# Direct observation of α- to β-glycine transformation during ionic liquid mediated crystallization process

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**Supplementary Information**

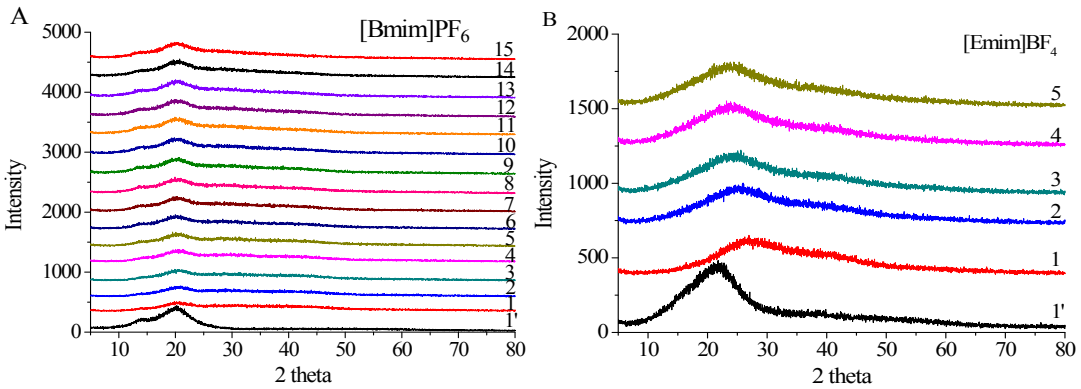



Figure S1 In situ powder XRD monitoring of glycine crystallization from [Bmim]$PF_6$ and [Emim]$BF_4$. (A) 80 μL of 50 mg/mL Aladdin glycine water solution spotted onto hydrophobic ionic liquid [Bmim]$PF_6$. (B) 80 μL of 50 mg/mL Sigma glycine water solution spotted onto hydrophilic ionic liquid [Emim]$BF_4$. XRD scan time: 190 s for the each interval; 2 Theta: 5-80°.The 1' scan represents the XRD patterns of ionic liquid.

Table S1 Phase identification results from the different scan times of glycine crystallization of Figure 1A.

| Scan | Peak position (2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **1-4** | No peaks | | | | | | | | |
| **5** | 18.904 | 29.764 | | | | | | | α |
| **6** | 14.729 | 18.930 | 29.734 | 44.185 | | | | | α |
| **7** | 14.717 | 18.938 | 20.085 | 29.745 | | | | | α |
| **8** | 14.768 | 18.934 | 29.781 | 38.351 | | | | | α |
| **9** | 14.749 | 17.869 | 18.941 | 29.783 | 36.221 | 36.603 | | | α+β |
| **10** | 14.750 | 17.869 | 18.941 | 29.778 | 36.210 | 36.583 | 39.033 | | α+β |
| **11** | 14.748 | 17.869 | 18.944 | 23.858 | 29.768 | 36.214 | 36.530 | 39.053 | α+β |
| **12** | 14.748 | 17.869 | 18.944 | 23.858 | 29.768 | 36.214 | 36.530 | 39.053 | α+β |
| **13** | 14.748 | 17.869 | 18.944 | 23.858 | 29.768 | 36.214 | 36.530 | 39.053 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively.

Table S2 Phase identification results from the different scan times of glycine crystallization of Figure 1B.

| Scan | Peak position (2θ) | | | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1-15** | No peaks | | | | | | | | | | |
| **16** | 17.952 | 20.315 | 29.306 | 30.938 | 35.334 | 36.274 | 39.025 | 53.121 | 70.531 | | α+β |
| **17** | 17.892 | 18.964 | 30.113 | 30.982 | 35.316 | 36.203 | 36.559 | 39.026 | 53.005 | 70.588 | α+β+γ |
| **18** | 17.895 | 18.954 | 30.170 | 30.966 | 35.330 | 36.199 | 36.563 | 39.021 | 53.116 | | α+β+γ |
| **19** | 17.889 | 18.935 | 29.253 | 30.162 | 30.981 | 35.324 | 36.192 | 36.636 | 39.026 | 53.117 | α+β+γ |
| **20** | 17.889 | 18.940 | 29.215 | 30.154 | 30.975 | 35.318 | 36.192 | 36.549 | 39.032 | 53.113 | α+β+γ |
| **21** | 17.890 | 18.967 | 21.837 | 29.242 | 30.157 | 30.974 | 35.337 | 36.195 | 36.632 | 39.026<br>53.139 | α+β+γ |

The values of the peak positions marked in red, blue and black belonged to β, γ and α-glycine, respectively.

Table S3 Phase identification results from the different scan times of glycine crystallization of Figure 1C.

| Scan | Peak position (2θ) | | | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1-5** | No peaks | | | | | | | | | | |
| **6** | 29.908 | 36.360 | 36.452 | 45.440 | | | | | | | α |
| **7** | 14.897 | 19.118 | 29.888 | 30.982 | 45.438 | 56.749 | 61.908 | | | | α |
| **8** | 14.910 | 19.115 | 28.507 | 29.906 | 36.280 | 38.583 | 45.439 | 56.733 | 61.915 | | α |
| **9** | 14.909 | 18.005 | 19.120 | 28.497 | 29.906 | 36.308 | 38.585 | 45.434 | 56.733 | 61.916 | α+β |
| **10** | 14.909 | 18.035 | 19.107 | 29.906 | 36.320 | 38.591 | 45.455 | 56.732 | 61.912 | | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. The purity of α-glycine was approximately 97.55% in the final products.

Table S4 Phase identification results from the different scan times of glycine crystallization of Figure 2A.

| Scan | Peak position (2θ) | | | | | Phases |
|---|---|---|---|---|---|---|
| **1'-1** | No peaks | | | | | |
| **2** | 61.982 | | | | | α |
| **3** | 14.949 | 29.925 | | | | α |
| **4** | 17.993 | 29.932 | 33.738 | 36.328 | 39.131 | α+β |
| **5** | 18.011 | 19.012 | 29.873 | 33.670 | 36.330 | α+β |
| **6** | 17.987 | 19.024 | 25.326 | 29.850 | 36.333 | α+β |
| **7** | 17.986 | 19.019 | 29.854 | 33.652 | 36.330 | α+β |
| **8** | 17.981 | 19.025 | 29.830 | 33.651 | 36.330 | α+β |
| **9** | 17.982 | 19.018 | 29.848 | 33.651 | 36.327 | α+β |
| **10** | 17.981 | 19.029 | 29.837 | 33.651 | 36.329 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. The "?" represents uncertainty of the peak.

Table S5 Phase identification results from the different scan times of glycine crystallization of Figure 2B.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1'-2** | No peaks | | | | | | | |
| **3** | 18.013 | 36.357 | | | | | | α+β |
| **4** | 18.019 | 36.321 | 53.083 | | | | | α+β |
| **5** | 17.989 | 25.329 | 36.303 | 57.794 | 70.632 | | | α+β |
| **6** | 17.978 | 36.303 | 70.609 | | | | | α+β |
| **7** | 17.976 | 35.402 | 36.302 | 57.748 | 70.585 | | | α+β |
| **8** | 17.975 | 18.986 | 35.455 | 36.303 | 57.773 | 70.624 | | α+β |
| **9** | 17.975 | 19.076 | 35.440 | 36.302 | 57.762 | 70.635 | | α+β |
| **10** | 17.976 | 19.069 | 25.328 | 35.380 | 36.302 | 57.856 | 70.720 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the table.

Table S6 Phase identification results from the different scan times of glycine crystallization of Figure 2C.

| Scan | Peak position (2θ) | | | | | | Phases |
|---|---|---|---|---|---|---|---|
| **1'-2** | No peaks | | | | | | |
| 3 | 55.866 | 56.559 | 59.345 | 60.875 | 69.240 | | α+β |
| 4 | 18.044 | 36.331 | 55.951 | | | | α+β |
| 5 | 18.024 | 36.315 | 39.204 | 55.939 | 76.941 | | α+β |
| 6 | 18.005 | 36.311 | 39.200 | 55.938 | 76.938 | | α+β |
| 7 | 18.003 | 36.296 | 39.190 | 55.694 | 56.356 | 76.938 | α+β |
| 8 | 18.002 | 36.296 | 39.199 | 55.768 | 56.367 | 76.937 | α+β |
| 9 | 18.001 | 36.295 | 39.192 | 55.681 | 56.372 | 76.937 | α+β |
| 10 | 18.002 | 36.296 | 39.197 | 55.691 | 56.372 | 76.937 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the table.

Table S7 Phase identification results from the different scan times of glycine crystallization of Figure 2D.

| Scan | Peak position (2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **1'-3** | No peaks | | | | | | | | |
| **4** | 18.008 | 36.717 | | | | | | | β |
| **5** | 18.019 | 23.798 | 31.105 | 35.410 | 36.366 | 36.686 | 39.173 | 57.714 | α+β |
| | 19.070 | 28.508 | 33.793 | | | | | | |
| **6** | 18.007 | 23.788 | 31.094 | 35.392 | 36.340 | 36.675 | 39.173 | 57.666 | α+β |
| | 19.076 | 28.504 | 33.788 | | | | | | |
| **7** | 18.010 | 23.790 | 29.897 | 33.759 | 35.418 | 36.678 | 53.139 | 57.706 | α+β |
| | 19.055 | 28.492 | 31.025 | 34.434 | 36.346 | 39.191 | | | |
| **8** | 18.012 | 23.783 | 29.890 | 33.779 | 35.410 | 36.671 | 56.435 | 57.712 | α+β |
| | 19.081 | 28.498 | 31.085 | 34.407 | 36.327 | 39.153 | | | |
| **9** | 18.003 | 23.797 | 29.895 | 33.774 | 36.351 | 39.181 | 53.181 | 57.711 | α+β |
| | 19.035 | 28.497 | 31.085 | 35.383 | 36.672 | | | | |
| **10** | 18.010 | 23.794 | 29.883 | 33.795 | 35.405 | 36.664 | 53.181 | 57.749 | α+β |
| | 19.040 | 28.497 | 31.063 | 34.442 | 36.336 | 39.156 | | | |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. The numerical values marked in green indicated that the mixture phase of β and α-glycine may be for the peak positions. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the table.

Table S8 Phase identification results from the different scan times of Aladdin glycine crystallization of Figure 3A.

| Scan | Peak position (2θ) | | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|---|
| **1'-7** | No peaks | | | | | | | | | |
| **8** | 17.921 | 36.219 | 76.840 | | | | | | | α+β |
| **9** | 17.902 | 18.968 | 29.288 | 30.132 | 33.592 | 35.299 | 36.277 | 39.023 | 76.881 | α+β+γ |
| **10** | 17.903 | 18.977 | 29.282 | 30.156 | 33.606 | 35.292 | 36.227 | 39.026 | 76.885 | α+β+γ |
| **11** | 17.901 | 18.969 | 29.280 | 30.138 | 33.595 | 35.292 | 36.227 | 39.023 | 76.888 | α+β+γ |
| **12** | 17.901 | 18.970 | 29.286 | 30.148 | 33.609 | 35.292 | 36.228 | 39.025 | 76.840 | α+β+γ |
| **13** | 17.902 | 18.967 | 29.286 | 30.149 | 33.589 | 35.298 | 36.228 | 39.026 | 76.890 | α+β+γ |

The values of the peak positions marked in red, blue and black belonged to β, γ and α-glycine, respectively. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the table.

Table S9 Phase identification results from the different scan times of Sinopharm glycine crystallization of Figure 3B.

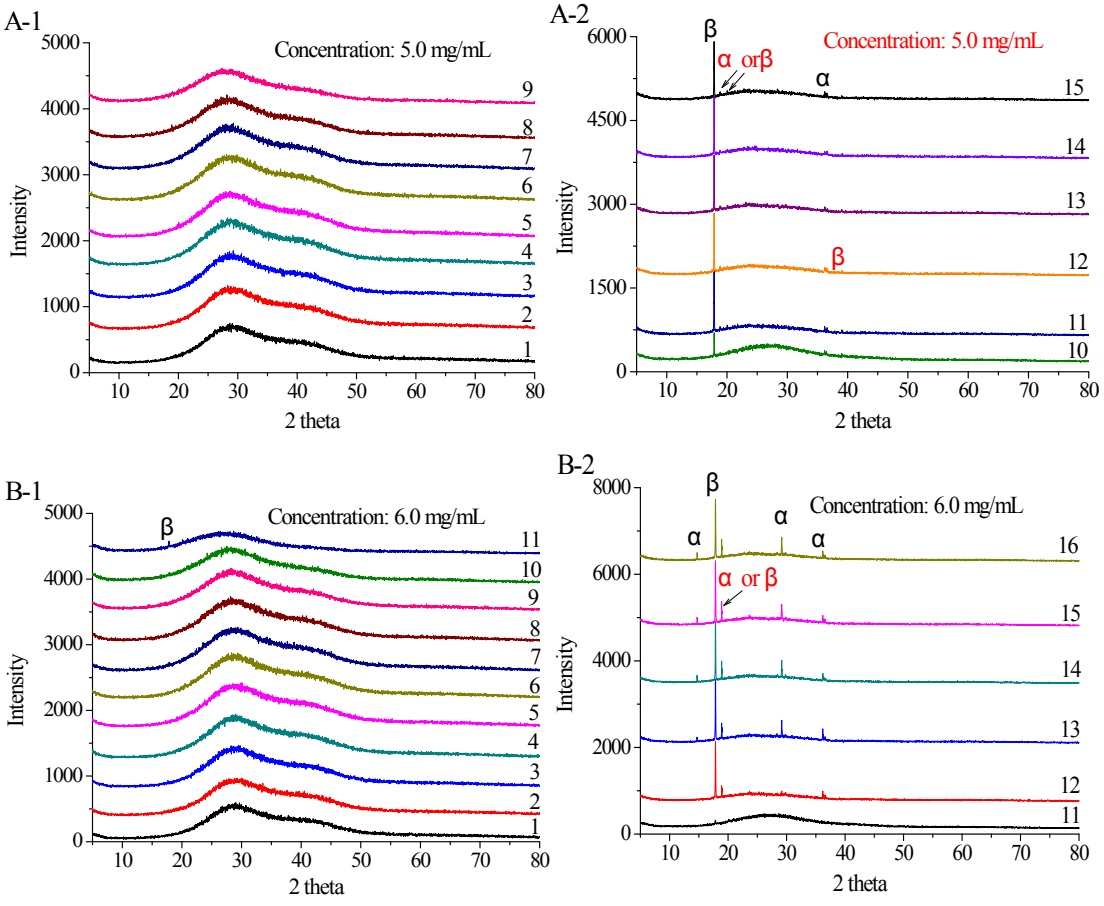
| Scan | Peak position (2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **1'-7** | No peaks | | | | | | | | |
| **8** | 17.956 | 18.939 | 30.116 | 31.070 | 33.565 | 35.305 | 36.265 | 64.615 | α+β+γ |
| **9** | 17.931 | 23.903 | 29.242 | 30.176 | 33.561 | 36.214 | 57.650 | | α+β+γ |
| | 18.951 | 28.408 | 29.751 | 31.058 | 35.339 | 56.345 | 64.623 | | |
| **10** | 17.924 | 23.868 | 30.162 | 33.564 | 36.213 | 57.629 | 76.878 | | α+β+γ |
| | 18.952 | 29.221 | 31.059 | 35.337 | 56.385 | 64.621 | | | |
| **11** | 17.926 | 23.870 | 30.165 | 33.564 | 36.214 | 57.800 | 76.877 | | α+β+γ |
| | 18.958 | 29.223 | 31.059 | 35.338 | 56.335 | 64.622 | | | |
| **12** | 17.929 | 23.892 | 30.168 | 33.565 | 36.213 | 57.651 | 76.871 | | α+β+γ |
| | 18.954 | 29.227 | 31.059 | 35.336 | 56.352 | 64.623 | | | |

The values of the peak positions marked in red, blue and black belonged to β, γ and α-glycine, respectively.

Table S10 Phase identification results from the different scan times of Sigma glycine crystallization of Figure 3C.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1'-6** | No peaks | | | | | | | |
| **7** | 17.933 | 36.201 | 58.849 | | | | | α+β |
| **8** | 17.946 | 18.929 | 33.639 | 35.310 | 36.270 | 37.949 | 39.032 | α+β |
| **9** | 17.958 | 18.960 | 33.629 | 35.284 | 36.295 | 37.963 | 39.027 | α+β |
| **10** | 17.972 | 28.439 | 33.630 | 36.293 | 39.035 | | | α+β |
| | 18.959 | 29.280 | 35.354 | 37.946 | | | | |
| **11** | 17.972 | 28.393 | 33.625 | 36.295 | 39.038 | | | α+β |
| | 18.963 | 29.282 | 35.286 | 37.948 | | | | |
| **12** | 17.975 | 28.381 | 33.627 | 36.294 | 39.039 | | | α+β |
| | 18.956 | 29.283 | 35.355 | 37.934 | | | | |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively.



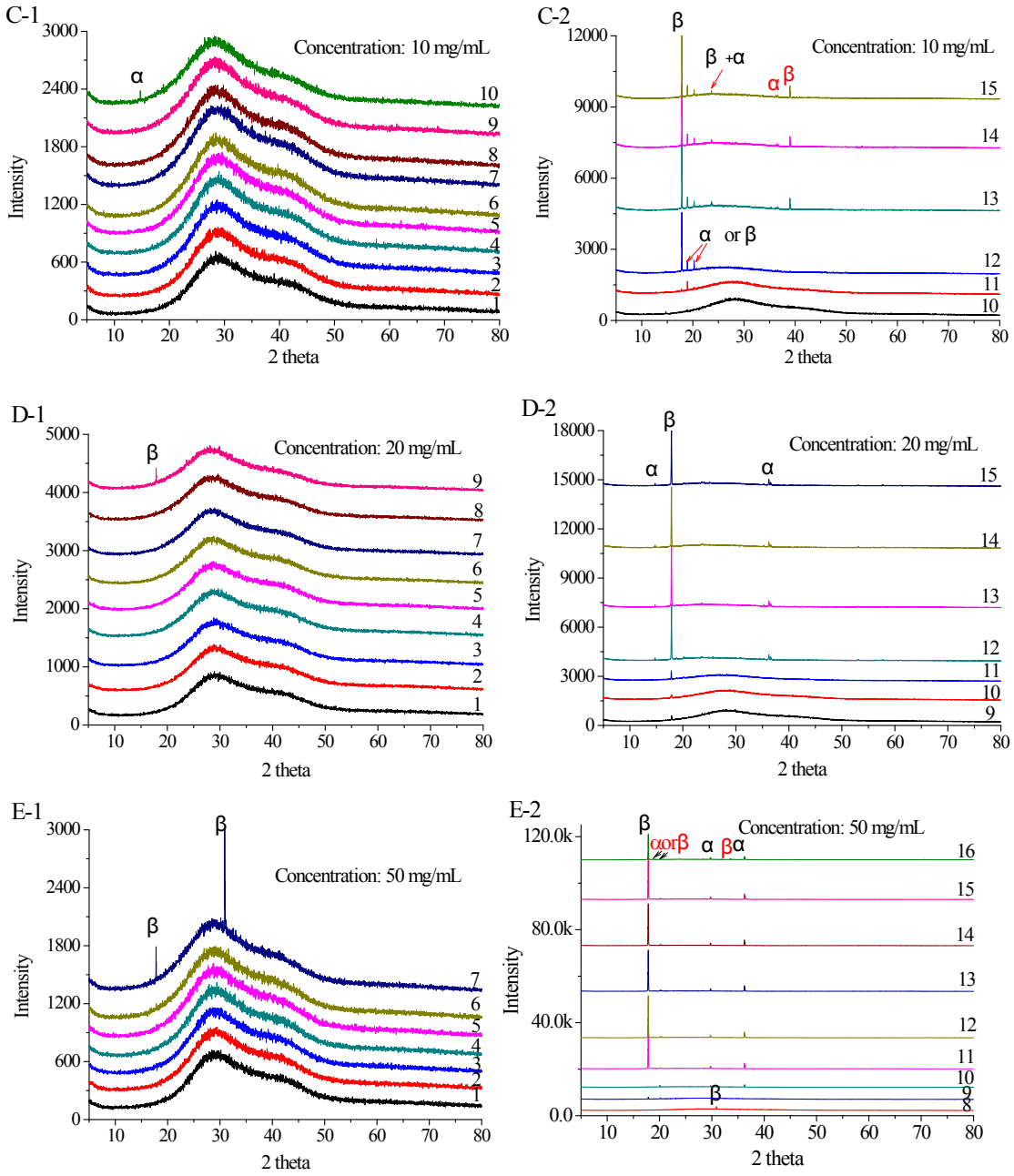



**Figure S2 In situ monitoring of glycine crystallization from aqueous solution using powder XRD with different concentration.** Individual concentrations are marked in each figure: 5.0 mg/mL s for (A-1 and -2); 6.0 mg/mL for (B-1 and -2); 10 mg/mL for (C-1 and -2) ; 20 mg/mL for (D-1 and -2); 50 mg/mL for (E-1 and -2). XRD program: Start angle, 5° (2 theta); End angle, 80° (2 theta); Step size, 0.0204479° (2 theta); Scan time, 381 s. 200 µL of 20.0 mg/mL Aladdin glycine solution was spotted in the sample holder for each experiment.

Table S11 Phase identification results from the different scan times of glycine solution crystallization of Figure S2A.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1-9** | No peaks | | | | | | | |
| **10** | 17.826 | 36.126 | 38.983 | | | | | α+β |
| **11** | 17.819 | 18.850 | 36.156 | 36.547 | 38.998 | | | α+β |
| **12** | 17.821 | 18.813 | 36.154 | 36.517 | 39.006 | | | α+β |
| **13** | 17.821 | 18.864 | 36.177 | 36.527 | 38.965 | | | α+β |
| **14** | 17.818 | 18.805 | 19.978 | 36.135 | 36.496 | 39.004 | | α+β |
| **15** | 17.818 | 18.791 | 19.964 | 28.335 | 36.162 | 36.537 | 38.947 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the tables S2A-E.
It must be noticed that the values of peak position at 18.8 and 19.9°(2θ) belonged to β-glycine. The identification of peak positions is based on the two rules. One is the degree of closeness to the standard card. The other is the condition of other peaks appear in the same time.

Table S12 Phase identification results from the different scan times of glycine solution crystallization of Figure S2B.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1-10** | No peaks | | | | | | | |
| **11** | 17.776 | | | | | | | β |
| **12** | 17.816 | 18.882 | 29.104 | 36.144 | 36.514 | | | α+β |
| **13** | 14.688 | 17.817 | 18.865 | 29.126 | 36.136 | 36.504 | | α+β |
| **14** | 14.690 | 17.817 | 18.880 | 29.122 | 36.165 | 36.524 | | α+β |
| **15** | 14.680 | 17.718 | 18.872 | 23.618 | 29.123 | 36.147 | 36.577 | α+β |
| **16** | 14.685 | 17.817 | 18.880 | 29.116 | 36.140 | 36.517 | | α+β |

Table S13 Phase identification results from the different scan times of glycine solution crystallization of Figure S2C.

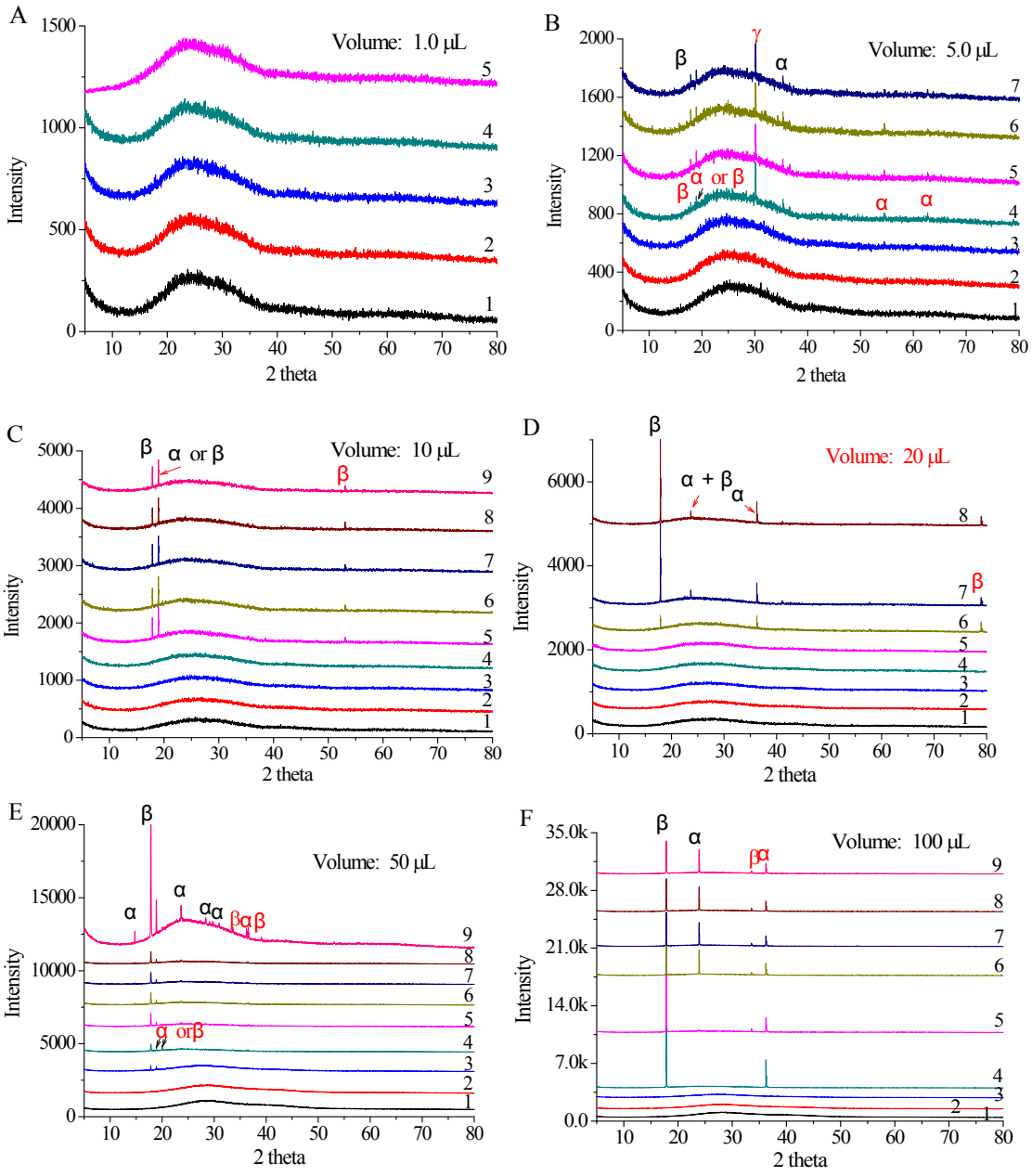
| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1-9** | No peaks | | | | | | | |
| **10** | 14.697 | | | | | | | α |
| **11** | 17.720 | 18.910 | | | | | | β |
| **12** | 14.702 | 17.815 | 18.910 | 20.200 | | | | α+β |
| **13** | 17.822 | 18.902 | 20.190 | 23.609 | 36.180 | 36.514 | 38.906 | α+β |
| **14** | 17.820 | 18.901 | 20.198 | 23.618 | 36.208 | 36.486 | 38.908 | α+β |
| **15** | 17.822 | 18.897 | 20.200 | 23.625 | 36.216 | 36.511 | 38.905 | α+β |

Table S14 Phase identification results from the different scan times of glycine solution crystallization of Figure S2D.

| Scan | Peak position (2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **1-8** | No peaks | | | | | | | | |
| **9** | 17.839 | | | | | | | | β |
| **10** | 17.818 | 20.221 | | | | | | | β |
| **11** | 17.792 | | | | | | | | β |
| **12** | 14.733 | 17.818 | 18.801 | 20.145 | 33.507 | 35.208 | 36.154 | 36.519 | α+β |
| **13** | 14.735 | 17.811 | 20.148 | 23.558 | 35.249 | 36.165 | 36.502 | | α+β |
| **14** | 14.727 | 17.812 | 23.594 | 33.546 | 36.159 | 36.507 | | | α+β |
| **15** | 14.734 | 17.812 | 20.123 | 23.576 | 28.228 | 33.531 | 36.162 | 36.508 | α+β |

Table S15 Phase identification results from the different scan times of glycine solution crystallization of Figure S2E.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| 1-6 | | | | | | | | |
| 7 | 17.746 | 30.848 | | | | | | β |
| 8 | 17.804 | 30.835 | | | | | | β |
| 9 | 17.821 | 18.844 | 20.063 | | | | | β |
| 10 | 17.824 | 18.891 | 20.064 | 28.297 | 29.710 | 36.140 | | α+β |
| 11 | 17.814 | 18.873 | 20.117 | 28.301 | 29.652 | 36.148 | | α+β |
| 12 | 17.814 | 18.857 | 20.292 | 28.291 | 29.652 | 36.148 | | α+β |
| 13 | 17.814 | 18.871 | 20.073 | 28.306 | 29.653 | 36.159 | | α+β |
| 14 | 17.814 | 18.868 | 20.077 | 20.305 | 28.310 | 29.655 | 36.148 | α+β |
| 15 | 14.674 | 17.813 | 18.879 | 20.064 | 28.314 | 29.668 | 36.148 | α+β |
| 16 | 14.667 | 18.861 | 28.303 | 33.477 | 36.153 | 38.990 | 52.960 | α+β |
| | 17.818 | 20.064 | 29.650 | | 36.504 | 43.774 | 57.614 | |



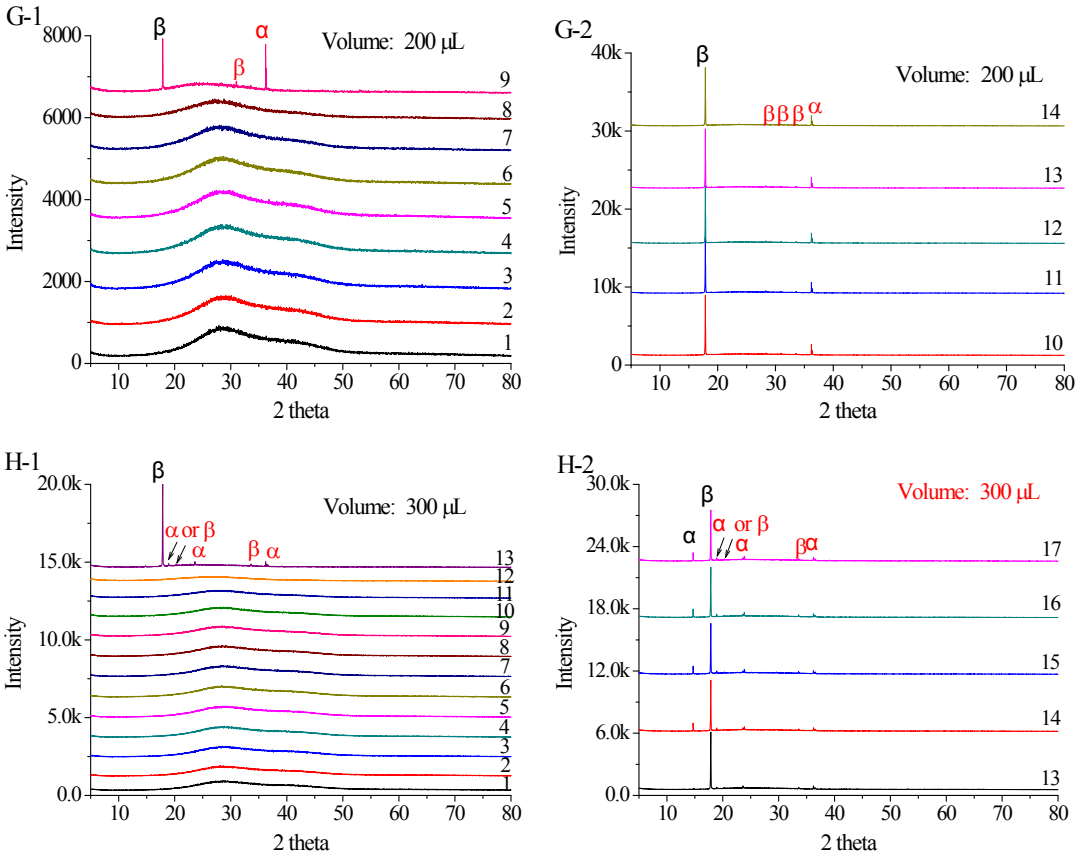



**Figure S3 In situ monitoring of glycine crystallization from aqueous solution using powder XRD with different volumes.** Spotted volumes are marked in each figure: 1.0 µL s for (A); 5.0 µL for (B); 10 µL for (C) ; 20 µL for (D) ; 50 µL s for (E), 100 µL for (F), 200 µL for (G), 300 µL for (H). XRD program: Start angle, 5° (2 theta); End angle, 80° (2 theta); Step size, 0.0204479° (2 theta); Scan time, 381 s. 20.0 mg/mL Sigma glycine solution was used for each experiment. 26 º and humidity 32%

Table S16 Phase identification results from the different scan times of glycine solution crystallization of Figure S3B.

| Scan | Peak position (2θ) | | | | | | Phases |
|---|---|---|---|---|---|---|---|
| **1-3** | No peaks | | | | | | |
| **4** | 17.853 | 18.893 | 30.094 | 35.266 | 54.433 | 62.595 | α+β+γ |
| **5** | 17.832 | 18.933 | 30.108 | 35.260 | 36.524 | 54.418 | α+β+γ |
| **6** | 17.853 | 18.895 | 30.107 | 35.258 | 54.535 | | α+β+γ |
| **7** | 17.851 | 18.909 | 30.082 | 35.249 | 54.481 | | α+β+γ |

The values of the peak positions marked in red, blue and black belonged to β, γ and α-glycine, respectively. It must be noticed that the peaks were not easily found in the figures with their intensities less than 2%, which was still listed in the tables S3B-H.

Table S17 Phase identification results from the different scan times of glycine solution crystallization of Figure S3C.

| Scan | Peak position (2θ) | | | Phases |
|---|---|---|---|---|
| **1-4** | No peaks | | | |
| **5** | 17.836 | 18.933 | 53.095 | β |
| **6** | 17.832 | 18.937 | 53.006 | β |
| **7** | 17.842 | 18.931 | 53.017 | β |
| **8** | 17.843 | 18.933 | 53.006 | β |
| **9** | 17.835 | 18.940 | 53.088 | β |

The values of the peak positions marked in red belonged to β-glycine. The numerical values marked in green indicated that the phase of β or α-glycine may be for the peak positions.

Table S18 Phase identification results from the different scan times of glycine solution crystallization of Figure S3D.

| Scan | Peak position (2θ) | | | | | Phases |
|---|---|---|---|---|---|---|
| **1-5** | No peaks | | | | | |
| **6** | 17.860 | 36.210 | 78.780? | | | α+β |
| **7** | 17.859 | 23.658 | 36.174 | 14.022 | 78.800? | α+β |
| **8** | 17.860 | 23.643 | 36.180 | 78.790? | | α+β |

Table S19 Phase identification results from the different scan times of glycine solution crystallization of Figure S3E.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1-2** | No peaks | | | | | | | |
| **3** | 17.779 | 18.858 | 57.562 | | | | | α+β |
| **4** | 17.815 | 18.859 | 19.994 | 36.177 | 36.536 | | | α+β |
| **5** | 14.737 | 17.807 | 18.841 | 23.587 | 36.198 | 36.489 | | α+β |
| **6** | 14.711 | 17.807 | 18.855 | 23.597 | 28.332 | 36.153 | 36.493 | α+β |
| **7** | 14.712 | 18.853 | 28.305 | 33.562 | 36.169 | 36.514 | | α+β |
| | 17.807 | 23.579 | ~~29.708~~ | | | | | |
| **8** | 14.707 | 17.807 | 18.857 | 23.594 | 36.183 | | | α+β |
| **9** | 14.712 | 18.859 | 28.325 | 29.686 | 33.533 | 38.984 | 36.519 | α+β |
| | 17.810 | 23.619 | 29.089 | 30.892 | 36.178 | | | |

Table S20 Phase identification results from the different scan times of glycine solution crystallization of Figure S3F.

| Scan | Peak position (2θ) | | | | Phases |
|---|---|---|---|---|---|
| **1-3** | No peaks | | | | |
| **4** | 17.845 | 23.675 | 33.533 | 36.148 | α+β |
| **5** | 17.827 | 23.836 | 33.501 | 36.151 | α+β |
| **6** | 17.816 | 23.851 | 33.502 | 36.149 | α+β |
| **7** | 17.812 | 23.851 | 33.502 | 36.147 | α+β |
| **8** | 17.841 | 23.851 | 33.502 | 36.150 | α+β |
| **9** | 17.831 | 23.851 | 33.499 | 36.148 | α+β |

Table S21 Phase identification results from the different scan times of glycine solution crystallization of Figure S3G.

| Scan | Peak position (2θ) | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|
| **1-8** | No peaks | | | | | | | |
| **9** | 17.846 | 30.947 | 33.569 | 36.156 | 36.498 | | | α+β |
| **10** | 17.825 | 28.276 | 30.946 | 33.519 | 36.183 | 36.494 | | α+β |
| **11** | 17.825 | 28.283 | 30.927 | 33.498 | 36.153 | 36.478 | | α+β |
| **12** | 17.826 | 28.298 | 30.986 | 33.524 | 36.154 | 36.496 | | α+β |
| **13** | 17.826 | 18.901 | 28.288 | 30.942 | 33.525 | 36.153 | 36.502 | α+β |
| **14** | 17.826 | 18.904 | 28.295 | 30.956 | 33.558 | 36.153 | | α+β |

Table S22 Phase identification results from the different scan times of glycine solution crystallization of Figure S3H.

| Scan | Peak position (2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **1-12** | No peaks | | | | | | | | |
| **13** | 14.772 | 17.823 | 18.911 | 23.596 | 33.540 | 36.173 | 36.503 | | α+β |
| **14** | 14.694 | 17.819 | 18.892 | 23.589 | 23.809 | 33.521 | 36.180 | 36.578 | α+β |
| **15** | 14.687 | 17.820 | 18.889 | 23.608 | 23.788 | 33.517 | 36.175 | 36.489 | α+β |
| **16** | 14.688 | 17.819 | 18.884 | 23.608 | 23.788 | 33.505 | 36.158 | 36.486 | α+β |

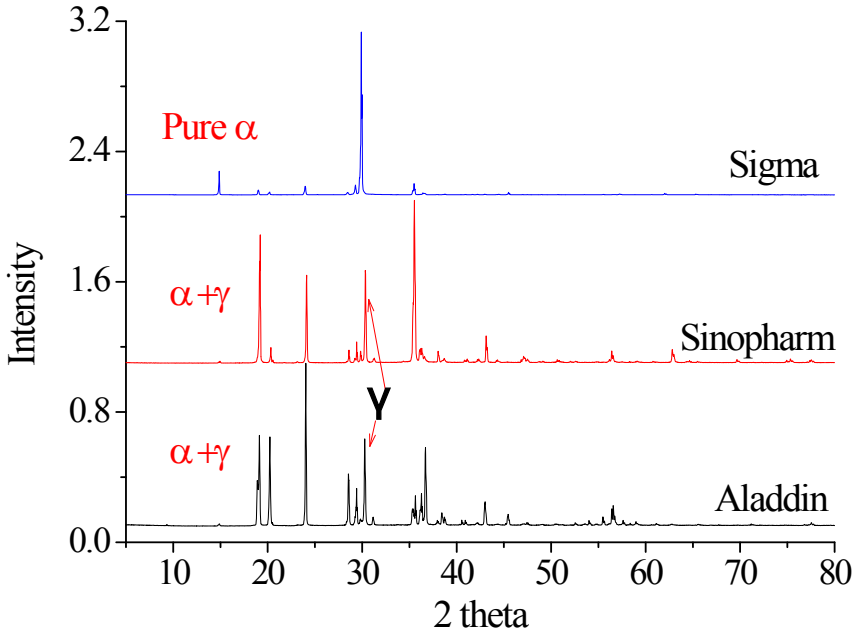


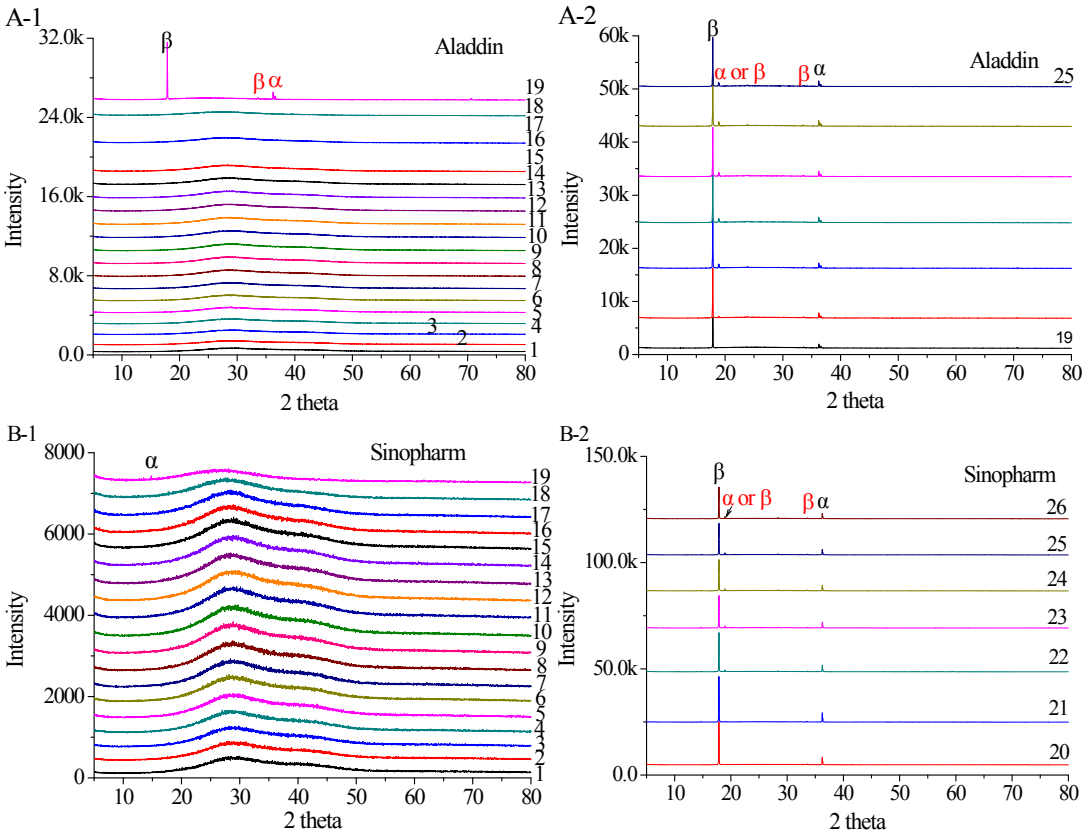

**Figure S4 XRD patterns of glycine powders from three brands.**

XRD program: Start angle, 5° (2 theta); End angle, 80° (2 theta); Step size, 0.0204479° (2 theta); Scan time, 762 s. No marked peaks belonged to α-forms glycine. Phase identifications of glycine crystals were compared with standard cards of PDF#06-0230 (γ-glycine), PDF#32-1702 (α-glycine) and PDF#02-0171 (β-glycine).

Table S23 Phase identification results from XRD patterns of three commercial brands of Figure S4.

| Brands | Peak positions(2θ) | | | | | | | | Phases |
|---|---|---|---|---|---|---|---|---|---|
| **Sigma** | 14.832 | 18.975 | 20.134 | 23.913 | 28.407 | 29.848 | 35.421 | | α |
| | 36.437 | 38.680 | 40.859 | 45.393 | 29.220 | | | | |
| **Aladdin** | 14.842 | 19.072 | 20.190 | 23.895 | 28.503 | 29.351 | 29.810 | 30.220 | α+γ |
| | 31.107 | 35.257 | 35.264 | 36.210 | 36.637 | 37.884 | 38.384 | 38.721 | |
| | 40.464 | 40.847 | 42.101 | 42.926 | 45.355 | 47.334 | 52.475 | 53.910 | |
| | 55.372 | 56.452 | 58.886 | 61.035 | 77.382 | α+β | | | |
| **Sinopharm** | 14.932 | 19.173 | 20.289 | 24.068 | 28.541 | 29.367 | 29.800 | 30.284 | α+γ |
| | 31.192 | 35.442 | 36.062 | 36.540 | 38.000 | 38.587 | 40.793 | 41.035 | |
| | 42.251 | 43.036 | 44.229 | 47.012 | 47.388 | 50.552 | 56.048 | 56.319 | |
| | 62.710 | 69.528 | 74.781 | 75.191 | 77.372 | | | | |

The values of the peak positions marked in blue and black belonged to γ and α-glycine, respectively.



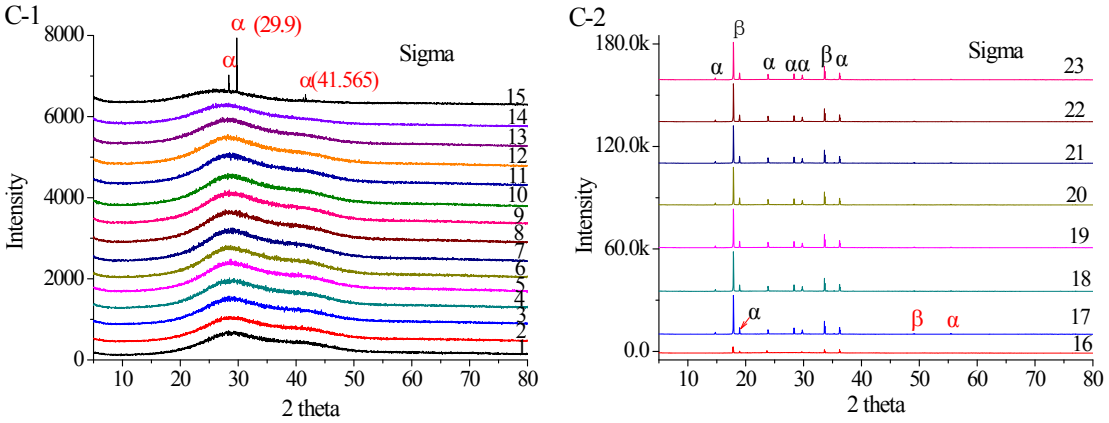



**Figure S5 In situ monitoring of glycine crystallization from aqueous solution using powder XRD with three commercial brands**. (A) Aladdin; (B)Sinopharm;(C) Sigma. XRD program: Start angle, 5° (2 theta); End angle, 80°(2 theta); Step size, 0.02° (2 theta); Scan time, 381 s. 400 µL of 20.0 mg/mL glycine solution was used for each experiment at 26 º and humidity 32%.

Table S24 Phase identification results from the different scan times of Figure S5A.

| Scan | Peak position (2θ) | | | | | Phases |
|---|---|---|---|---|---|---|
| **1-18** | No peaks | | | | | |
| **19** | 17.845 | 33.545 | 36.169 | 36.518 | | α+β |
| **20** | 17.828 | 18.868 | 33.518 | 36.155 | 36.509 | α+β |
| **21** | 17.828 | 18.868 | 33.519 | 36.154 | 36.501 | α+β |
| **22** | 17.828 | 18.871 | 33.526 | 36.155 | 36.509 | α+β |
| **23** | 17.829 | 18.842 | 33.530 | 36.156 | 36.511 | α+β |
| **24** | 17.829 | 18.871 | 33.534 | 36.154 | 36.508 | α+β |
| **25** | 17.828 | 18.872 | 33.497 | 36.154 | 36.500 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively.

Table S25 Phase identification results from the different scan times of Figure S5B.

| Scan | Peak position (2θ) | | | | | | Phases |
|---|---|---|---|---|---|---|---|
| **1-18** | No peaks | | | | | | |
| **19** | 14.816 | | | | | | α |
| **20** | 14.785 | 17.838 | 33.519 | 36.166 | | | α+β |
| **21** | 14.758 | 17.842 | 18.911 | 28.302 | 33.503 | 36.167 | α+β |
| **22** | 14.741 | 17.841 | 18.899 | 28.351 | 33.516 | 36.167 | α+β |
| **23** | 14.752 | 17.838 | 18.897 | 28.339 | 33.511 | 36.168 | α+β |
| **24** | 14.752 | 17.838 | 18.902 | 28.329 | 33.516 | 36.168 | α+β |
| **25** | 14.750 | 17.839 | 18.906 | 28.324 | 33.515 | 36.171 | α+β |
| **26** | 14.744 | 17.838 | 18.900 | 28.346 | 33.501 | 36.170 | α+β |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively.

Table S26 Phase identification results from the different scan times of Figure S5C.

| Scan | Peak position (2θ) | | | | | Phases |
|---|---|---|---|---|---|---|
| **1-14** | No peaks | | | | | |
| **15** | 28.345 | 29.704 | 41.565 | | | α |
| **16** | 17.778 | 23.639 | 29.632 | 33.535 | 76.828 | α+β |
| | 18.918 | 28.346 | 30.913 | 36.148 | | |
| **17** | 14.717 | 18.923 | 28.300 | 33.535 | 49.000 | α+β |
| | 17.848 | 23.832 | 29.738 | 36.166 | 55.354 | |
| **18** | 14.718 | 18.923 | 28.299 | 33.535 | 49.001 | α+β |
| | 17.849 | 23.834 | 29.731 | 36.157 | 55.348 | |
| **19** | 14.718 | 18.924 | 28.299 | 33.536 | 48.996 | α+β |
| | 17.849 | 23.832 | 29.729 | 36.166 | 55.348 | |
| **20** | 14.719 | 18.910 | 28.299 | 33.535 | 48.998 | α+β |
| | 17.849 | 23.834 | 29.731 | 36.157 | 55.347 | |
| **21** | 14.715 | 18.910 | 28.299 | 33.535 | 48.997 | α+β |
| | 17.849 | 23.833 | 29.731 | 36.166 | 55.346 | |
| **22** | 14.719 | 18.910 | 28.299 | 33.535 | 48.999 | α+β |
| | 17.848 | 23.832 | 29.731 | 36.157 | 55.348 | |
| **23** | 14.718 | 18.911 | 28.299 | 33.535 | 49.001 | α+β |
| | 17.849 | 23.834 | 29.730 | 36.166 | 55.348 | |

The values of the peak positions marked in red and black belonged to β and α-glycine, respectively.

## Table S27 Crystallization condition of β-glycine from references 42-52

| Concentration | Volume | Ambient conditions | Substrate | Crystallization Time | Solution | Ref. |
|---|---|---|---|---|---|---|
| 4.0-35.9 g/mL | unknown | 25°C | Crystallizing dishes | unknown | Methanol or Ethanol-water | 42 |
| 10 g/30 mL | unknown | room temperature | Crystallizing dishes | unknown | α-amino acids in water | 43 |
| Supersaturated | unknown | 25°C | Macroemulsions | 5 h | water in oil | 44 |
| 30.78 g/100 g | unknown | 80°C | Emulsions | unknown | water in oil | 45 |
| 3.0 M | unknown | 40 °C to 2°C | SAMs/Au/Si | 12.6-633.0h or >200 | Pure water | 46 |
| 3.2 M | unknown | 23°C, 35% | SAMs/Au/Si | 5-450 min | Pure water | 47 |
| 1-133 mg/mL | 50 µL | 21°C, 30% | Pt/SiO2/Si | unknown | Pure water | 48 |
| 18% | unknown | vacuum | p-PS-PDMA monoliths | 6 h | Pure water | 49 |
| 5% -18% | unknown | vacuum | CPG and p-PS-PDMA monoliths | 6 h | Pure water | 50 |
| 10-17.5% | unknown | 90-180°C | unknown | unknown | Pure water | 51 |
| 16.6 mg/mL | unknown | dry air | unknown | unknown | Pure water | 52 |
| 5-50 mg/mL (0.0666-0.666M) | 1-400 µL | 26°C, 32% | XRD glass sample holder | 30-150 min | Pure water or ILs-water | This paper |

Table S28 The percentage of β-glycine crystals from different crystallization condition

| Brand | Solvent | The percentage of β-glycine | Figure |
|---|---|---|---|
| Aladdin | Water | 45.71% | Figure 1A |
| Aladdin | [Bmim]$PF_6$-water | 35.50% | Figure 1B |
| Aladdin | [Emim]$BF_4$- water | 86.38% | Figure 2A |
| Aladdin | [Emim]$BF_4$- water | 89.89% | Figure 2B |
| Aladdin | [Emim]$BF_4$- water | 60.34% | Figure 2C |
| Aladdin | [Emim]$BF_4$- water | 56.42% | Figure 2D |
| Aladdin | [Bmim]$PF_6$-water | 41.33% | Figure 3A |
| Sigma | [Emim]$BF_4$- water | 2.45% | Figure 1C |
| Sigma | [Bmim]$PF_6$-water | 55.96% | Figure 3C |
| Sigma | Water | 62.46% | Figure S5C |

The percentage of β-glycine was calculated according to the peak areas.