Electronic Supplementary Material (ESI) for Polymer Chemistry.


**Supporting Information**

# Designed Enzymatically Degradable Amphiphilic Conetworks by Radical Ring-Opening Polymerization

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## Homopolymerization behavior of VCP

The homopolymerization behavior of the monomer VCP under radical ring-opening polymerization condition at 120 °C was studied. After purification, the polymers were obtained as white solid. The representative $^1$H NMR spectrum of VCP homopolymer is shown in Figure S1. The characteristic proton signals of VCP units after polymerization are marked. According to the previous report of T. Endo *et al.*[1], the structures of both ring-opened and ring-closed VCP units coexist in the VCP homopolymer. In the $^1$H NMR spectrum, the peak at $\delta$ = 5.2 ppm corresponds to the double bond protons from the VCP ring-opened structure (Structure **1** in Figure S1). The broad signals between 1.5-2.5 ppm can be assigned to the protons from the VCP ring-closed structure (Structure **2** in Figure S1). The peaks at $\delta$ = 1.1 ppm and $\delta$ = 4.1 ppm

correspond to the $CH_3CH_2O$- group, which exists in both - the ring-opened and ring-closed - structure. Through comparing the total peak areas of double bond protons (peak *c* in Figure S1, $\delta$ = 5.2 ppm) and methyl group (peak *a* in Figure S1, $\delta$ = 1.2 ppm) the fraction of VCP units with ring-opened structure was calculated to be 52 mol%.

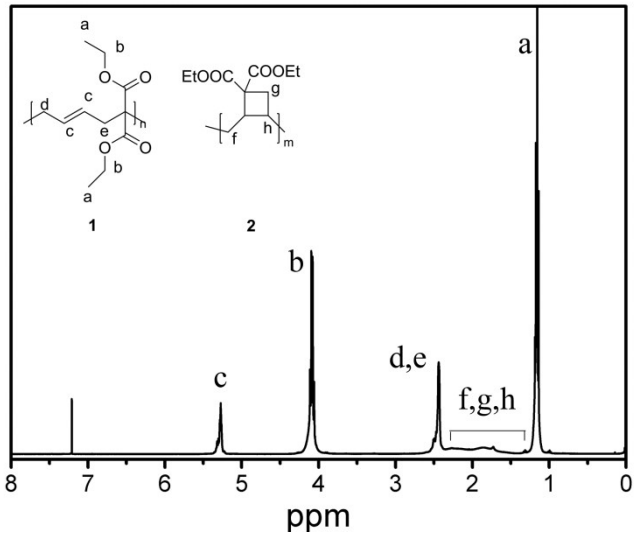


**Figure S1.** $^1$H-NMR spectrum of VCP homopolymer prepared at 120 °C. Structure **1**: VCP unit with ring-opened structure in PVCP; structure **2**: VCP unit with ring-closed structure in PVCP.

**Structural characterization of APCNs**

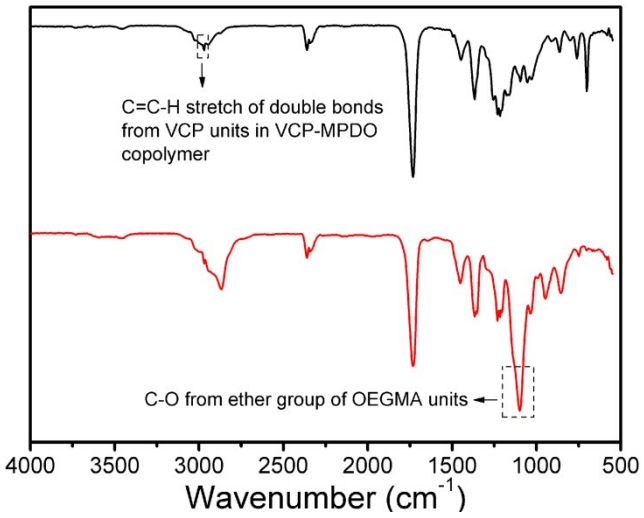


**Figure S2.** IR spectra of original VCP-MPDO copolymers (black) and APCNs (gel-3) after purification (red).

**Calculation of reactivity ratios for VCP and MPDO copolymerization**

The copolymerization of VCP and MPDO was carried out with various monomer feed ratios till low conversions (~5%) to determine the reactivity ratios using kelen-Tüdõs method. The feed ratios and compositions of the resulting copolymers are summarized in Table S1.

**Table S1.** VCP-MPDO copolymerization for determining reactivity ratios

| entry [a] | VCP:MPDO in feed (mol-%) | Yield (%) | VCP:MPDO in Copolymer (mol-%) [b] |
|---|---|---|---|
| Copolymer I | 80:20 | 5.7 | 67:33 |
| Copolymer II | 59:41 | 7.8 | 53:47 |
| Copolymer III | 39:61 | 4.2 | 46:54 |
| Copolymer IV | 28:72 | 5.1 | 42:58 |
| Copolymer V | 13:87 | 4.4 | 34:66 |

[a] reaction time: 6 h; reaction temperature: 120 °C; initiator: di-*tert*-butyl peroxide (1 wt% of monomer)

[b] Determined using $^{1}$H-NMR of the resulting VCP-MPDO copolymers.

The *r*-parameters are determined applying the Kelen-Tüdõs method as follows (Table S2).[2]

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right] \cdot \xi - \frac{r_2}{\alpha} \quad (\mathbf{1})$$

$$\eta = \frac{G}{\alpha + F} \quad (\mathbf{2})$$

$$\xi = \frac{F}{\alpha + F} \quad (\mathbf{3})$$

$$G = \frac{x(y-1)}{y} \quad (\mathbf{4})$$

$$F = \frac{x^2}{y} \quad (\mathbf{5})$$

x = molar ratio of comonomers in feed = $m_1/m_2$ ; y = molar composition of the copolymer = $M_1/M_2$

$\alpha$ = constant = $\sqrt{F_m F_M}$ ($F_m$ = smallest *F*-value; $F_M$ = biggest *F*-value)

**Table S2.** *r*-parameters calculation using Kelen-Tüdõs method

| | x | y | G | F | η | ξ |
|---|---|---|---|---|---|---|
| Copolymer I | 4.04 | 2.04 | 2.06 | 8.00 | 0.24 | 0.93 |
| Copolymer II | 1.41 | 1.12 | 0.16 | 1.77 | 0.07 | 0.75 |
| Copolymer III | 0.65 | 0.86 | -0.10 | 0.49 | -0.10 | 0.45 |
| Copolymer IV | 0.39 | 0.71 | -0.16 | 0.21 | -0.19 | 0.26 |
| Copolymer V | 0.15 | 0.51 | -0.14 | 0.04 | -0.22 | 0.07 |

$\alpha = \sqrt{F_m F_M} = 0.5923$

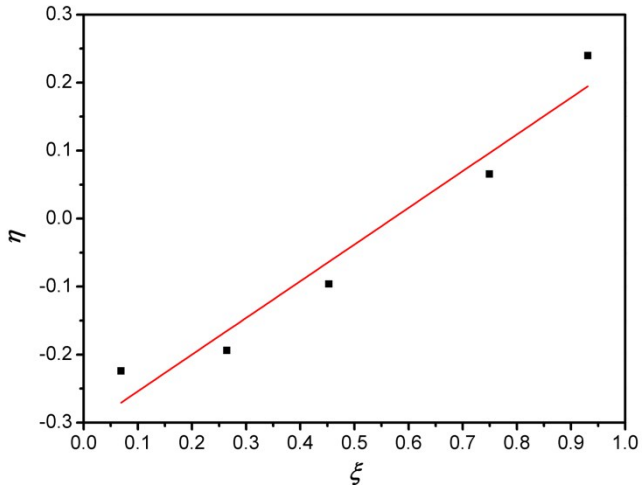


**Figure S3.** Kelen-Tüdõs plot for the determination of VCP and MPDO reactivity ratios (linear fit to the experimental data: $R^2 = 0.953$).

The plot of $\eta$ vs. $\xi$ is shown in Figure S3. From the slope and intercept of the linear fit, the monomer reactivity ratios of VCP and MPDO were determined to $r_{VCP} = 0.23 \pm 0.08$ and $r_{MPDO} = 0.18 \pm 0.02$. A comparison of the experimental data from Table S1 with the calculated copolymerization diagram, using the *r*-values determined by the Kelen-Tüdõs method, shows an excellent agreement.

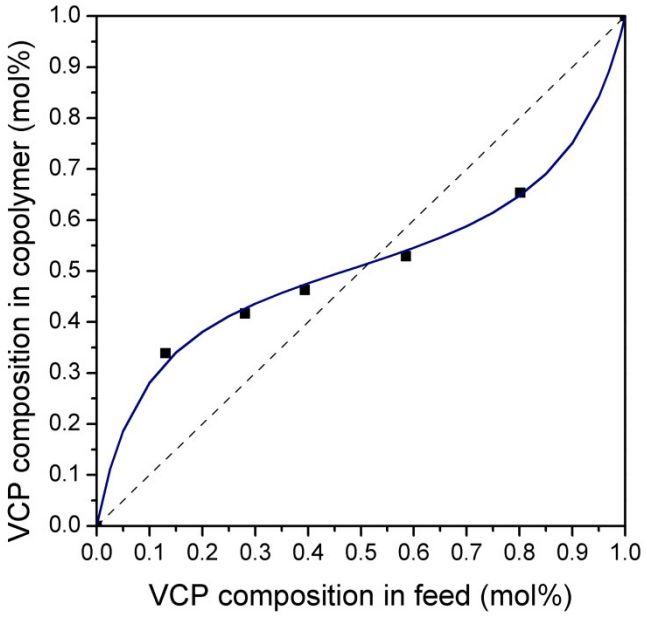


**Figure S4.** Calculated copolymerization diagram (blue curve) and comparison with experimental data (squares) from Table S1.

**Thermal properties of VCP-MPDO copolymers**

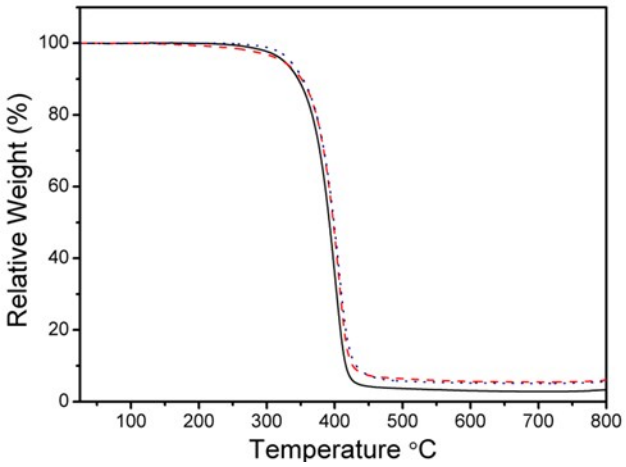


**Figure S5.** TGA profiles of VCP-MPDO copolymers with different comonomer ratios in feed. Black-solid line: VCP:MPDO = 30:70; red-broken line: VCP:MPDO = 50:50; blue-dotted line: VCP:MPDO = 70:30.

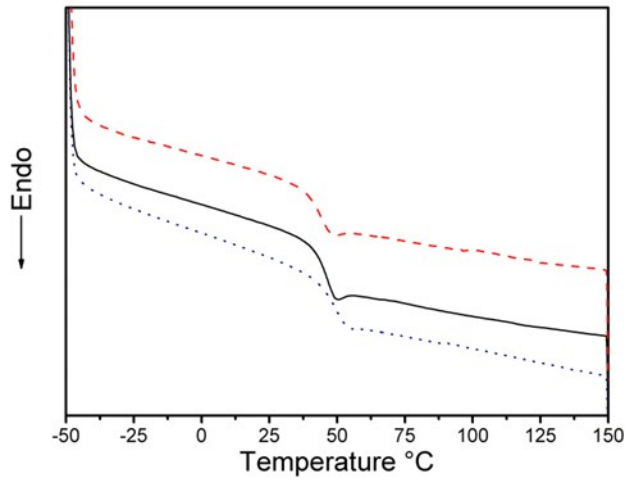


**Figure S6.** DSC heating traces of VCP-MPDO copolymers with different comonomer ratios in feed. Black-solid line: VCP:MPDO = 30:70; red-broken line: VCP:MPDO = 50:50; blue-dotted line: VCP:MPDO = 70:30.

**Reference**


(1) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818-1824.

(2) Kelen, T.; Tüdõs, F. *J. Macromol. Sci., Part A: Chem.* **1975**, *9*, 1-27.