Explore diacetylene-based C$_{2h}$-symmetric monomers for two dimensional polymers’ synthesis

General information on synthesis, purification and characterization

All reagents were purchased from Aladdin and Xiyareagent, and used without further purification.

Nuclear Magnetic Resonance (NMR) spectra were recorded on WIPM 400 ($^1$H: 400 MHz, $^{13}$C: 100 MHz) and Varian Inova 600 ($^1$H: 600 MHz, $^{13}$C: 150 MHz) using CDCl$_3$ and $d_6$-DMSO as solvent. Solvent signals were used as internal standards for chemical shifts ($^1$H: $\delta$ = 7.26 ppm and $^{13}$C: $\delta$ = 77.16 ppm for CDCl$_3$; $^1$H: $\delta$ = 2.50 ppm and $^{13}$C: $\delta$ = 39.52 ppm for $d_6$-DMSO).

High resolution mass spectrometry (HRMS) analyses were performed with an Agilent LC-MS TOF 1260-6224.

Crystallographic data (CCDC number: monomer 1, 1493349; monomer 2, 1474129; compound 4, 1474130; compound 9, 1474925) was collected by the X-ray analysis service at Huazhong Normal University (SMART APEX CCD, monomer 2, 9) or Wuhan University (Bruker SMART APEX2, monomer 1) and cif files are attached.

Melting point was recorded on a WRS-2A digital melting point instrument.

The Raman spectroscopy measurement was conducted with an Invia Raman spectroscope (λ = 785 nm). Materials were milled between two glass slides and measured directly on a glass slide.

For the Infrared (IR) spectra, Materials were mixed with KBr and measured with an Nicolet iS10 Infrared spectroscope.

The optical microscopy measurement was performed with a transflective polarized microscope (Shanghai Tuming CP-602C).

The differential scanning calorimetry (DSC) spectrometry was measured by Shimadzu DSC-60 under a nitrogen atmosphere.

The Thermal Gravimetric Analysis (TGA) was performed with Perkin elmer Diamond TG/DTG under a nitrogen atmosphere.

S2
Synthesis procedures, analytical data and original spectra

**Compound 3:**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{OH}
\end{align*}
\]

The known compound hexa-2,4-diyne-1,6-diol (3) (CAS:3031-68-3) was prepared according to ref. 18 with minor modifications.

A beaker was charged with a mixture of CuCl (CAS:7758-89-6, 4.1 g, 41 mmol), TMEDA (CAS:110-18-9, 6.3 mL, 42 mmol), acetone (CAS:67-64-1, 350 mL) and propargyl alcohol (CAS:107-19-7, 50 mL, 860 mmol). The mixture was stirred at room temperature (31-23 °C) overnight. After reaction, ether (CAS:60-29-7, 300 mL) was added and the mixture was washed with saturated NH4Cl (CAS:12125-02-9, 100 mL X 2) and brine (70 mL X 2). The yellow organic extracts was concentrated and then redissolved in hot THF (CAS:109-99-9,150 mL). After cooling, compound 3 was obtained as light yellow solid (34.7 g, 73%). M.p. 112 °C.

\[^1\text{H-NMR (d}_6\text{DMSO)} \delta/\text{ppm: 5.41 (t, } J = 4 \text{ Hz, } 2H, \text{ OH); 4.17 (d, } J = 4 \text{ Hz, } 4H, \text{ CH}_2).\]

**Compound 1:**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]
Figure S1: $^1$H- (a) and $^{13}$C-NMR spectra (b) of compound I.
Figure S2: Crystal structure of monomer 1. (a) The ellipsoid plot; (b) CheckCIF report.
Compound 2:

Figure S3: $^1$H- (a) and $^{13}$C-NMR spectra (b) of compound 2.
Figure S4: Crystal structure of monomer 2. (a) The ellipsoid plot; (b) CheckCIF report.
Compound 4:

CuCl (0.207 g, 2 mmol) and TMEDA (0.233 g, 2 mmol) were dissolved in acetone (2 mL) in an open beaker. After stirring for 3 min, compound 5 (0.406 g, 2 mmol) was added to the solution. The reaction was carried out at 40 °C for 16 h. The product mixture was washed with water and a white precipitate was collected by centrifugation (0.350 g, 0.86 mmol, 86.5%). M.p. 188.7 °C.

\[ \text{1H-NMR (400 MHz, CDCl}_3\text{)} \delta/\text{ppm}: 6.52 (s, 4 H, H-1), 5.29 (s, 4 H, H-2), 4.27 (s, 2 H, H-4), 2.89 (s, 4 H, H-3). \]

\[ \text{13C-NMR (150 MHz, d}_6\text{-DMSO)} \delta/\text{ppm: 175.53, 136.71, 80.53, 73.33, 66.02, 47.55, 27.90.} \]

HRMS (LC-MS TOF, Formic acid) calcd. for C\text{22H}_{16}N\text{2O}_6[MNa]^+ 427.0901, found 427.0941.
Figure S5: $^1$H- (a) and $^{13}$C-NMR spectra (b) of compound 4.
Figure S6: Crystal structure of compound 4. (a) The ellipsoid plot; (b) CheckCIF report.

**Compound 5:**

Propargyl bromide (CAS:106-96-7, 0.238 g, 2 mmol), compound 6 (0.495 g, 3 mmol) and K₂CO₃ (CAS:584-08-7, 0.828 g, 6 mmol) were dissolved in anhydrous DMF (CAS:68-12-2, 5 mL). The mixture was purged with Ar gas and stirred at 60 °C for 3 h. After reaction, the volatile was removed and the remains were extracted by CH₂Cl₂ (CAS:79-09-2). Evaporation of the solvent under reduced pressure afforded product as a white solid (0.274 g, 1.35 mmol, 67.4%). M.p. 138.6 °C.
\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 6.52\) (s, 2 H, H-1), 5.30 (s, 2 H, H-2), 4.24 (s, 2 H, H-4), 2.91 (s, 2 H, H-3), 2.20 (s, 1 H, H-5).

**Compound 6:**

A round flask with a condenser was charged with compound 7 (30 g, 0.181 mol), ammonia liquor (CAS:1336-21-6, 100 mL) and water (20 mL). The mixture was refluxed for 2 h and then cooled to room temperature. Crystalline needles were formed overnight. Compound 6 was obtained by filtration as white crystals. (26.9 g, 0.163 mol, 90%). M.p. 156.2 °C.

\(^1\)H-NMR (400 MHz, d\(_6\)-DMSO) \(\delta/\text{ppm}: 6.53\) (s, 2 H, H-1), 5.11 (s, 2 H, H-2), 2.85 (s, 2 H, H-3).

**Compound 7:**

A mixture of maleic anhydride (CAS 108-31-6) (10 g, 102 mmol), furan (CAS:110-00-9, 20 mL, 28 mmol) and diethyl ether (60 mL) was stirred at room temperature for 2 h. The product precipitated out and was collected by vacuum filtration. The colorless product was used without further purification. Yield (15.312 g, 92 mmol, 90.4%). M.p. 108 °C, ref. (118 °C), Z. Kolodynska, *Acta Poloniae Pharmaceutica, 1975*, 32, 133 - 137.

**Compound 8:**

A round flask was charged with maleic anhydride (5.10 g, 52 mmol) dissolved in a refluxing acetone (25 mL). Propargylamine (CAS:68-12-2, 3.43 mL, 50 mmol) was slowly dropped in this solution and the reaction continued for 2 h with refluxing. After cooling, the solvent was removed under vacuum and the reddish remains was recrystallized from an ether/methanol mixture (1:4) to afford colorless needles of N-propargylmonoamic maleic acid (5.2 g, 67.9%). M.p.141°C. \(^1\)H-NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 13.88\) (s, 1 H, COOH), 9.15 (t, 1 H, \(\text{J} = 6\) Hz, NH), 6.32 (d, 1 H, \(\text{J} = 12.2\) Hz, CH=CH), 6.26 (d, 1 H, \(\text{J} = 12.2\) Hz, CH=CH), 3.97 (dd, 2 H, \(\text{J}_1 = 6\) Hz, \(\text{J}_2 = 2.6\) Hz, CH\(_2\)), 3.19 (t, 1 H, \(\text{J} = 2.6\), CH).

N-propargylmonoamic maleic acid (3.072 g, 20.0 mmol) was further
dehydration-cyclized by refluxing in 80 mL of xylene, under a Dean-Stark trap for 4 h. After reaction, the hot solution was filtered to remove insoluble byproducts and dried to yield 6 as colorless oil (0.654 g, 4.84 mmol, 24.2%).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 6.76 (\text{s}, 2 \text{ H, H-1}), 4.29 (\text{s}, 2 \text{ H, H-2}), 2.21 (\text{s}, 1 \text{ H, H-3}).\)

**Compound 9:**

![Chemical structure of Compound 9](image)

Bismaleimide 9 is a known compound and was synthesized according to ref. 20 with minor modifications.

4,4'-oxydianiline (CAS:101-80-4, 2.0 g, 10 mmol) and maleic anhydride (2.15 g, 22 mmol) in acetone (45 mL) was refluxed for 10 mins and then added NaOAc (CAS:127-09-3, 5.83 g, 71 mmol) and acetic anhydride (CAS:108-24-7, 10 mL). The mixture was further heated at 60 °C over night. After reaction, volatile was removed and the remains passed a silica-column (ethyl acetate: petroleum ether = 4:1) affording a bright yellow solid 9 (3.46 g, 9.6 mmol, 96%). M.p. 180 °C.

\(^1\)H-NMR (400 MHz, \(d_6\)-DMSO) \(\delta/\text{ppm}: 7.40 (\text{d, } J = 7.8 \text{ Hz, 4H, benzene}), 7.15 (\text{d, } J = 7.8 \text{ Hz, 4H, benzene}), 6.79-6.71 (\text{s, 4H, maleimide}).\)
Figure S7: Crystal structure of compound 9. (a) The ellipsoid plot; (b) CheckCIF report.

**Compound 10:**

![Chemical structure of Compound 10](image)

N-Ethylmaleimide (CAS:128-53-0, 60 mg, 0.479 mmol) in acetonitrile (CAS:75-05-8, 2 mL) was degassed with argon for 1 min and irradiated (365 nm) in a glass bottle for 24 h. Bulk colorless crystals precipitated our and were filtered (60 mg, 0.479 mmol, 100%). M.p. > 250 °C.
$^1$H-NMR (600 MHz, CDCl$_3$) δ/ppm: 3.65 (q, 4 H, $J = 6$ Hz, CH$_2$), 3.36 (s, 4 H, CH), 1.22 (t, 6 H, $J = 6$ Hz, CH$_3$).

**Compound 11:**

![Chemical structure of Compound 11]

A glass flask was charged with maleimide (CAS:541-59-3, 100 mg, 1.042 mmol) and acetonitrile (3 mL). The resulting solution was degassed with argon for 1 min and irradiated (365 nm) for 24 h. Bulk colorless crystals precipitated out and were filtered (100 mg, 1.042 mmol, 100%). M.p. > 250 °C. $^1$H-NMR (600 MHz, d$_6$-DMSO) δ/ppm: 11.67 (s, 2 H, NH), 3.29 (s, 4 H, CH).

**Irradiation experiment**

The photo reactor was self-made and equipped with four UV-lamps (365 nm, 4*9 W, gross power = 36 W) and a cooling fan on the ceiling.

![Photo reactor diagram]

Figure S8: photo reactor for the irradiation experiment.
Figure S9: Infrared spectra of the N-ethylmaleimide (top) and its photodimer (bottom).
Figure S10: Infrared spectra of the maleimide (top) and its photodimer (bottom).
Figure S11: Raman spectra of the \( N \)-ethyl maleimide (top) and its photodimer (bottom).
Figure S12: Raman spectra of the maleimide (top) and its photodimer (bottom).
Figure S13. The DSC measurement of irradiated materials from 15 – 300 °C.

Figure S14. The TGA measurement of irradiated materials from 30 – 800 °C.