Supplementary Information

Rational Design of Soluble and Clickable Polymers Prepared by Conventional Free Radical Polymerization of Acetylene-Functionalized Acrylate

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Experimental Section
Materials
1-ethynyl-1-cyclohexanol, 2-hydroxy-2-methyl propiophenone (PI 1173), (2,4,6-Trimethylbenzoyl) diphenylphosphine oxide (TPO) and trimethylol propane tris(3-mercaptopropionate) (MTP) were purchased from Tianjin Jiuri Chemicals, China, and directly used without further purification. Ethynyl-1-cyclohexanol, Propargyl Acrylate (PA), AIBN were purchased from Aladdin Chemical CO., China, and AIBN was recrystallized twice from absolute methanol. (Meth)acryloyl chloride was freshly prepared and distilled before use. Methyl methacrylate was purified twice by passing a column filled with basic alumina to remove the inhibitor. Other solvents and common chemicals were used as received without further purification.

Synthesis of 1-ethynylcyclohexyl acrylate (ECA)
Ethynyl-1-cyclohexanol (30 g, 0.24 mol), triethylamine (31.36 g, 0.31 mol), and 150 mL of anhydrous dichloromethane were charged in a 500 mL dried round-bottom flask immersed in an ice bath at 0 °C. Freshly prepared and distilled acryloyl chloride (26.26 g, 0.29 mol) was added dropwisely for 2 h. Then the mixture was stirred at 10 °C for 12 h. After filtration and concentration with a rotavapor the crude product was diluted with cyclohexane. Then the solution was extracted
subsequently with saturated aqueous solution of NaHCO₃, the mixture of methanol:water=3:4(wt/wt), distilled water until neutralization. The organic layer was dried over anhydrous MgSO₄ and distilled off under vacuum to give a transparent liquid product. Weight: 29.4 g; yield: 69%. ¹H-NMR (400MHz, CDCl₃) : δ ppm, 2.51 (1H, H-C≡C), 6.31,6.11,5.81 (3H,CH₂=CH-), 2.14-1.74 (4H, CH₂ of cyclohexyl adjacent to the tertiary Carbon), 1.61-1.20 (6H of cyclohexyl). ¹³C-NMR (400MHz, CDCl₃): δ ppm,130.47 (CH₂=CH-), 129.04(CH₂=CH-), 74.45 (H-C≡C), 75.43 (H-C≡C), 164.35 (CH₂=CH-COO-), 83.41(-COO- of C₆H₁₀), 36.81, 22.20 and 24.84 (the other carbons of the cyclohexyl).

**Ploymerization of ECA**

A typical polymerization procedure for ECA was as follows. ECA (2g, 11 mmol), AIBN (0.01g, 0.06 mmol), 3g ethyl acetate were charged in a 25 mL round-bottom flask equipped with magnetic stirrer and capped with rubber septa. After purging with highly pure nitrogen gas for 20 min, the system was polymerized at 70°C for 8h. At the end of the reaction, polymer was precipitated in methanol and dried in vacuum. Bulk photopolymerization was similar but without the addition of solvent.

**Photopolymerization of ECA**

ECA (2g, 11 mmol), TPO (0.035g, 0.10 mmol), 2g ethyl acetate were charged in a 25 mL round-bottom flask equipped with magnetic stirrer and capped with rubber septa. After purging with highly pure nitrogen gas for 20 min, the solution was irradiated with 1000w medium-pressure mercury lamp at 25°C for 2.5 h. At the end of the reaction, polymer was precipitated in methanol and dried in vacuum.

**Analysis**

NMR spectroscopy: ¹H- NMR and ¹³C- NMR spectra (400 MHz) were recorded with a Bruker AC200 spectrometer, withCDCl₃ used as solvents. All chemical shifts are stated in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (¹H and ¹³C). FT-IR measurements were carried out with a Nicolet iS10 Fourier Transform spectrometer equipped with a tungsten halogen lamp, a KBr beam splitter, and a DTGS detector. Each spectrum in the spectral region of 4000-400 cm⁻¹ with resolution of 4 cm⁻¹.
Figure S1. $^{13}$C NMR spectra of ECA in CDCl$_3$

Figure S2. FT-IR spectra of the PECA
Figure S3 $^1$H-NMR spectra of mixtures obtained from bulk polymerization of ECA in CDCl$_3$

The bulk polymerization of ECA was thermal initiated or photo-initiated, and the resulting polymer together with the unreacted monomers were characterized by $^1$H-NMR spectroscopy, as shown in Figure S3, the conversion can be calculated through the following formulation:

$$\text{Conversion \%} = (1 - \frac{I_a + I_b + I_c}{3(I_{d+a'})}) \times 100\%$$

Where:

The $I_{d+a'}$ represents the integration of 2.5-2.6 ppm corresponding to the protons from terminal alkyne of unreacted monomers and that from the polymer pedant acetylene group, while the $I_a$, the $I_b$, the $I_c$ is the integration of the three proton of double bond from the unreacted monomers approximately at 5.8-6.4 ppm, respectively.
Figure S4 ¹H-NMR spectra of mixtures obtained from copolymerization of ECA and MA (polymerization was carried in ethyl acetate) in CDCl₃

After copolymerizing in ethyl acetate for a certain time, the yielded solution was characterized by ¹H-NMR spectroscope. As shown in Figure S4, both the characteristic peak of the products and that of reactants were observed. The $I_f$ is the integration of proton from methyl of unreacted monomers, while $I_{f'}$ is the integration of proton from methyl of polymer chain; the $I_a, I_b, I_c, I_{d+d'}$ were the same as figure S3 described. Conversion can be calculated through the following formulation:

**a:** Conversion (MA) $\% = \frac{I_{f'}}{I_f + I_{f'}} \times 100\%$

**b:** Conversion (ECA) $\% = (1 - \frac{I_a + I_b + I_c}{3(I_{d+d'})}) \times 100\%$

When feed ration (mol) was [MA]:[ECA] = m:n, then the total conversion can be calculated through the following formulation

Conversion $\% = (a \times \frac{m}{m+n} + b \times \frac{n}{m+n}) \times 100\%$
### Table S1 Solubility test of acetylene containing polymer

<table>
<thead>
<tr>
<th>Samples</th>
<th>MA</th>
<th>ECA</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Diethyl Ether</th>
<th>Hexane</th>
<th>Acetone</th>
<th>DCM</th>
<th>TCM</th>
<th>DMF</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0</td>
<td>100</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>P2</td>
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<td>90</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<td>√</td>
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<tr>
<td>P3</td>
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<td>80</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>√</td>
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<td>√</td>
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<tr>
<td>P4</td>
<td>30</td>
<td>70</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>√</td>
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</tr>
<tr>
<td>P5</td>
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<td>50</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>√</td>
<td>√</td>
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<td>√</td>
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</tr>
</tbody>
</table>

√: soluble  ×: insoluble  
DCM: dichloromethane  TCM: trichloromethane  DMF: dimethyl formamide  
THF: tetrahydrofuran  
Soluble means samples completely dissolve in the corresponding solvent forming homogeneous solution. Insoluble means samples could not dissolve in the corresponding solvent generating heterogeneous solution.