of C=O bond and the bending vibrations of N-H bond on the amide moiety in the range around 1660 to 1630 cm<sup>-1</sup> and 1570 to 1550 cm<sup>-1</sup>, respectively. On the other hand, FT-IR spectra of **Poly-2a** and **Poly-2b** showed characteristics two carbonyl peaks of different intensities, which were related to asymmetric

and symmetric stretching vibration of typical polyimides, these typical absorptions were observed in the range of 1740 to 1730  $\text{cm}^{-1}$  and of 1690 to 1670  $\text{cm}^{-1}$ .<sup>[16]</sup> Additionally, the C-N stretching vibrations of polyimides were observed in the range of 1370 to 1340  $\text{cm}^{-1}$ . The above vibrational frequencies from FT-IR analysis reveals the successful formation of polyimides from chemical/thermal imidization methods. **Poly-1a** and **Poly-1b** were subjected to differential scanning calorimetry (DSC) and the results were shown in Figure 2. **Poly-1a** did not exhibit neither glass transition nor melting points in the range from 50 to 250 °C, whereas the DSC curve of **Poly-1b** exhibited the glass transition temperature ( $T_g$ ) at 63.1 °C because of the flexible aliphatic chain of hexamethylene moiety. As the specific peaks, the DSC curves of **Poly-1a** and **Poly-1b** showed their large endothermic peaks around 207 °C and 188 °C, respectively, which suggests their cyclization temperatures transforming into polyimides together with dehydration from the polyamic acid units in the main-chain. On the other hand, the DSC curves of **Poly-2a** and **Poly-2b** did not show anything peaks in the range from 50 to 250 °C. The thermal decomposition behaviour of **Poly-1** and **Poly-2** was investigated by thermogravimetric analysis (TGA) analysis in a nitrogen atmosphere at a heating range of 10 °C/min as shown in Figure 3. The TGA curves of **Poly-1a** and **Poly-1b** showed the decomposition behaviour of 2-steps. The first decomposition temperature of **Poly-1a** and **Poly-1b** were observed at 219 °C and 190 °C, which roughly agreed with the large endothermic peaks observed by DSC measurement. This means that the first

decomposition step of **Poly-1a** and **Poly-1b** were assigned to the thermal cyclization transforming into polyimides. Actually, the weight loss at first step of **Poly-1a** and **Poly-1b**, which were 11.8% and 14.6%, respectively, approached to theoretical weight loss of 11% due to the dehydration from the polyamic acid units in the main-chain. The second decomposition happened at high temperature region as the major degradation of polyimides. This hypothesis was revealed by the TGA results of **Poly-2a** and **Poly-2b**, because their TGA curves showed the one-step decomposition behaviour and the decomposition temperatures estimated by DTG curves were roughly agreed with that of **Poly-1a** and **Poly-1b**. Moreover, the 10% weight loss temperature ( $T_{d10}$ ) of **Poly-2a** and **Poly-2b** were observed at 301 °C and 320 °C as the thermal properties of six-membered cyclic polyimides bearing EDTA moieties, although the  $T_{d10}$  values of **Poly-1a** and **Poly-1b** could not be estimated strictly owing to the multi decomposition behaviour based on the thermal imidization process. These results also indicate the successful cyclization of polyamic acids into their polyimides by chemical/thermal imidization methods.

On the basis of the results as described above, the optimized polyaddition methods were further applied to the synthesis of networked polyamic acid and its polyimide as shown in Scheme 2. The networked polyamic acid (**Poly-3**) was successfully synthesized from EDTA anhydride and tris(2-aminoethyl)amine using optimized conditions with 56% yield as a brown color powder. The corresponding networked polyimide (**Poly-4**) was also achieved

by the chemical and thermally imidization with 68% yield as a black color solid. The obtained networked polymers were insoluble in any solvents. The chemical structures of **Poly-3** and **Poly-4** were characterized by FT-IR spectroscopy as shown in Figure 4. FT-IR spectrum of **Poly-3** exhibited two characteristics bands at  $1744\text{ cm}^{-1}$  and  $1531\text{ cm}^{-1}$ , which can be assigned to the stretching vibrations of C=O bond and the bending vibrations of N-H bond of -NH-CO- functional groups, respectively. In the spectrum of **Poly-4**, similar bands of symmetrical and asymmetrical vibrational stretching's of the networked polyimide were appeared at  $1736\text{ cm}^{-1}$  and  $1671\text{ cm}^{-1}$ , respectively, and also the C-N stretching vibrations of polyimides were observed at  $1346\text{ cm}^{-1}$ . This result indicates successful networked polyimide formation using chemical/thermal imidization methods. Next, the thermal properties of **Poly-3** and **Poly-4** were investigated by DSC and TGA analysis as shown in Figure 5. Due to the flexible aliphatic cross-linking chain of networked polyamic acid revealed the  $T_g$  at  $94.3\text{ }^\circ\text{C}$ , whereas the networked polyimide thermogram did not show any thermal transition in DSC analysis. Additionally, in the DSC curve of **Poly-3**, two kinds of the endothermic peaks were observed at  $197\text{ }^\circ\text{C}$  and  $231\text{ }^\circ\text{C}$ , which might be attributable to the partial cyclization of the polyamic acid moieties into poly(amic acid-imide) and subsequently complete imidization of the unreacted polyamic acid moieties, respectively. To prove the hypothesis, TGA measurements of **Poly-3** and **Poly-4** were performed as shown in Figures 5b and 5c. The TGA curves of **Poly-3** and **Poly-4** showed roughly 2-steps and single decomposition behavior, respectively.

In the first decomposition, further 2-steps weight loss of 6.1% and 19.9% were observed around 200 °C and 230 °C, which might be attributable to the partial and complete thermal imidization of polyamic acid moieties together with the dehydration, respectively, because their decomposition temperature specifically agreed with the temperature of endothermic peaks observed by DSC curve of **Poly-3**. In addition, the total weight loss at first step (19.9%) of **Poly-3** was in accord with theoretical weight loss of 20% due to the dehydration from the polyamic acid units in the main-chain. The major decomposition temperatures of **Poly-3** and **Poly-4** were observed at 365 °C and 368 °C by DTG curve, respectively. The agreement of decomposition temperatures indicates that the chemical and thermal cyclization of polyamic acid bearing EDTA moieties into six-membered cyclic polyimide is successfully applicable to the polyamic acid having networked structure. Moreover, **Poly-4** exhibited the  $T_{d10}$  value at 355 °C and the residue of 73.8% at 500 °C, indicating significantly high thermal stability due to the networked structure consisted with the six-membered cyclic polyimide originated from EDTA.

### **Conclusion:**

The polyaddition of aromatic and aliphatic bifunctional amines with EDTA-anhydride afforded the polyamic acids which were successfully further cyclized by thermally to afford the six membered cyclic polyimides. The detailed structural analysis of polyamic acids and



polyimides confirmed by FT-IR spectra. As the thermal properties of the obtained polymers, DSC and TGA measurements of polyamic acids successfully showed the cyclization temperatures transforming into polyimides. In addition, 10% weight loss temperatures of six-membered cyclic polyimides bearing EDTA moieties were confirmed by TGA analysis. Given the accessibility of this methodology, we also investigated the synthesis and thermal properties of the networked polyamic acid and its polyimide by FT-IR, DSC, and TGA analyses. The networked polyamic acid was successfully achieved by polyaddition of EDTA anhydride and trifunctional amine, and subsequently the corresponding networked polyimide was also achieved by the chemical and thermally imidization in the networked polymer chain. The networked six-membered cyclic polyimide exhibited significantly high thermal stability.

## **Experimental Details:**

### **Materials**

Ethylenediaminetetraacetic acid (EDTA) (99%), Acetic anhydride (99.5%), Pyridine (99.5%), 1,3-dimethyl-imidazolidinone (DMI) (99.5%), N,N-Dimethyl Formamide (99%), Sodium acetate (99.5%), Diethyl ether (99%), were purchased from Wako Pure Chemical Industries Co., Ltd. and used as received. 1,4-Phenylenediamine (99.4%), 1,6-diaminohexane (99%), and tris(2-aminoethyl)amine (98%) were purchased from Tokyo

Chemical Industry Co., Ltd. Dimethyl sulfoxide-d<sub>6</sub> (99% D) were obtained from Kanto Chemical Co., Inc. and used as received.

## Measurements

Infrared spectra were recorded on a Thermo Fischer Scientific Nicolet iS10 spectrometer with a smart iTR diamond ATR sampling accessory in the range of 4000-650 cm<sup>-1</sup>. TGA was carried out on a Seiko Instrument Inc. TG-DTA 6200 with an aluminum pan under 200 mL/min N<sub>2</sub> flow at a heating rate of 10 °C/min. DSC analysis was carried out on a SHIMADZU DSC-60A with an aluminum pan under 50 mL/min N<sub>2</sub> flow at a heating rate of 10 °C/min. <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR recorded with a JEOL ECS-400 spectrometer, and chemical shifts  $\delta$  and coupling constant  $J$  were given in ppm and Hz using DMSO-d<sub>6</sub> as internal standard.

## Synthesis of Ethylenediaminetetraacetic dianhydride (EDTAA)

EDTA **1** (10.0 g, 1.00 mmol) was dissolved in acetic anhydride (0.51 g, 5.00 mmol) in a 200 mL flask under argon atmosphere and suspension was allowed to stir for 10 min at room temperature. To this stirred suspension, pyridine (0.40 g, 5.00 mmol) was added slowly under same atmosphere. Next, temperature of reaction mixture was initiated to 70 °C for 24 h. During the reaction, the color of the reaction mass was changes to light yellow to medium

yellow. After 24 h, the reaction mixture was cooled to room temperature and filtered and washed with Et<sub>2</sub>O and hexanes three times to obtain pure EDTAA **2** in 99% yield (Scheme 3). The EDTAA **2** was obtained as a white solid and its structure was confirmed by <sup>1</sup>H- and <sup>13</sup>C-NMR analyses. The NMR data were identical with the reported one.<sup>[17]</sup>

**Typical procedure for the synthesis of polyamic acids (Poly-1a and Poly-1b) via polyaddition of EDTA-anhydride using bifunctional diamines**

EDTAA (0.500 g, 1.00 mmol) was taken in 50 mL of flask containing DMI (5 mL) solvent at room temperature. Next, the bifunctional diamines (1.00 mmol) were added at same temperature and reaction mixture were allowed to stir at 100 °C for 12 h. After completion of reaction time, the suspension was dissolved in 2 mL of DMF, it was purified by reprecipitation into large excess of acetone, and the polyamic acids were dried under the vacuum at 50 °C for overnight (Scheme 1).

**Poly-1a:** Synthesized according to the general procedure, the polyaddition of EDTAA (0.50 g, 1.00 mmol) with 1,4-diaminobenzene (0.21 g, 1.00 mmol) was carried out to give **Poly-1a** (0.48 g, 68%) as a grey powder. FT-IR (ATR): 3259, 2963, 1616, 1658, 1571, 1515, 1406, 1309, 1231, 839, 688 cm<sup>-1</sup>. (<sup>1</sup>H NMR in DMSO-d<sub>6</sub>): d (ppm): 10.05 (s, 1H), 9.64 (s, 1H),

7.25 (s, 2H), 6.94 (s, 2H), 3.63 (bs, 4H), 3.43 (s, 4H), 2.80 (s, 4H). ( $^{13}\text{C}$  NMR in DMSO- $d_6$ ):  
d (ppm): 173.4, 168.9, 145.3, 127.8, 121.3, 114.3, 58.7, 56.2, 52.8

**Poly-1b**: Synthesized according to the general procedure, the polyaddition of EDTAA (0.50 g, 1.00 mmol) with 1,6-diaminohexane (0.23 g, 1.00 mmol) was carried out to give **Poly-1b** (0.43 g, 59%) as a white powder. FT-IR (ATR): 3212, 2952, 1636, 1559, 1541, 1434, 1386, 1212, 1134, 1072, 697  $\text{cm}^{-1}$ . ( $^1\text{H}$  NMR in  $\text{D}_2\text{O}$ ): d (ppm): 3.85-3.65 (m, 2), 3.56-3.43 (m, 2), 3.20 (bs, 4H), 2.95 (s, 4H), 2.10 (s, 4H), 1.62-1.57 (m, 4), 1.36-1.26 (m, 4). ( $^{13}\text{C}$  NMR in  $\text{D}_2\text{O}$ ): d (ppm): 174.0, 169.1, 57.4, 56.7, 51.6, 39.3, 28.2, 26.6, 25.7, 25.4, 25.1

**Typical procedure for the synthesis of polyimides (Poly-2a and Poly-2b) via chemical/thermal imidization of polyamic acids**

The polyamic acids (1.00 mmol) were taken in 50 mL flask containing NaOAc (3.00 mmol) and acetic anhydride 5 mL and allowed to reflux at 145 °C for 2 h. After cooling at room temperature the suspension were reprecipitated into a large excess of water. And the polyimides were dried under the vacuum at 60 °C for overnight. Further, additionally obtained polyimides were thermally cyclized at 200 °C for 4 h, the resulting polyimides were obtained as insoluble solids in solvents.

**Poly-2a:** Synthesized according to the general procedure. The chemical imidization of **Poly-1a** (0.40 g, 1.00 mmol) with NaOAc (0.21 g, 3.00 mmol) in Ac<sub>2</sub>O (5 mL), followed by thermal imidization (at 200 °C for 4 h) was carried out to give **Poly-2a** (0.20 g, 50%) as a black color solid. FT-IR (ATR): 1741, 1678, 1511, 1405, 1367, 1311, 1255, 1017, 837 cm<sup>-1</sup>.

**Poly-2b:** Synthesized according to the general procedure. The chemical imidization of **Poly-1b** (0.40 g, 1.00 mmol) with NaOAc (0.26 g, 3.00 mmol) in AC<sub>2</sub>O (5 mL), followed by thermal imidization (at 200 °C for 4 h) was carried out to give **Poly-2b** (0.11 g, 28%) as a black color solid. FT-IR (ATR): 2946, 2863, 1732, 1671, 1433, 1400, 1348, 1257, 1162, 972, 943 cm<sup>-1</sup>.

### **Synthesis of networked polyamic acid (Poly-3)**

EDTAA (5.25 g, 1.50 mmol) was taken in 50 mL of flask containing DMI (5 mL) solvent at room temperature. Next, tris(2-aminoethyl)amine (2.00 g, 1.00 mmol) was added at same temperature and reaction mixture were allowed to stir at 100 °C for 12 h. After completion of reaction time, the suspension was dissolved in 8 mL of DMF, it was purified by reprecipitation into large excess of acetone, and then was dried under the vacuum at 50 °C for overnight to give **Poly-3** (4.38 g, 60%). FT-IR (ATR): 2952, 2831, 1644, 1531, 1459, 1387, 1294, 1125, 1094, 713 cm<sup>-1</sup>.

### Synthesis of networked polyimide (Poly-4)

The chemical imidization of **Poly-3** (3.00 g, 1.00 mmol) with NaOAc (4.50 g, 3.00 mmol) in AC<sub>2</sub>O (10 mL), followed by thermal imidization (at 200 °C for 4 h) was carried out to give **Poly-4** (1.50 g, 50%) as a black color solid. FT-IR (ATR): 2911, 2781, 1736, 1671, 1346, 1158, 1021, 755 cm<sup>-1</sup>.

### Acknowledgements:

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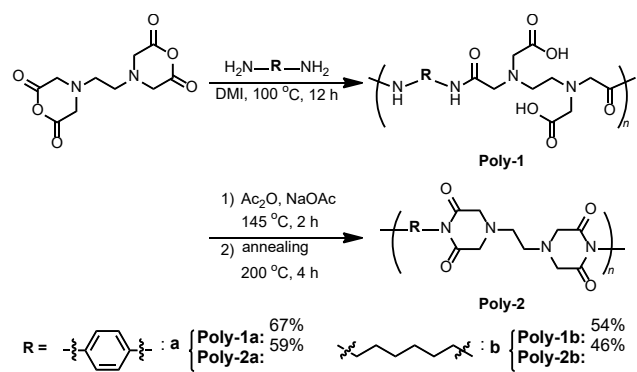
### References:

- [1] P. Matteo. *Bulletin for the history of chemistry*. **2017**, *42*, 133-140.
- [2] a) T. Furia, *Food Technology*. **1964**, *18*, 1874-1882. b) B. Nortemann. *Applied Microbiology and Biotechnology*. **1999**, *51*, 751-759. c) A. Piechalak, B. Tomaszewska, D. Baralkiewicz. *Phytochemistry*. **2003**, *64*, 1239-1251. d) E. Bloem, S. Haneklaus, R. Haensch, E. Schnug. *Science of the total environment*. **2017**, *577*, 166-173.
- [3] a) B. Francois, C. M. Bourg Alain. *Aquatic Geochemistry*, **1998**, *4*, 201-214, b) S. Pozdniakova. *Analyst*, **1998**, *123*, 1497-1500. c) F. Munoz, C. Von Sonntag. *Perkin 2*. **2000**, *10*, 2029-2033.
- [4] A. M. Senna, M. K. Novack, R. V. Botaro. *Carbohydrate Polymers*. **2014**, *114*, 260-268.

- [5] a) X.-Y. Liu, M.-S. Zhan, K. Wang. *High Performance Polymers*. **2012**, *24*, 373-378. b) Y. Li, X. Yan, M.-S. Zhan, K. Wang. *J. Appl. Polym. Sci.* **2012**, *125*, 4128-4134.
- [6] a) D. Liaw, K. Wang, Y. Huang, K. Lee, J. Lai, C. Ha. *Prog. Polym. Sci.* **2017**, *37*, 907-974. b) C. E. Sroog. *Prog. Polym. Sci.* **1991**, *16*, 561-694.
- [7] a) H. Deligoz, S. Ozgumus, T. Yalcinyuva, S. Yildirim, D. Deger, K. Ulutas. *Polymer*. **2005**, *46*, 3720-3729. B) T. F. Conceicao, N. Scharnagl, C. Blawert, W. Dietzel. K. U. Kainer. *Corros. Sci.* **2011**, *53*, 338-346.
- [8] a) M. M. Taheri, A. Kadir, M. Rafiq, S. Tolou, H. Azhang. A. Mahtab, S. Mostafa Rezazzadeh. M. Abolfazl. *Ceramics International*. **2015**, *41*, 9867-9872. b) Q. Hongfei, Y. Zhihong, R. Hailong, C. Nana, Z. Qingyan. W. Xianglong. L. Tingli. *Life Sciences*. **2016**, *148*, 139-144.
- [9] a) C. E. Sroog, *Progress in Polymer Science*. **1991**, *16*, 561-694. b) C. E. Sroog. *Journal of Polymer Science, Part D: Macromolecular Reviews*. **1976**, *11*, 161-208. c) D. Mengxian. *Prog. Polym. Sci.* **2007**, *32*, 623-668. d) M. Sato. *Plastics Engineering*. **1997**, *41*, 665-699. e) H. D. Stenzenberger. *Adv. Polym. Sci.* **1994**, *117*, 165-220.
- [10] a) Y. Okada, Y. Yamashita, H. Itaya. (JAPAN) *Jp2011132611 A 2011-07-07*. b) T. Ueda, T. Nishio, S. Inoue. *Open Journal of Organic Polymer Materials*. **2017**, *7*, 47-60. c) V. Gabara. United States. *US20090053500 A1 2009-02-26*. d) D. A. Rau, J. Herzberger, T. E. Long, C. B. Williams. *ACS. Appl. Mater. Interfaces*. **2018**, *10*, 34828-34833.

- [11] S. Panja, S. Hanson, C. Wang. *ACS. Appl. Mater. Interfaces*. **2020**, *12*, 25276-25285.
- [12] Y. Jiang, C. Liu, A. Huang. *ACS. Appl. Mater. Interfaces*. **2019**, *11*, 32186-32191.
- [13] K. Netsomboon, W. Suchaoin, F. Laffluer, F. Prüfert, A. Bernkop-Schnürch. *Eur. J. of Pharmaceutics and Biopharmaceutics*. **2017**, *111*, 26-32.
- [14] S.-Y. Wu, L.-T. Chang, S. Peng, H.-C. Tsai. *Int. J. Nanomedicine*. **2015**, *10*, 1637-1647.
- [15] Y. Mukoyama and H. Sugitani. *Anal. Sci. Aug*. **1985**, *1*, 299-300.
- [16] B. Rukmanikrishnan and S. Muthusamy. *Adv. Polym. Technol*. **2018**, *37*, 21641.
- [17] Q. Peng, Y. Yuan, H. Zhang, S. Bo, S. Chen, Z. Yang, X. Zhou, Z-X. Jiang. *Org. Biomol. Chem*. **2017**, *15*, 6441-6446



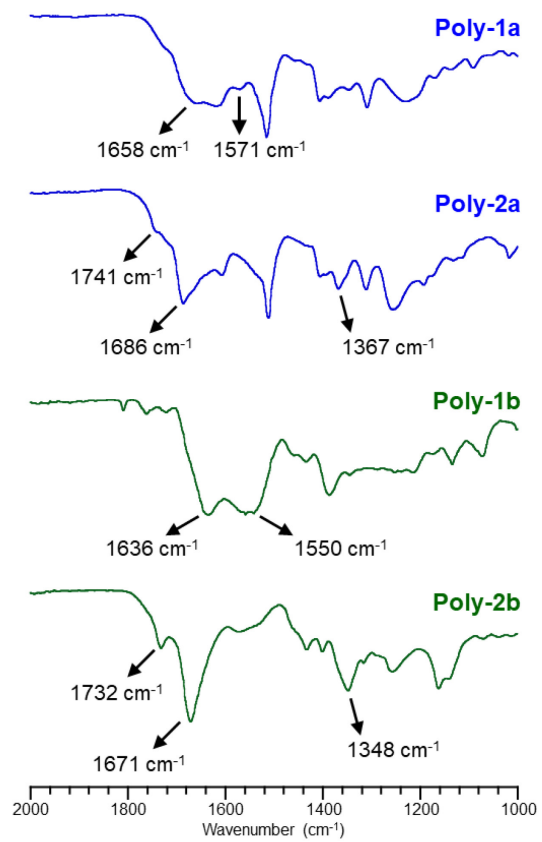


**Scheme 1.** Synthesis of polyamic acids (**Poly-1**) and polyimides (**Poly-2**)

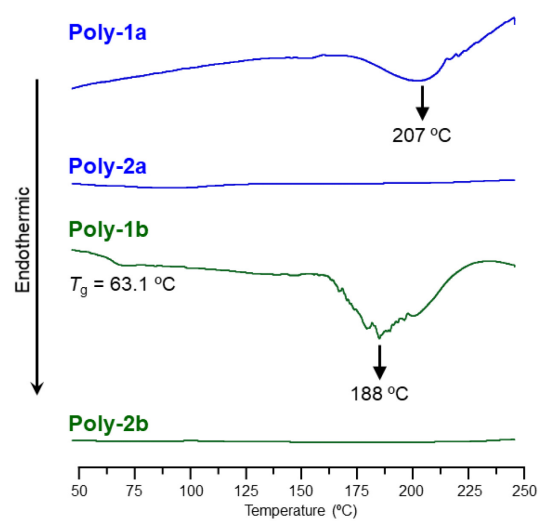
**Table 1. Solubility of Poly-1 in various solvent and their molecular weights**

entry	solubility <sup>a</sup>					
	H <sub>2</sub> O	THF	CHCl <sub>3</sub>	DMF	DMSO	NMP
<b>Poly-1a</b>	–	–	–	+	+	+
<b>Poly-1b</b>	+	–	–	+	+	+

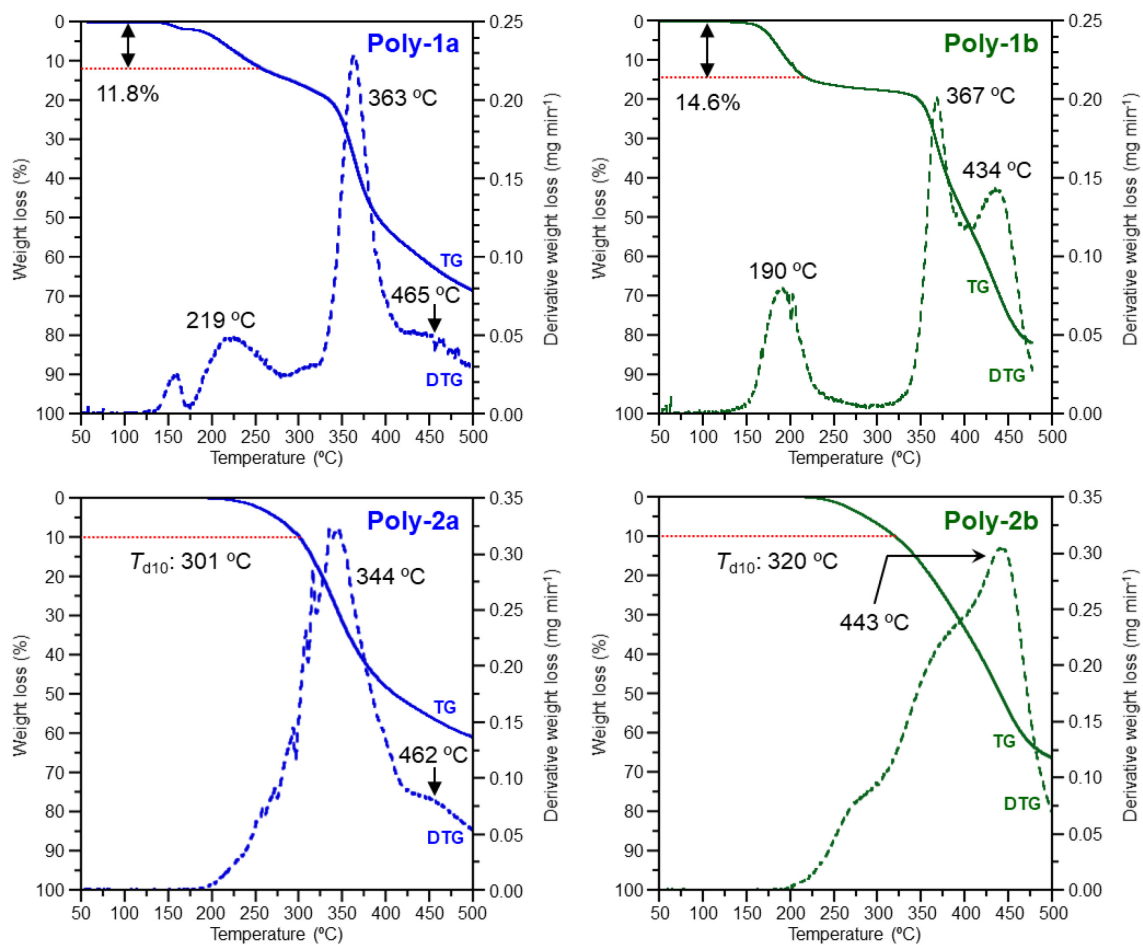
<sup>a</sup> The qualitative solubility was tested with 50 mg of polyamic acids in 1ml of solvent at room temperature. – insoluble at room temperature, + soluble at room temperature. THF: tetrahydrofuran, CHCl<sub>3</sub>: chloroform, DMF: *N,N*-dimethyl formamide, DMSO: dimethyl sulfoxide, NMP: *N*-methyl pyrrolidine.



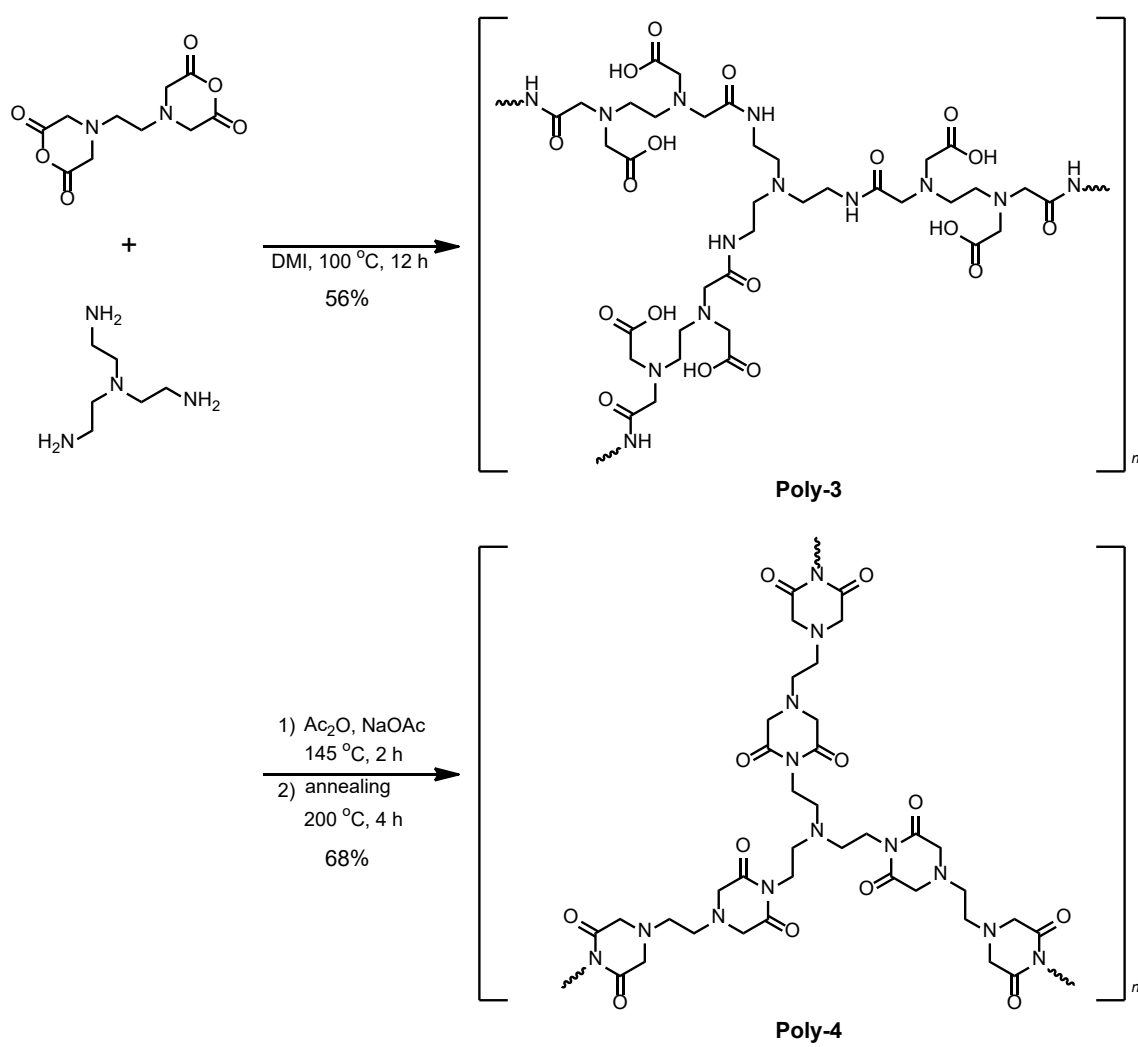
**Figure 1.** FT-IR spectra of **Poly-1** and **Poly-2**



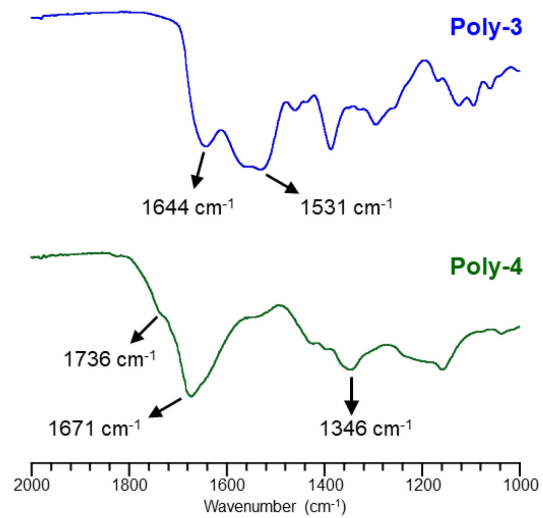
**Figure 2.** DSC curves of **Poly-1** and **Poly-2**



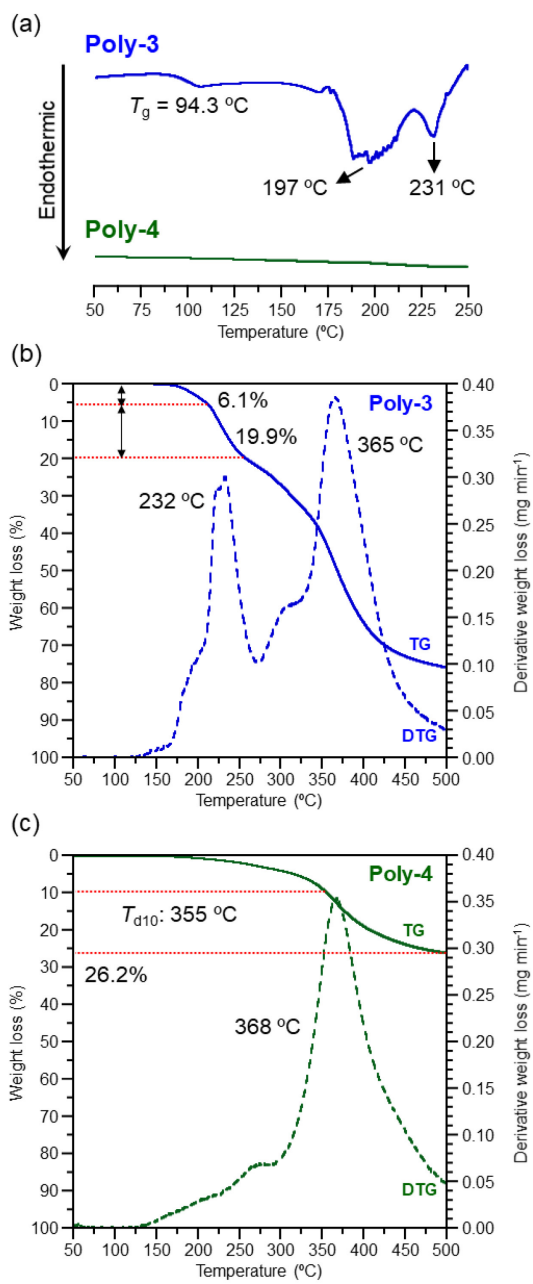
**Figure 3.** TGA curves of Poly-1 and Poly-2



**Scheme 2.** Synthesis of networked polyamic acid (**Poly-3**) and its polyimide (**Poly-4**)

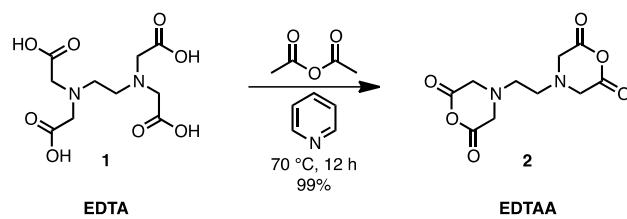


**Figure 4.** FT-IR spectra of **Poly-3** and **Poly-4**



**Figure 5.** (a) DSC curves of **Poly-3** and **Poly-4**, (b) TGA curve of **Poly-3**, and (c) TGA curve of **Poly-4**





**Scheme 3.** Preparation of EDTAA