

# **The Existence Region and Composition of a Polymer–Induced Liquid Precursor Phase to DL-Glutamic Acid Crystals**

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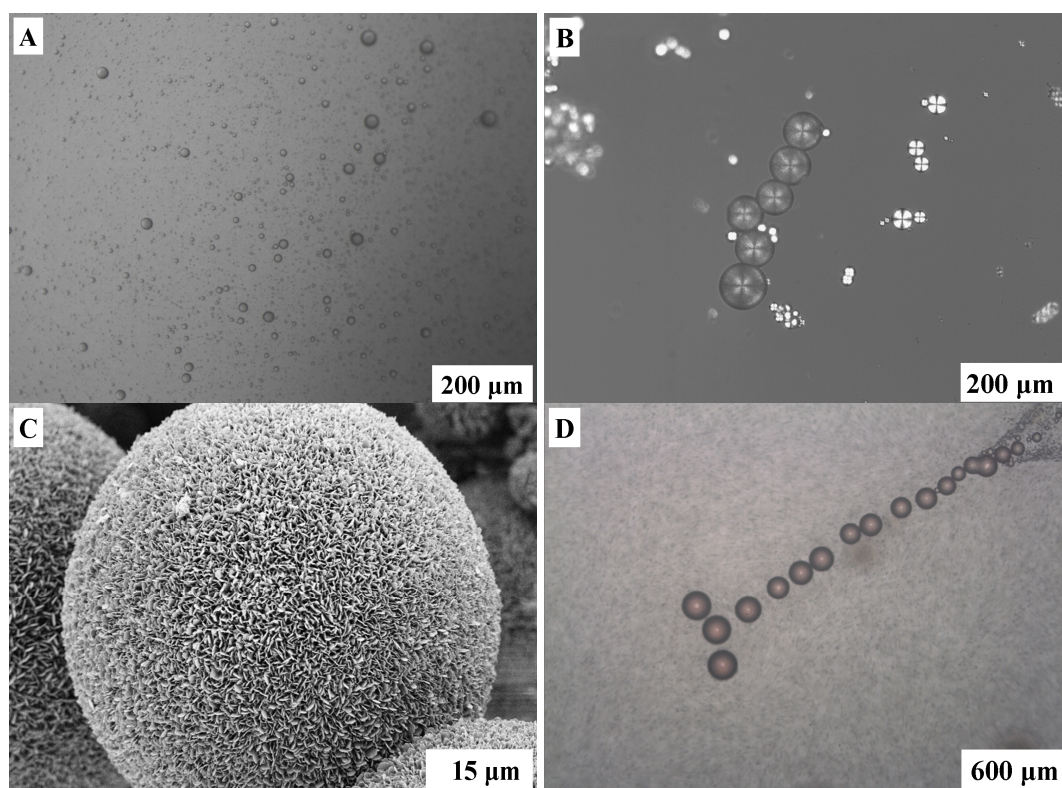
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### A. Microscopy images of the PILP phase, microspheres and coacervate droplets



**Figure 1.** Image **A** is an optical micrograph (OM), showing the existence of PILP droplets. Images **B** and **C** are polarized OM and scanning electron microscopy images, respectively, demonstrating the microspheres formed via PILP route. The composition of initial aqueous solution: [Glu] = 0.36 mol %, [EI] = 0.072 mol % (the sample was heated to 60 °C before it was mixed with EtOH). Image **D** shows the existence of coacervate droplets (OM). The composition: [Glu] = 0.6 mol % and [EI] = 1 mol %. The value of  $V_{EtOH}/V_{water}$  was kept constant at 9 in both cases.

**B. Titration experimental results**

**Table 1.** The summary of  $V_{EtOH}/V_{water}$  values for the determination of the phase boundaries in three series of systems with the values of  $n_{Glu}/n_{EI}$  at 1.5 (**A**), 3.1 (**B**), and 6.2 (**C**), respectively.

| A. Glu–PEI aqueous solution                         |                          |                           |
|-----------------------------------------------------|--------------------------|---------------------------|
| $n_{Glu}/n_{EI} = 1.5, [Glu] = 0.18 \text{ mol \%}$ |                          |                           |
| Dilution                                            | $V_{EtOH}/V_{water}^{'}$ | $V_{EtOH}/V_{water}^{''}$ |
| 0                                                   | 1.5 – 1.6                | > 1000                    |
| 1                                                   | 1.8 – 1.9                | > 1000                    |
| 5                                                   | 2.4 – 2.6                | > 200                     |

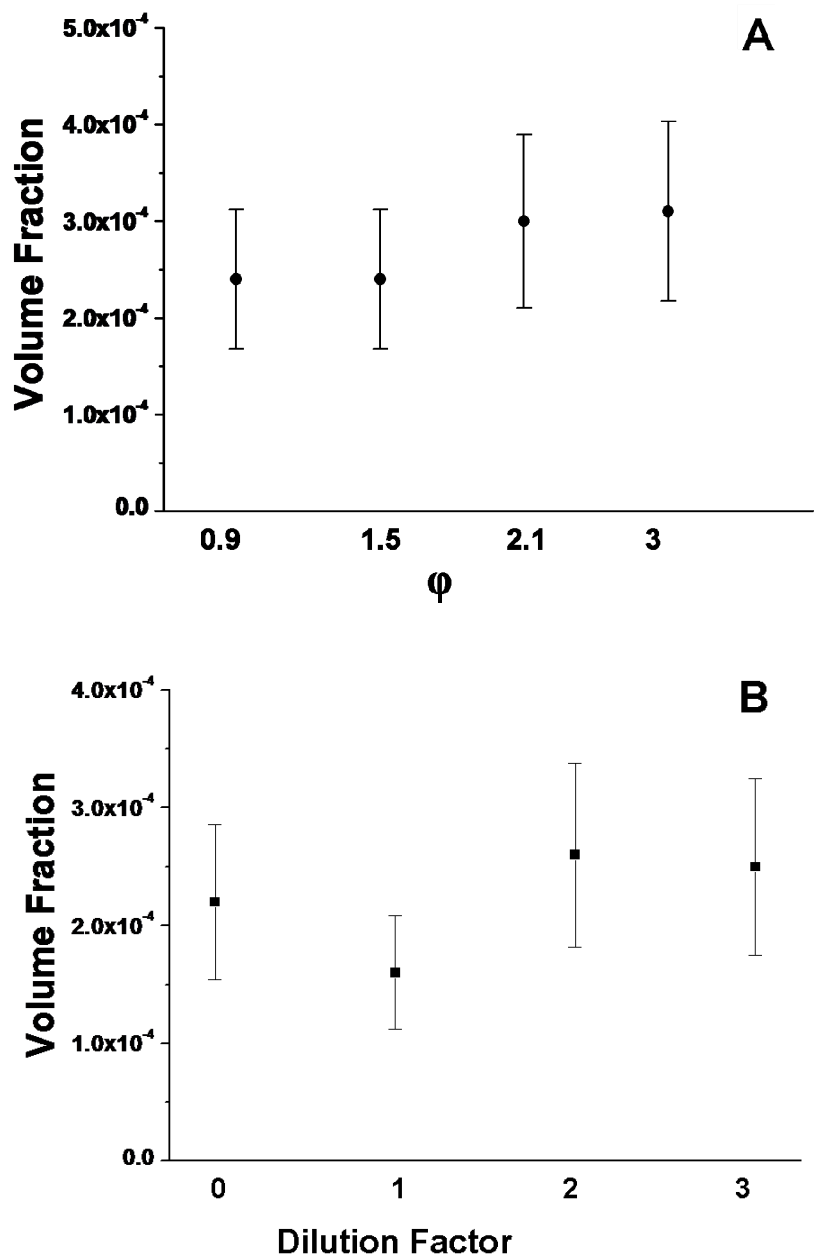
  

| B. Glu–PEI aqueous solution                         |                          |                           |
|-----------------------------------------------------|--------------------------|---------------------------|
| $n_{Glu}/n_{EI} = 3.1, [Glu] = 0.12 \text{ mol \%}$ |                          |                           |
| Dilution                                            | $V_{EtOH}/V_{water}^{'}$ | $V_{EtOH}/V_{water}^{''}$ |
| 0                                                   | 2 – 2.2                  | 38 – 40                   |
| 1                                                   | 2.4 – 2.6                | 16 – 18                   |
| 5                                                   | Transparent              |                           |

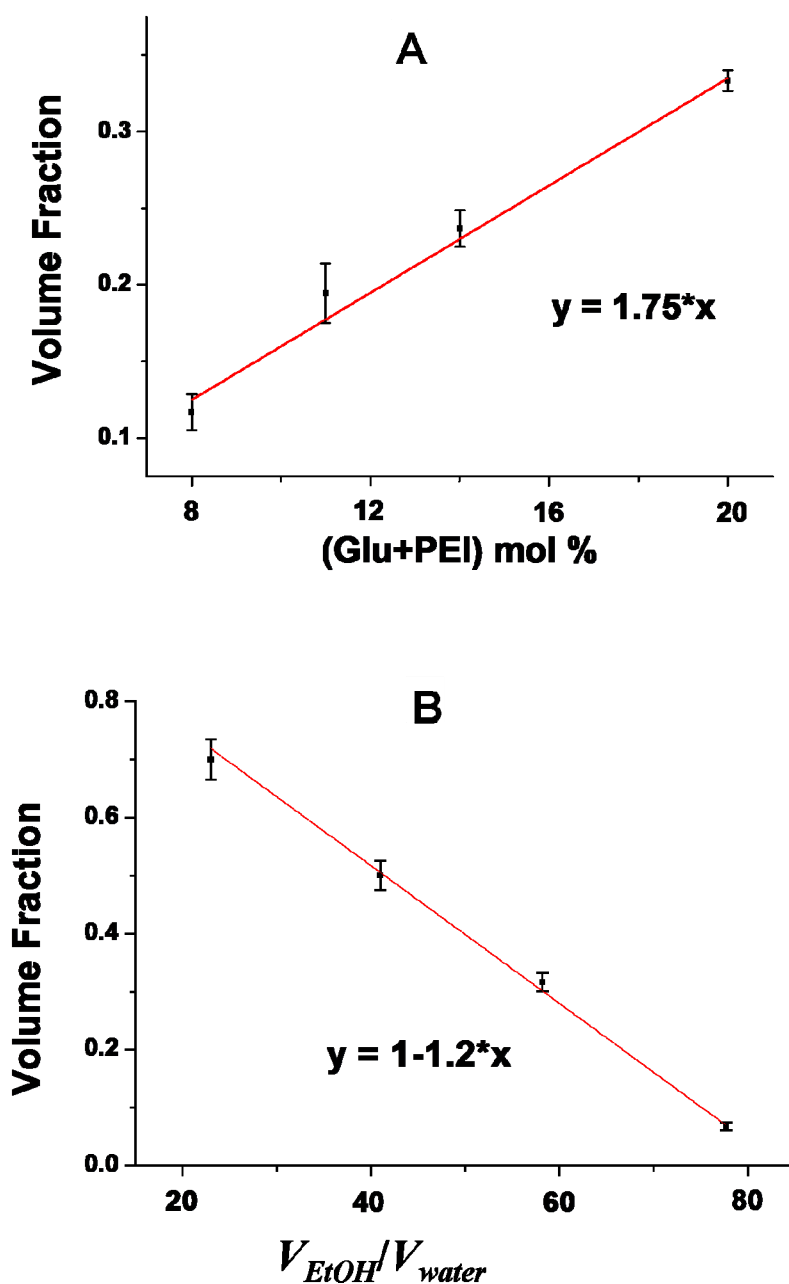
  

| C. Glu–PEI aqueous solution                         |                          |                           |
|-----------------------------------------------------|--------------------------|---------------------------|
| $n_{Glu}/n_{EI} = 6.2, [Glu] = 0.12 \text{ mol \%}$ |                          |                           |
| Dilution                                            | $V_{EtOH}/V_{water}^{'}$ | $V_{EtOH}/V_{water}^{''}$ |
| 0                                                   | 2.2 – 2.4                | 19 – 20                   |
| 1                                                   | 2.8 – 3.0                | 12 – 14                   |
| 5                                                   | Transparent              |                           |

C. Ultracentrifugation results of the PILP and the coacervation systems

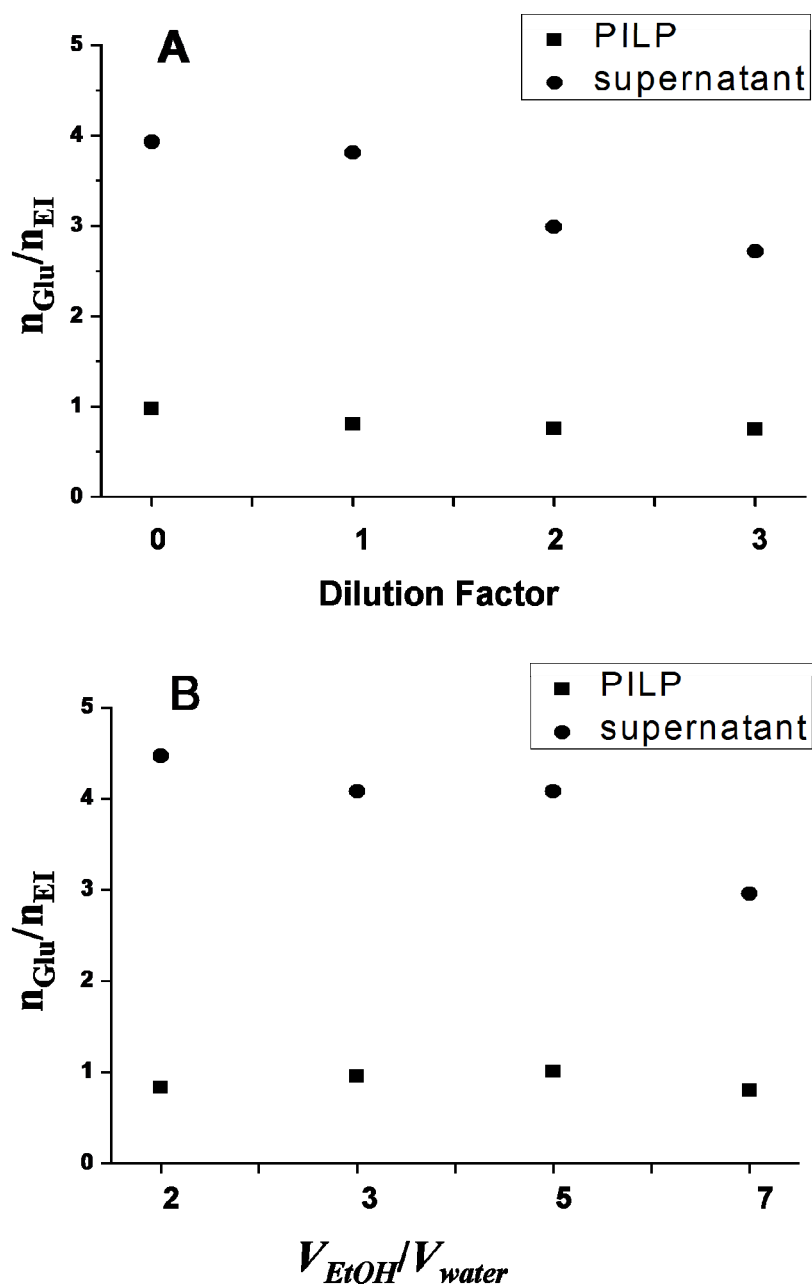


**Figure 2.** AUC results of PILP volume fractions in a series of measurements. Image **A**: [Glu] = 0.12 mol % in aqueous solution;  $V_{EtOH}/V_{water} = 3$ ; [EI] is variable. Image **B**: The original Glu-PEI aqueous solution composition: [Glu] = 0.18 mol % &  $n_{Glu}/n_{EI} = 1.5$ ; this solution was diluted with water by using three dilution factors at 1, 2, and 3 before the new mixture was mixed with EtOH with  $V_{EtOH}/V_{water}$  at 3.

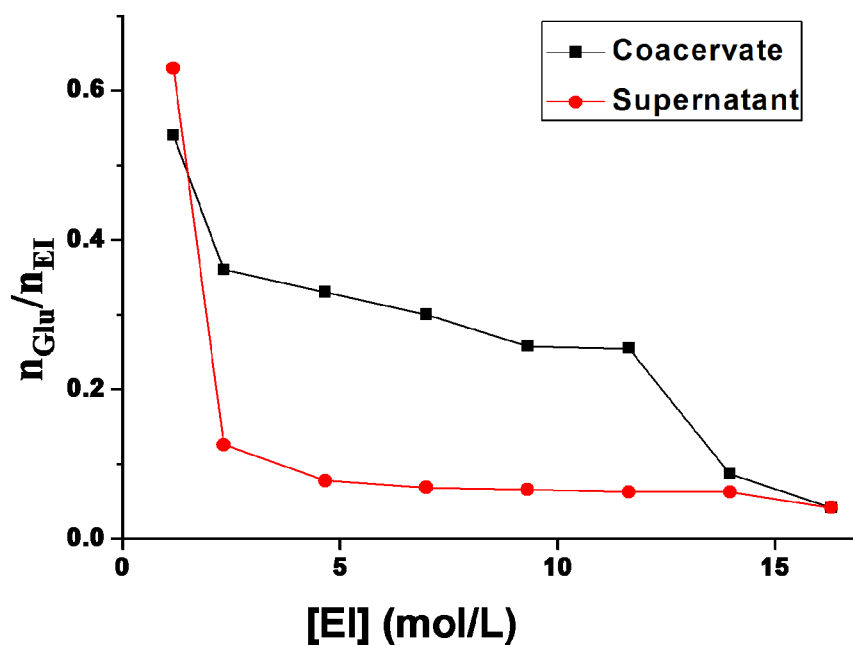


**Figure 3.** AUC results show the relationship between the volume fraction of the coacervates and the (Glu+PEI) mol % in the quaternary system. Image A:  $n_{Glu}/n_{EI} = 0.6$ ;  $V_{EtOH}/V_{water} = 1$ . Image B: the same Glu–PEI aqueous solution was mixed with EtOH at different values of  $V_{EtOH}/V_{water}$ ; the composition of aqueous solution [Glu] = 1.8 mol %,  $n_{Glu}/n_{EI} = 0.15$ .

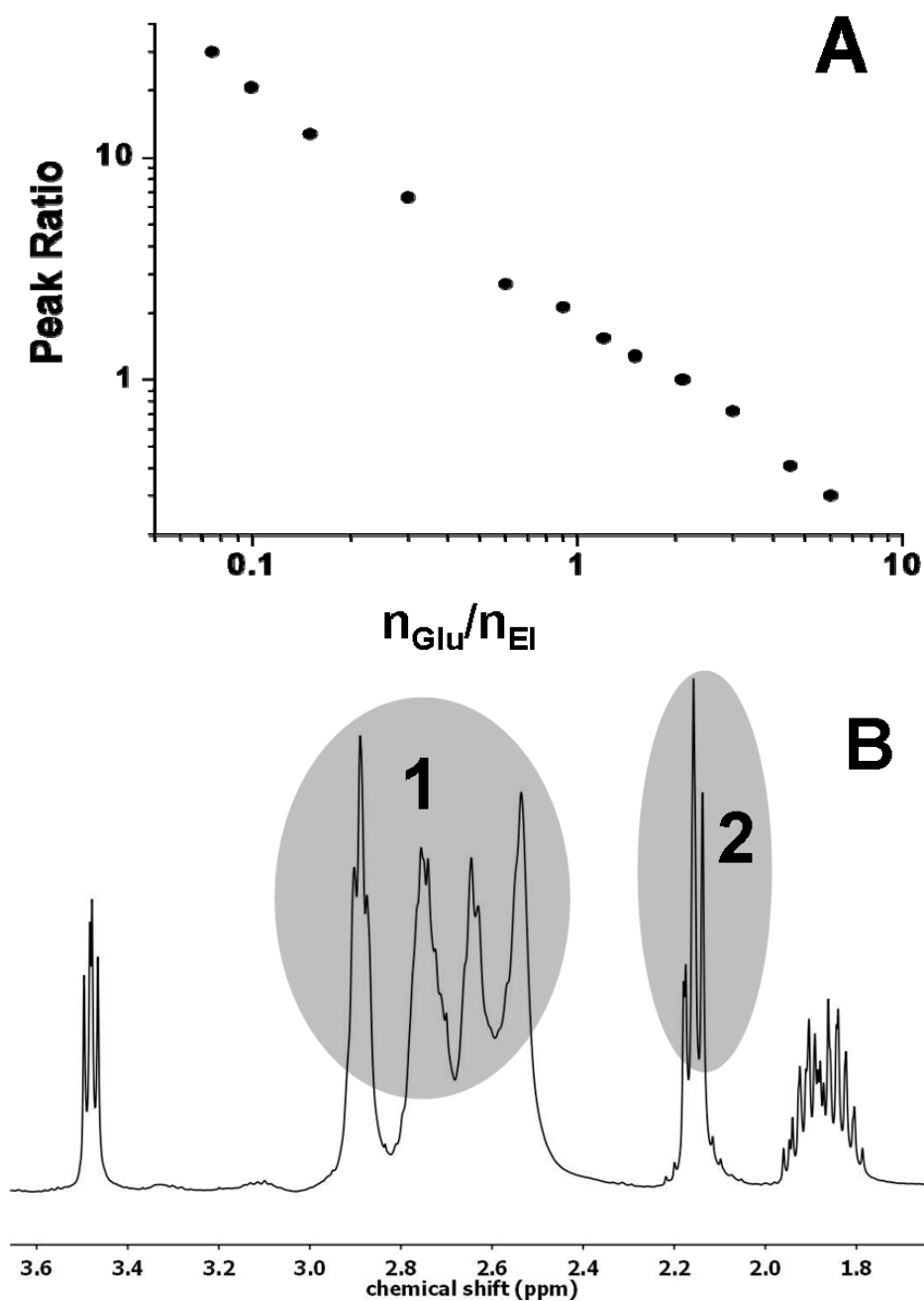
#### D. NMR Results



**Figure 4.** Image **A**: the relationship between the dilution effect in Glu-PEI aqueous solutions and the peak ratio in NMR measurements. The Glu-PEI aqueous solution used was diluted by a factor 2, 3, and 4 before they were mixed with EtOH at  $V_{\text{EtOH}}/V_{\text{water}} = 3$ . Image **B**: the relationship between  $V_{\text{EtOH}}/V_{\text{water}}$  and  $n_{\text{Glu}}/n_{\text{EI}}$ . The composition of the starting aqueous solution:  $[\text{Glu}] = 0.36 \text{ mol } \%$  and  $n_{\text{Glu}}/n_{\text{EI}} = 1.5$ .



**Figure 5.** The relationship between the [EI] in the Glu-PEI aqueous solution and the values of  $n_{\text{Glu}}/n_{\text{EI}}$  in the coacervate and supernatant phases from a coacervation process. [Glu] = 0.12 mol %;  $V_{\text{EtOH}}/V_{\text{water}} = 9$ .



**Figure 6.** Image A shows the relation between  $n_{\text{Glu}}/n_{\text{EI}}$  and the ratio of peak areas between the broad peaks on PEI (hydrocarbons) and the peaks of  $\gamma\text{-CH}_2$  on Glu. Image B is an example NMR spectrum of a Glu-PEI mixture in  $\text{D}_2\text{O}$ . The broad peaks (1) belong to the hydrogen of hydrocarbons on PEI, and the peaks (2) are  $\gamma\text{-CH}_2$  on Glu.