



CO₂-triggered and Temperature-switchable Crystallization-driven Self-assembly of Semicrystalline Block Copolymer in Aqueous Medium

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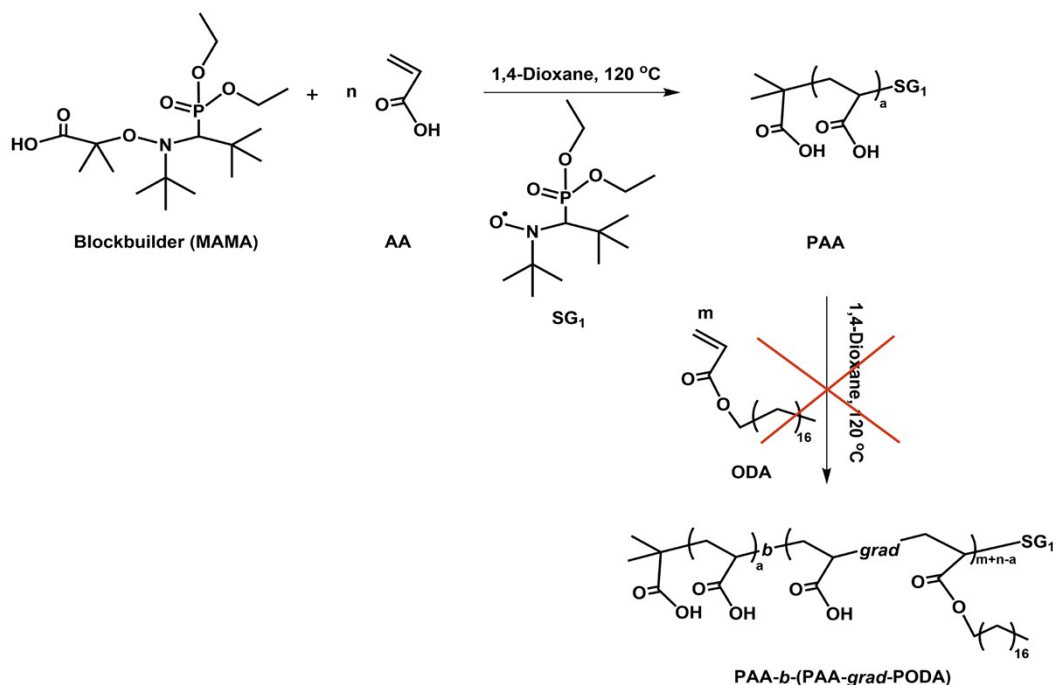
S1. Characterization

Conversion of ODA homopolymer was determined by ^1H NMR in CDCl_3 on a Bruker 400 MHz instrument at room temperature.

Differential scanning calorimetry (DSC) experiments were performed using a DSC Q100 instrument (TA Instruments, Inc., USA). The PODA sample was heated or cooled under nitrogen atmosphere between -10 $^\circ\text{C}$ and 80 $^\circ\text{C}$ with heat rate of 5 $^\circ\text{C}/\text{min}$ or -5 $^\circ\text{C}/\text{min}$. Other samples were heated under nitrogen atmosphere between 25 $^\circ\text{C}$ and 80 $^\circ\text{C}$ with rate of 1 $^\circ\text{C}/\text{min}$.

S2. Attempt to synthesize PAA-*b*-(PAA-grad-PODA) in one step

We attempt to directly synthesize PAA-*b*-(PAA-grad-PODA) in one step (Scheme S1). The synthesis of the block gradient copolymers was performed, as described in previous publications.^{S1} The NMP of AA was performed in 1,4-dioxane with MAMA as initiator ($[\text{M}]/[\text{I}]=200$ with $[\text{M}]=3$ $\text{mol}\cdot\text{L}^{-1}$) and a slight excess of SG1 ($[\text{SG1}]/[\text{I}]=0.09$). However, after 4 hours of reaction of AA, the ODA precipitated in 5 min after we added the monomer in the mixture solvent (Figure S1). And the precipitation process happened even the amount of ODA is very low (3 mol% in totally amount of AA). The attempt to synthesize PAA-*b*-(PAA-grad-PODA) has been failed.



Scheme S1 The reaction to attempt to prepare PAA-*b*-(PAA-grad-PODA).

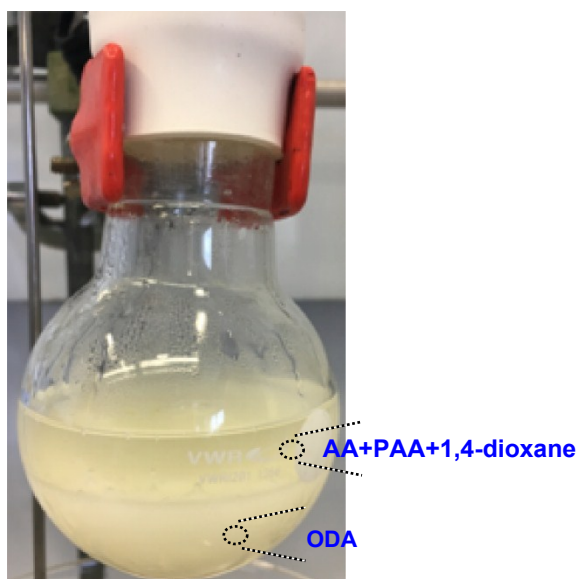


Fig. S1 The reaction to attempt to prepare PAA-*b*-(PAA-*grad*-PODA).

S3. Attempt to synthesize PAA-*b*-(PAA-*r*-PODA) with different ODA content in the feed.

In the first step of NMP, we tried different feed ratio of AA and ODA, and the ratio were listed in Table S1. And found if the amount of ODA is higher, even the ratio of AA and ODA in the feed is 87:13, the PAA-*r*-PODA precursor would precipitate when the AA added in the second step. It is interesting that the ODA and AA can coexist in 1,4-dioxane and even polymerized. But once there are polymer and AA, the precipitation occurred. But when we tried to control the ratio of AA:ODA=90:10 in the first synthesis step, there is no precipitation occurred.

Table S1 The Formulations of AA and ODA Used for Block-random Precursor Synthesis and the Experimental Result.

Sample code	Molar ratio AA:ODA	Experimental Result
D1	20:80	Precipitate
D2	40:60	Precipitate
D3	60:40	Precipitate
D4	80:20	Precipitate
D5	87:13	Precipitate
D6	90:10	No Precipitate

S4. Determination of reactivity ratios and the microstructure of PAA-*b*-(PAA-*r*-PODA).

The reactivity ratios of octadecyl acrylate and acrylic acid were determined from kinetic measurements in four experiments with different initial monomer ratios: the fraction of acrylic acid was varied from 20%, 40%, 60% and 80% in the co-monomer mixture. The aliquots were taken during copolymerization and the

copolymer composition, monomer ratios and conversion of each monomer were determined by ^1H NMR. The conditions of the experiment were the same as for the synthesis of PAA-*r*-PODA copolymers.

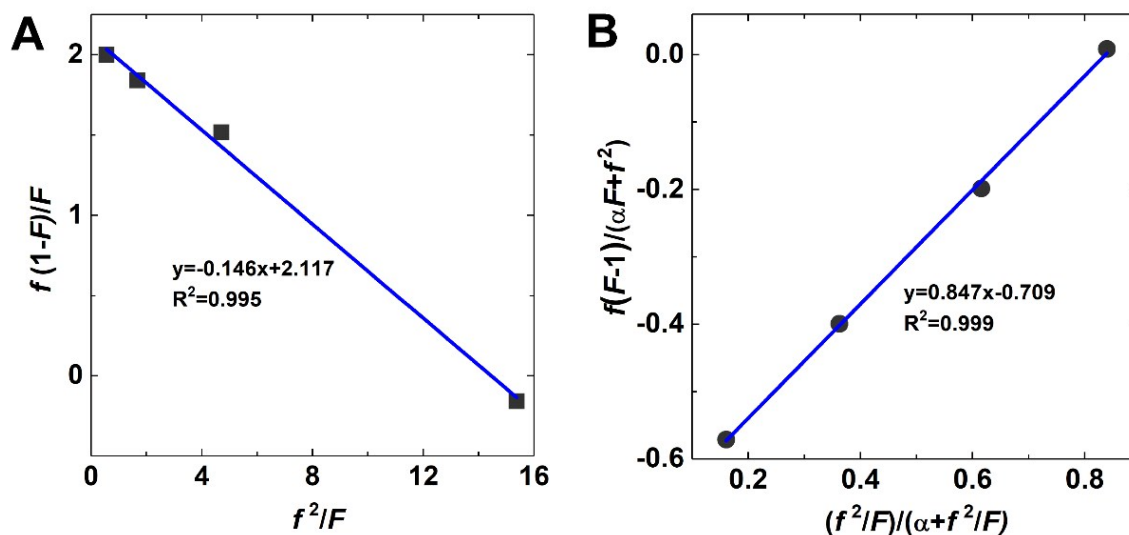
In the Fineman-Ross method,^{S2} the equation

$$\frac{f}{F}(1-F) = r_2 - r_1 \frac{f^2}{F} \quad (\text{S1})$$

is used, where $f=[\text{M}_1]/[\text{M}_2]$ presents the ratio of monomer in the monomer mixture, $F=m_1/m_2$ refers to the ratio of copolymer composition. The reactivity ratios for both monomers are derived from the slope and the intercept of the plot whose $f(1-F)/F$ is as ordinate and (f^2/F) is as abscissa (See Figure S2A). In the Kelen-Tüdös method,^{S3} one arbitrary constant α is introduced to the equation and the equation write

$$y = \left(r_1 + \frac{r_2}{\alpha} \right) x - \frac{r_2}{\alpha} \quad (\text{S2})$$

where $\alpha = \sqrt{\left(\frac{f^2}{F}\right)_{\min}} \sqrt{\left(\frac{f^2}{F}\right)_{\max}}$, $y = \frac{f(F-1)}{\alpha F + f^2}$ and $x = \frac{f^2/F}{\alpha + f^2/F}$. The reactivity ratios for monomers are derived from



the slope and the intercept of the curve plotted in the coordinates of eq. S2 (Figure S2B).

Fig. S2 Kinetic data plotted in coordinates of (A) Fineman-Ross equation; and (B) Kelen-Tüdös equation for determination of reactivity ratios of ODA and AA.

S5. Synthesis of homopolymer PODA by NMP.

The NMP of ODA was performed in 1,4-dioxane with MAMA as initiator ($[M]/[I]=200$ with $[M]=3 \text{ mol}\cdot\text{L}^{-1}$) and a slight excess of SG1 ($[SG1]/[I] = 0.09$). After four hours of polymerization at $120 \text{ }^\circ\text{C}$, the conversion is evaluated from sampling by ^1H NMR (CDCl_3 as solvent) and the product was precipitated in ethyl acetate. ^1H NMR (δ , ppm, CDCl_3): 4.06 ($-\text{CH}_2\text{OCO}-$), 2.27 ($-\text{CH}_2\text{CH}-$), 1.91 ($-\text{CH}_2\text{CH}-$), 1.53-1.24 ($-\text{CH}_2\text{CH}_2\text{O}-$), 0.90-0.84 ($-\text{CH}_2\text{CH}_3$). The molecular weights are $M_{n,\text{NMR}}=38880 \text{ g mol}^{-1}$, $M_{n,\text{SEC}}=38000 \text{ g mol}^{-1}$, and $M_w/M_n = 1.35$.

S6. Crystallization of PODA in solid.

Crystallinity of ODA homopolymer in solid was analyzed by DSC (Figure S3).

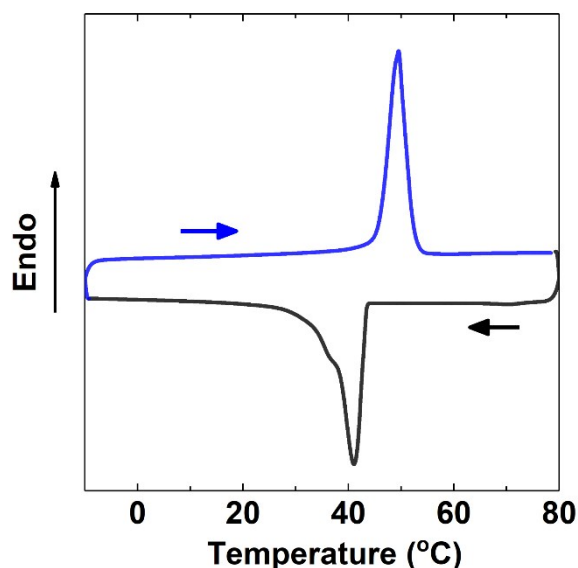


Fig. S3 DSC curves of ODA homopolymer: heating or cooling between $-10 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ at heat rate of $5 \text{ }^\circ\text{C}/\text{min}$ or $-5 \text{ }^\circ\text{C}/\text{min}$.

S7. DSC of $\text{PAA}_{103}\text{-}r\text{-PODA}_{10}$ in solid.

The solid polymers were obtained as follows: the $\text{PAA}_{103}\text{-}r\text{-PODA}_{10}$ was dissolving in 0.015 M NaOH and 0.01 M NaCl. After totally dissolving, the solvent was deal with no gas treatment, CO_2 , CO_2/N_2 and $\text{CO}_2/50 \text{ }^\circ\text{C}$ to reach pH to 9.5, 5.2, 7.8, 8.0 respectively and then quickly froze by liquid nitrogen and freeze-dried under vacuum at $-80 \text{ }^\circ\text{C}$ to avoid the reassembly and aggregation of the micelles during the drying process. The polymer samples were further analyzed by DSC as shown in Figure S4, we can see melting temperature for samples in bulk and the one dissolving in solvent and treated with CO_2 .

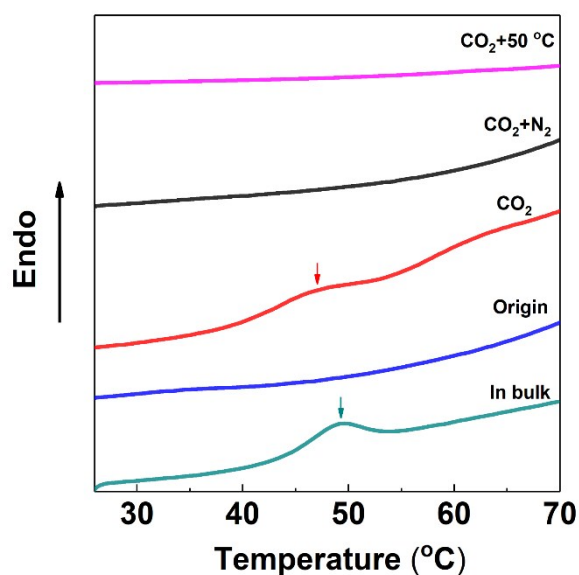


Fig. S4 DSC curves of PAA₁₀₃-r-PODA₁₀ in bulk and freeze-drying samples dissolving in 0.015 M NaOH and 0.01 M NaCl treated without gas and with CO₂, CO₂/N₂ and CO₂/50 °C.

S8. WAXS of NaCl.

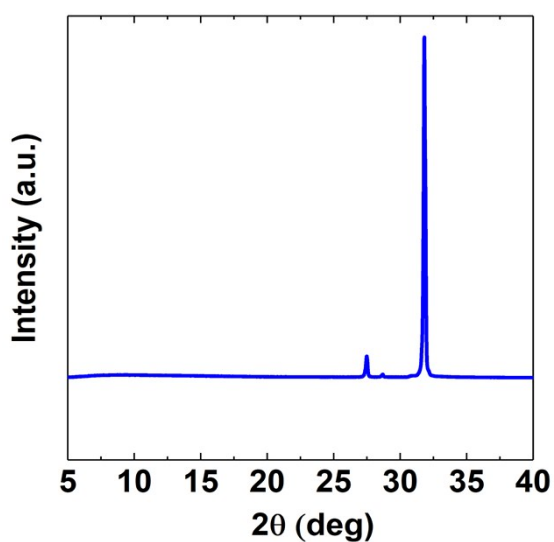


Fig. S5 WAXD result of solid NaCl at 25 °C.

References

- S1 O. Borisova, L. Billon, M. Zaremski, B. Grassl, Z. Bakaeva, A. Lapp, P. Stepanek and O. Borisov, *Soft Matter*, 2012, **8**, 7649.
- S2 M. Fineman and S. D. Ross, *J. Polym. Sci., Part A: Polym. Chem.*, 1950, **5**, 259.
- S3 T. Kelen and F. Tüdős, *J. Macromol. Sci., Chem.*, 1975, **9**, 1.