# Sol-gel transition in liquid polymer nanocomposites using trace amount of amine: Thickening of the glassy layer

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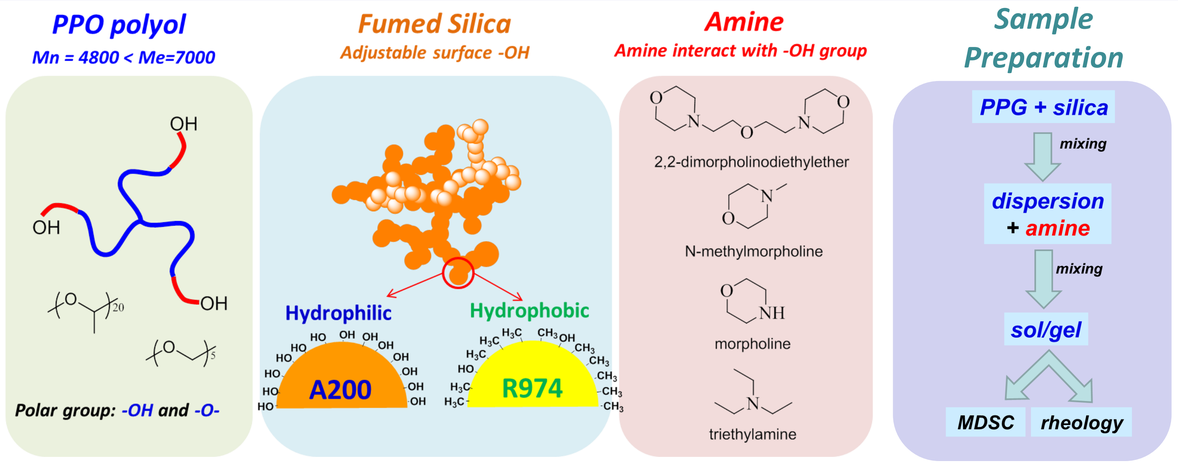
## Introduction



Liquid polymer nanocomposites (LPNCs) have attracted much attention due to their widespread applications in coatings, adhesives, lithium batteries, etc., while immobilized polymer layers surrounding nanoparticles are proposed to be of essentially vital importance for the reinforcement of LPNCs. However, there is still a need to clarify its contribution to diverse rheological performance like colloidal stability and gelation.

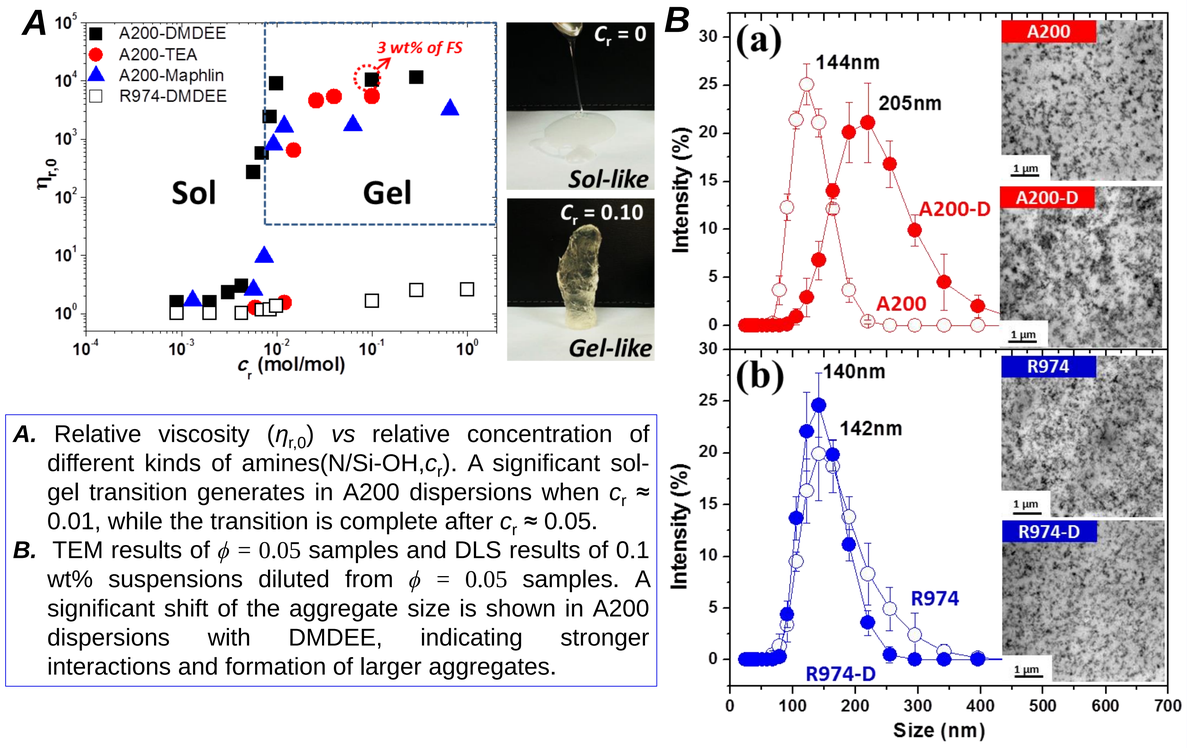
In our previous study, we accidentally find that introducing a trace amount tertiary amine obviously promotes the mechanical properties of the colloidal gels composed by fumed silica (FS) and urethane prepolymer.[1] We also find amines efficient to promote gelation of FS/PPG dispersion, a more simplified model system. We are interested in amine-mediated gelation mechanism in relation to molecular dynamics in the vicinity of NPs. Thus, in this work, we take advantage of MDSC method to investigate changes in heat capacity of PPG in FS dispersions with addition of amine during glass transition and try to correlate them with very unusual amine-initiated rheological response.

## Experimental




## Results and Discussion

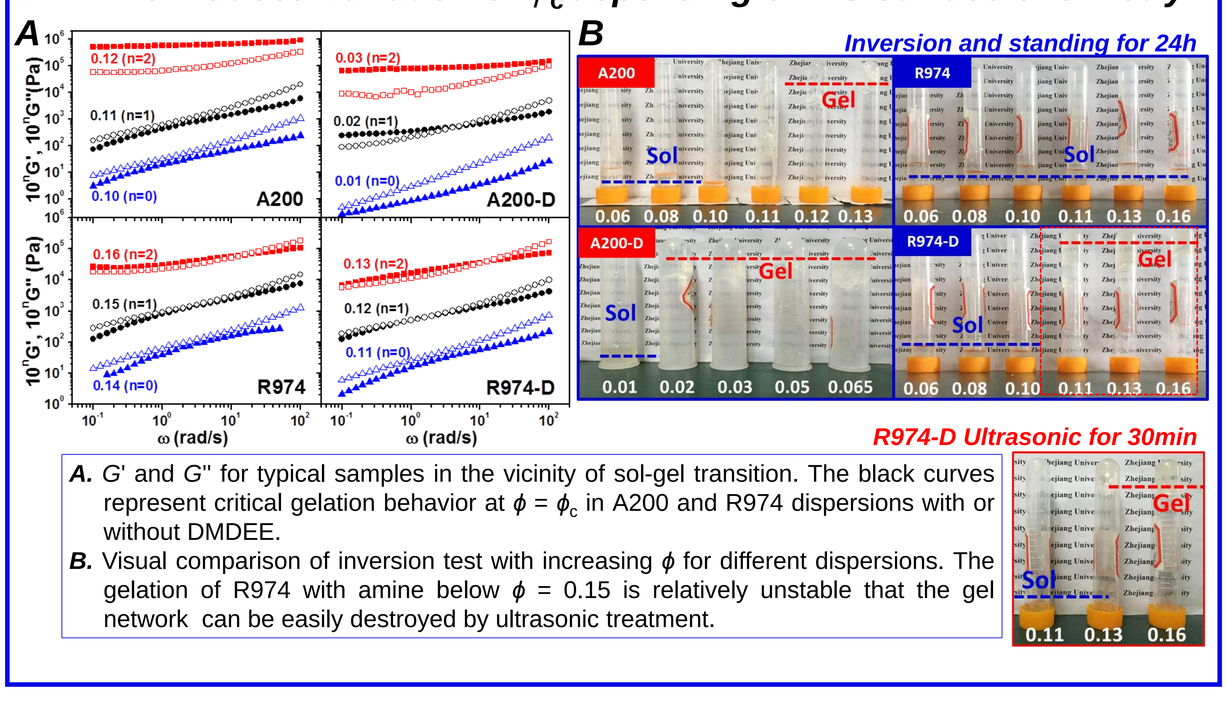
### 1. Effects of amine on rheology and dispersity of FS-PPG dispersions




***A.*** Relative viscosity ($\eta_{r,0}$) *vs* relative concentration of different kinds of amines(N/Si-OH,$c_r$). A significant sol-gel transition generates in A200 dispersions when $c_r \approx 0.01$, while the transition is complete after $c_r \approx 0.05$.

***B.*** TEM results of $\phi = 0.05$ samples and DLS results of 0.1 wt% suspensions diluted from $\phi = 0.05$ samples. A significant shift of the aggregate size is shown in A200 dispersions with DMDEE, indicating stronger interactions and formation of larger aggregates.

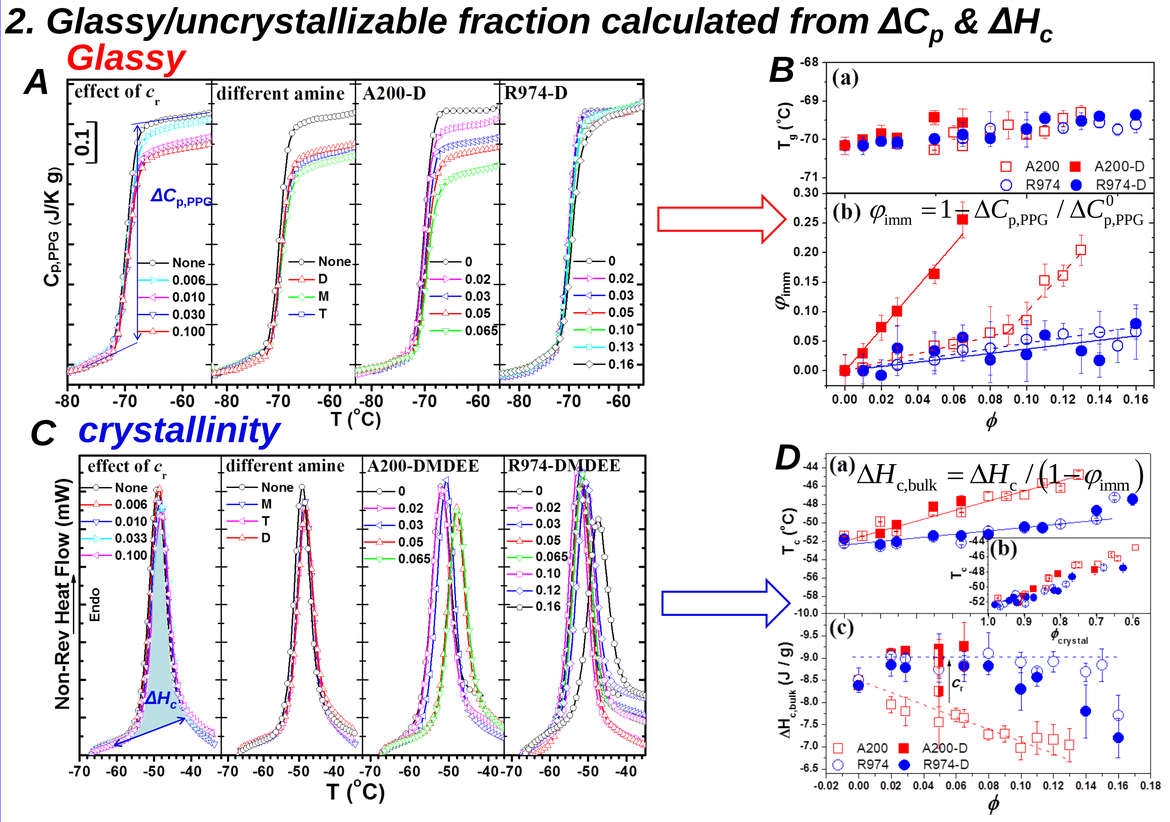
### 2. Amine induced variation of $\phi_c$ depending on FS surface chemistry



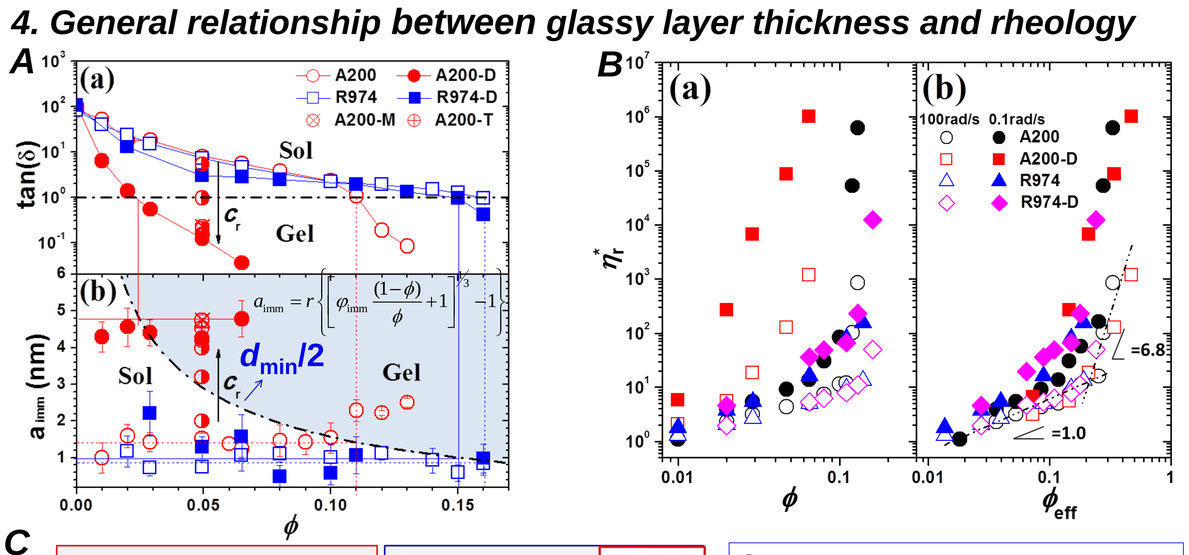

***A.*** *G'* and *G''* for typical samples in the vicinity of sol-gel transition. The black curves represent critical gelation behavior at $\phi = \phi_c$ in A200 and R974 dispersions with or without DMDEE.

***B.*** Visual comparison of inversion test with increasing $\phi$ for different dispersions. The gelation of R974 with amine below $\phi = 0.15$ is relatively unstable that the gel network can be easily destroyed by ultrasonic treatment.

### 2. Glassy/uncrystallizable fraction calculated from $\Delta C_p$ & $\Delta H_c$




### 4. General relationship between glassy layer thickness and rheology




***A.*** tanδ of PPG-FS dispersions and the estimated thickness of glassy layer comparing with the nearest distance between two ideal particles *vs* particle volume fraction. The sol-gel transitions (tanδ = 1) coincide with the percolation of the glassy layer.

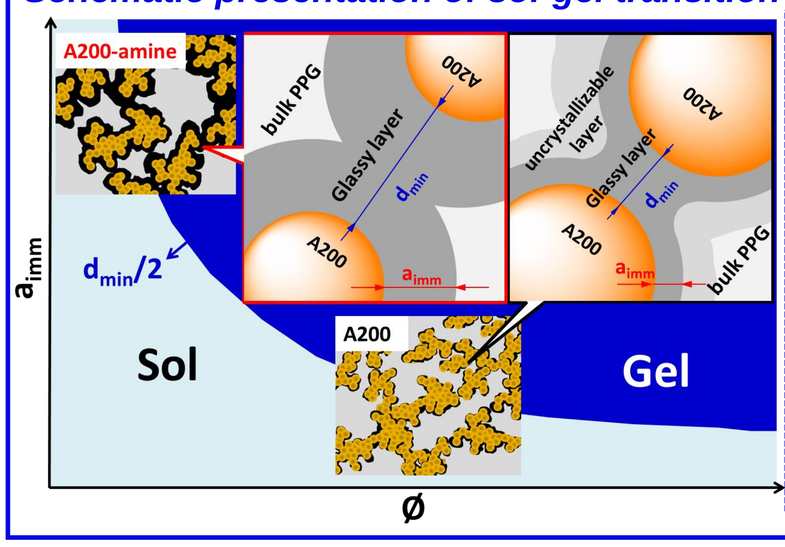
***B.*** $\eta^*_r$ of PPG-FS dispersions as a function of $\phi$ and $\phi_{eff}$ where

$$\phi_{eff} = k\phi \qquad k = \left(1 + \frac{a_{imm}}{r}\right)^3$$

***C.*** Evolution of the layer structure after adding amine into PPG-hydrophilic FS dispersions as well as layer thickness with or without amine.

## Conclusions

### Schematic presentation of sol-gel transition




### Summary

1. Direct evidence that percolation of glassy layer along the nearest neighbor nanoparticles is responsible for the sol-gel transition.[2]
2. The amine-promoted gelation is due to thickening and easy-percolation of the inner glassy layer converted from an outer uncrystallizable layer.[3]
3. The dispersion rheology could be well normalized within the framework of a two-phase model incorporating effective volume fraction of nanoparticles plus the glassy layers.

## References & Acknowledgement

[1] Zheng Z.; Song YH.; Wang X.; Zheng Q., ***Journal of Rheology*** **2015,** 59, 971−993
[2] Zheng Z.; Song YH.; Yang RQ.; Zheng Q., ***Langmuir*** **2015,** 31, 13478−13487
[3] Zheng Z.; Song YH.; Xu HL.; Zheng Q., ***Macromolecules*** **2015,** 48, 9015−9023

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