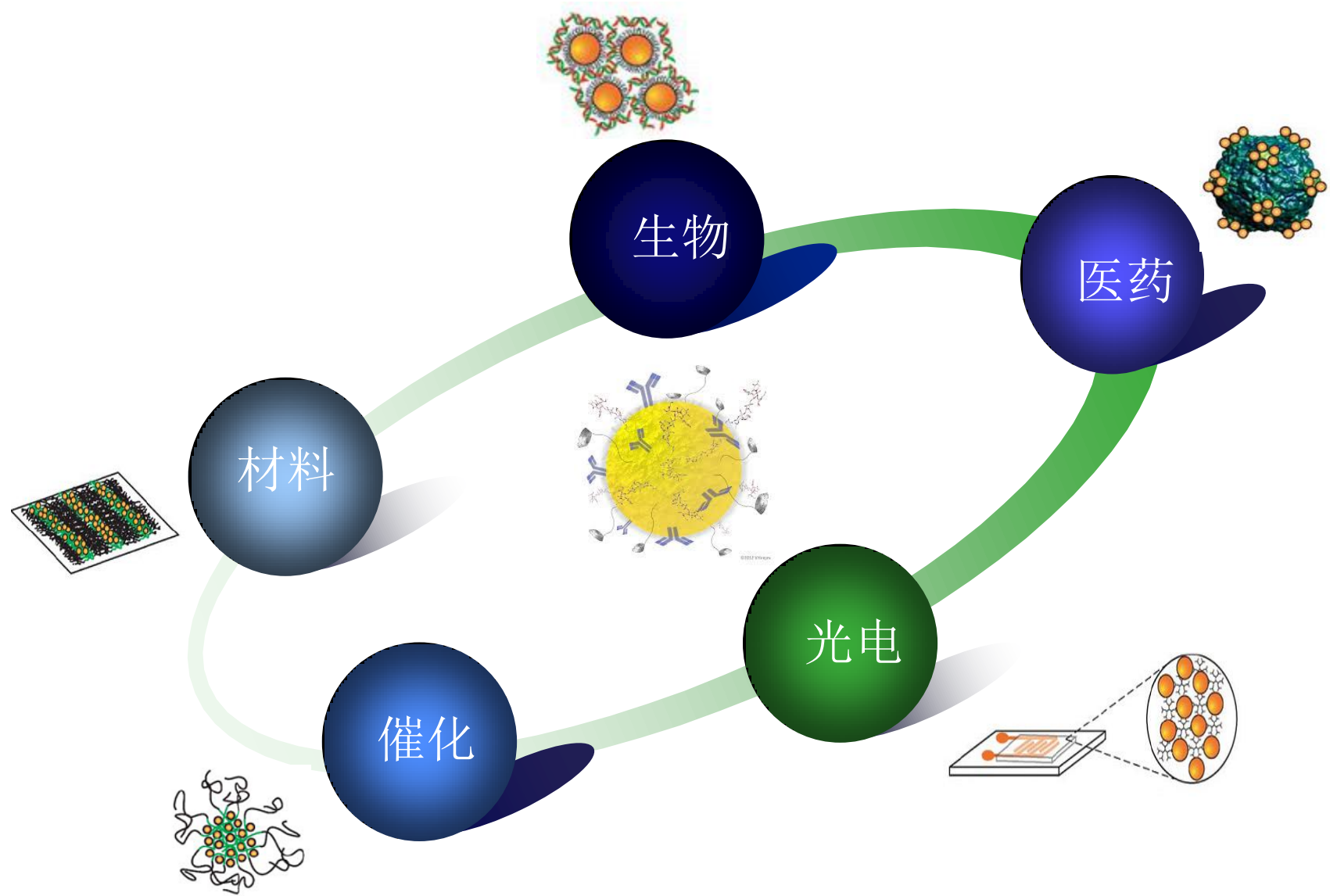
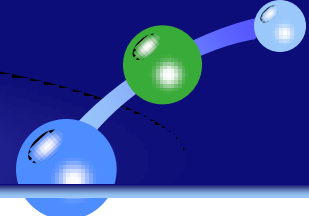


金纳米粒子表面受限的高分子的 玻璃化转变行为

朱丽丽

2013-12-08



博士论文工作

机理

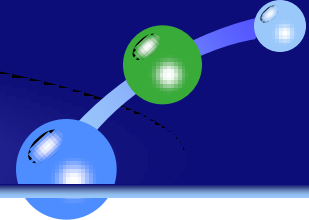
纳米表面
物质检测

纳米表面
化学反应

纳米材料

Lili Zhu, Xiaoliang Wang, Qiang Gu, Wei Chen, Pingchuan Sun and Gi Xue * *Macromolecules* 2013, 46, 2292-2297.
Lili Zhu, Chen Zhang, Chenchen Guo, Xiaoliang Wang, Pingchuan Sun, Dongshan Zhou, Wei Chen, and Gi Xue* *J. Phys. Chem. C* 2013, 117, 11399-11404.
Lili Zhu, Qiang Gu, Pingchuan Sun, Wei Chen, Xiaoliang Wang and Gi Xue.* *ACS Appl. Mater. Interfaces* 2013, 5, 10352-10356.

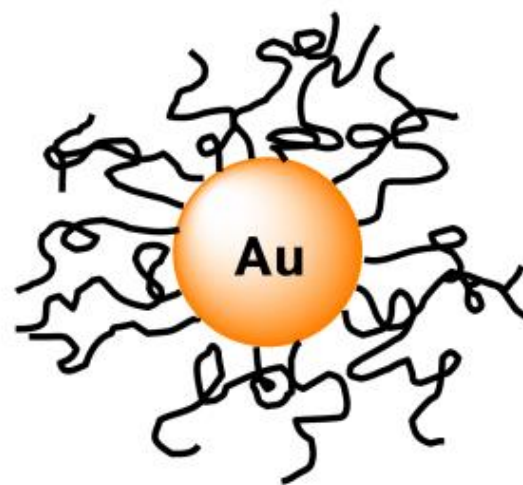
金纳米粒子表面受限的高分子的 玻璃化转变行为



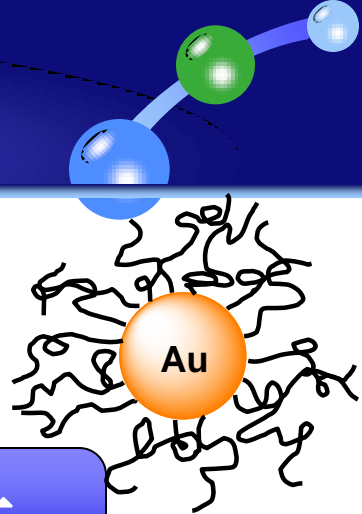
^1H SSNMR

高速魔角旋转，偶极滤波

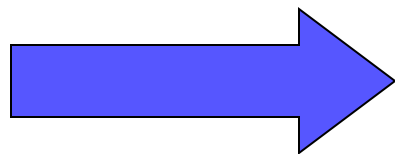
差热扫描量热法
(DSC)



金纳米粒子表面受限的高分子的 玻璃化转变行为

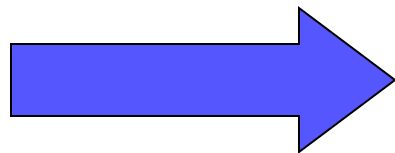


^1H SSNMR
偶极滤波

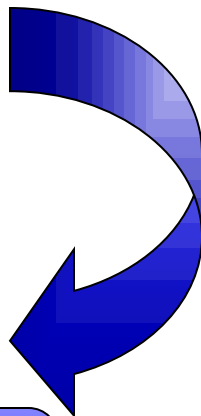


受限态

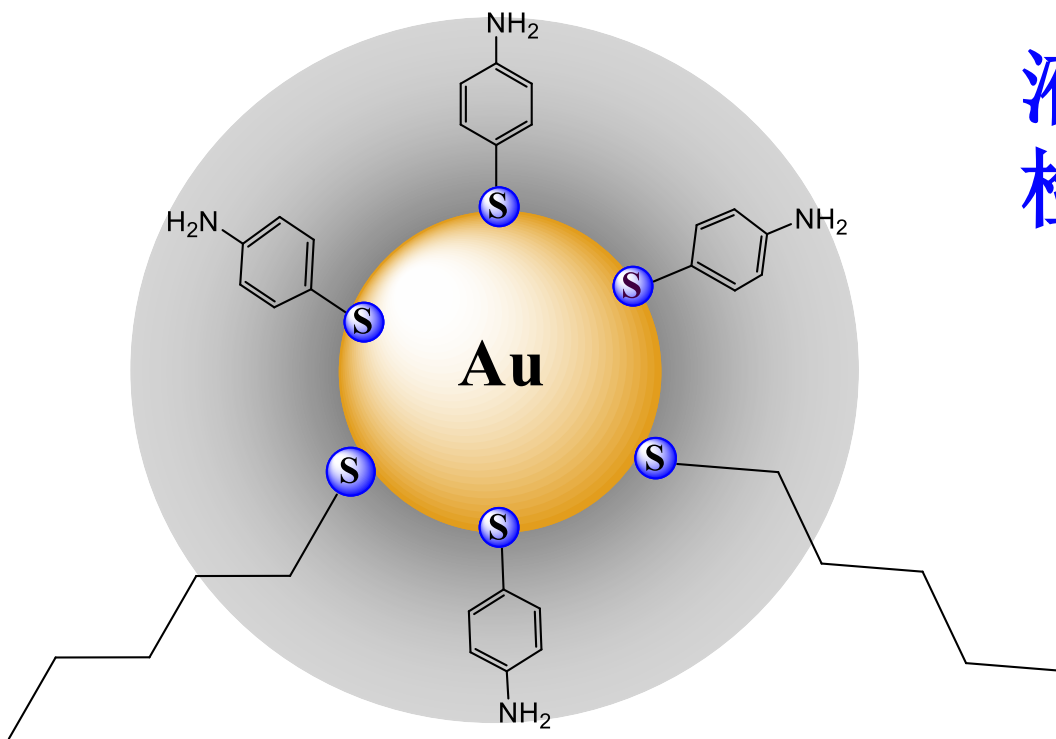
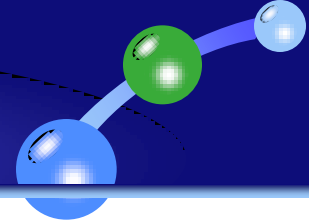
差热扫描量热
(DSC)



T_g

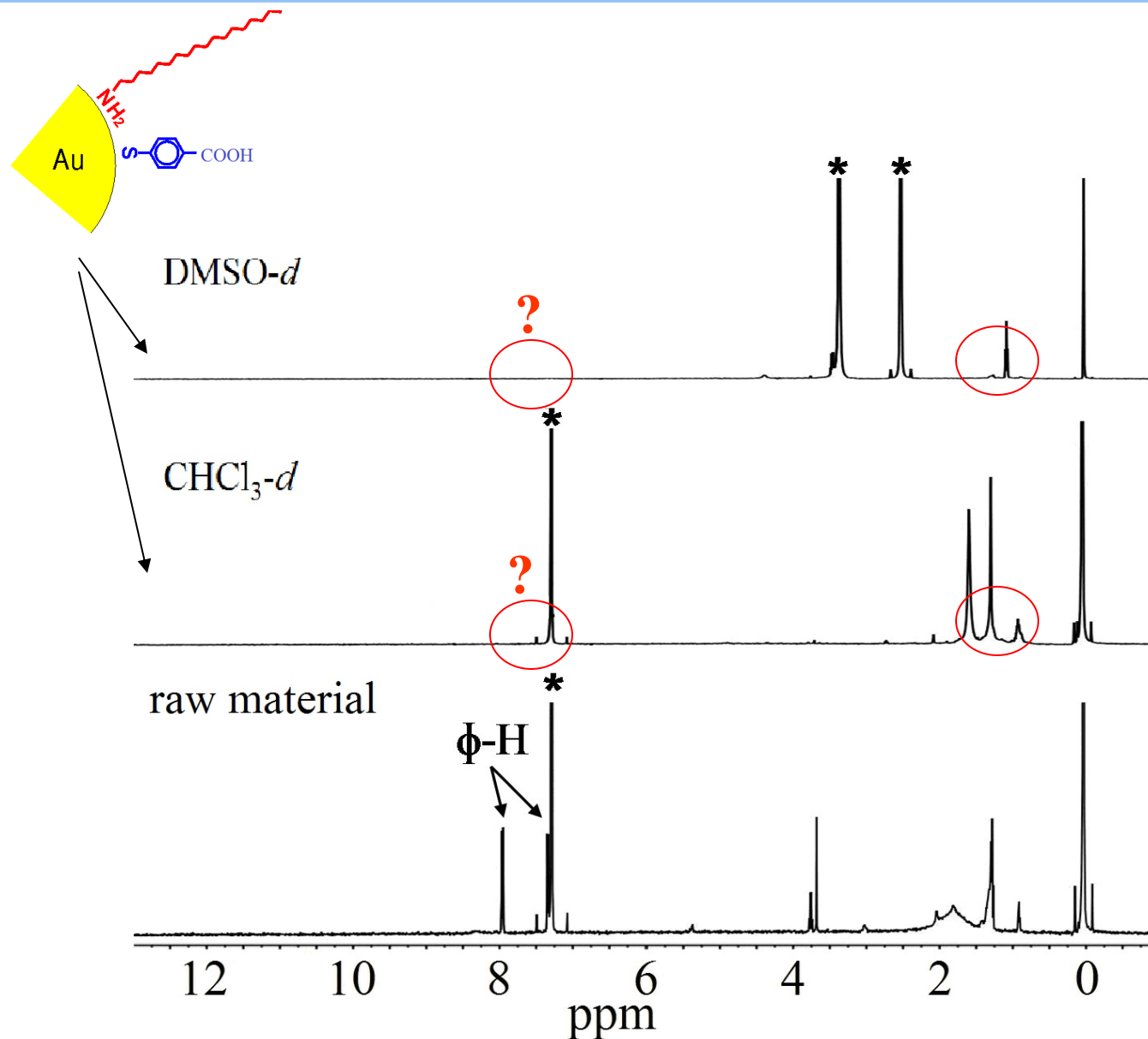
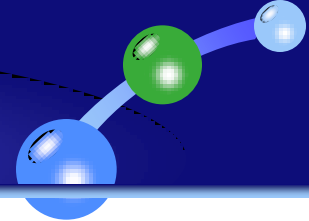


金纳米粒子表面受限配体的检测

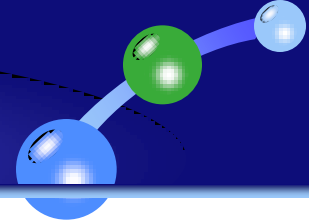


液体核磁
检测盲区

金纳米粒子表面受限配体的检测



静态哈密顿量和核磁谱线宽度之间的关系



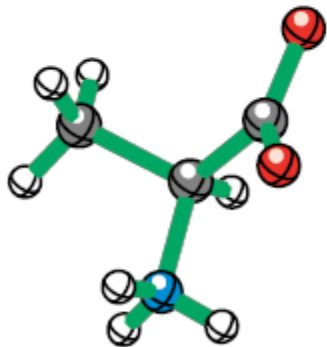
The Static Hamiltonian:

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_{cs} + \mathcal{H}_J + \dots$$

anisotropic homonuclear and heteronuclear dipolar interactions ($\sim 0-20$ kHz)

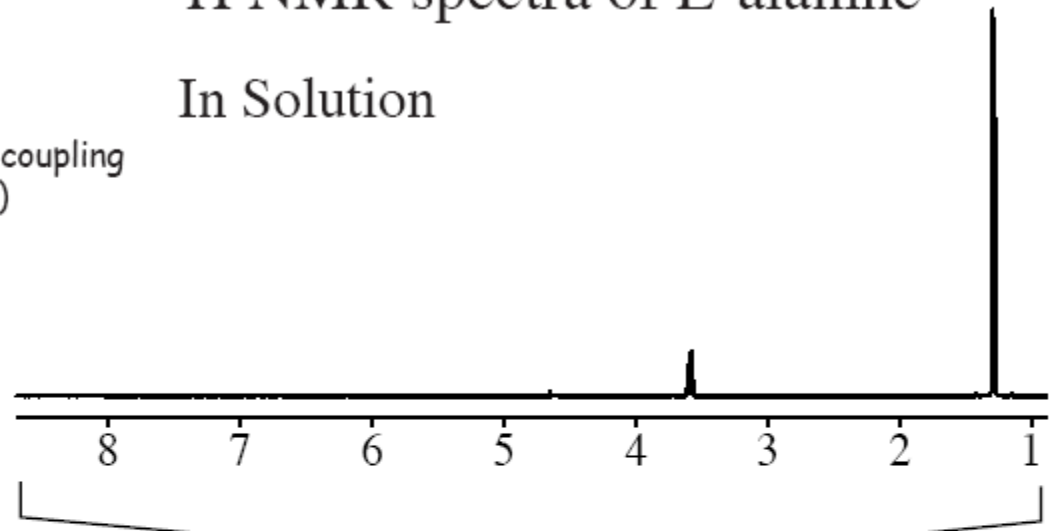
anisotropic chemical shift ($\delta \sim 0-10$ kHz)

isotropic J coupling (0-150 Hz)

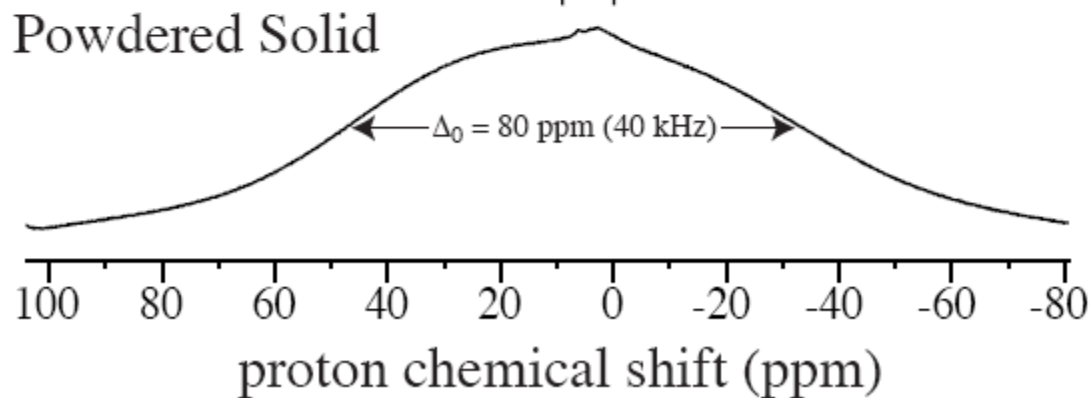


^1H NMR spectra of L-alanine

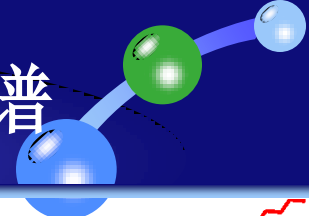
In Solution



Powdered Solid

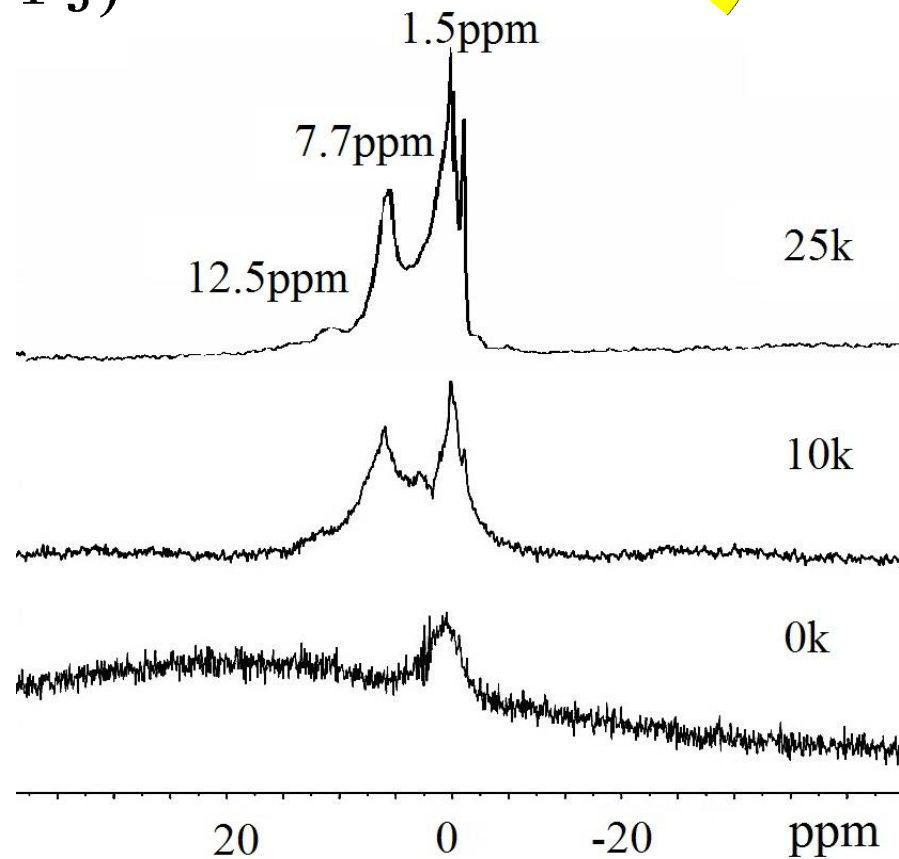
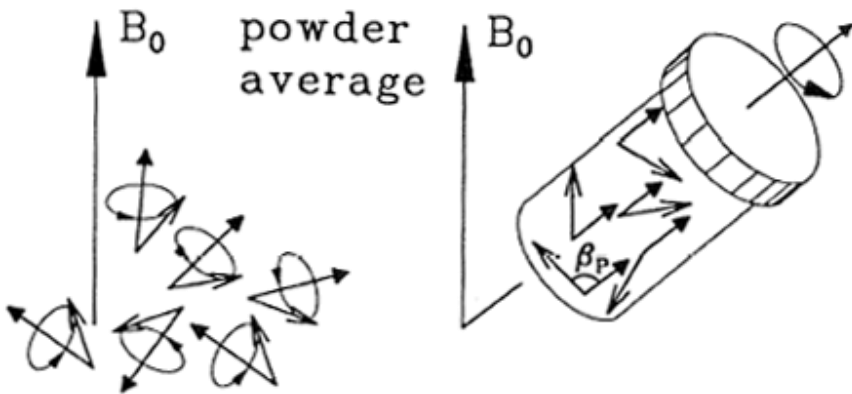
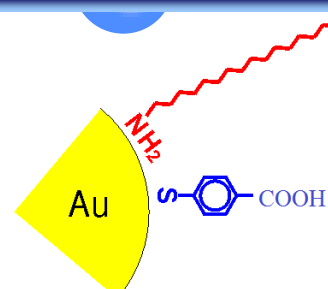


超高速魔角旋转固体核磁共振氢(^1H SSNMR)谱

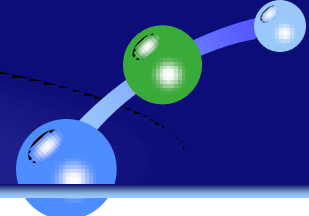


魔角旋转 (MAS) :

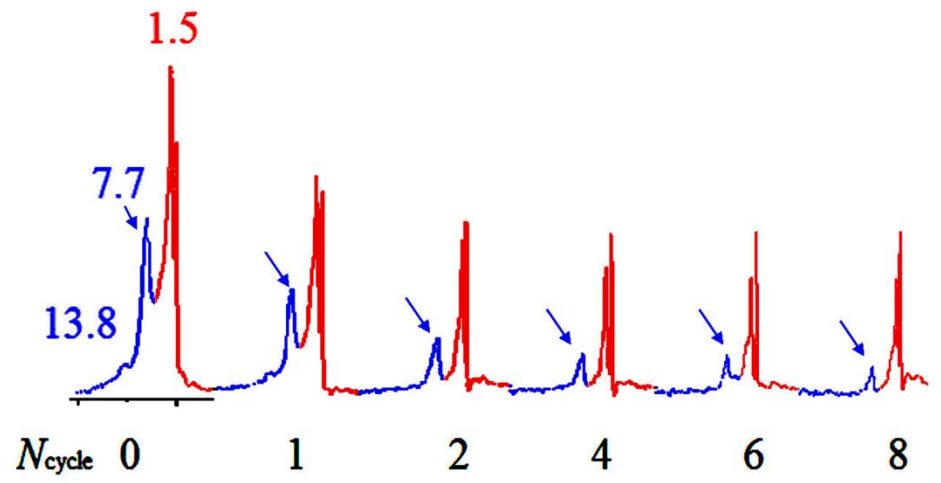
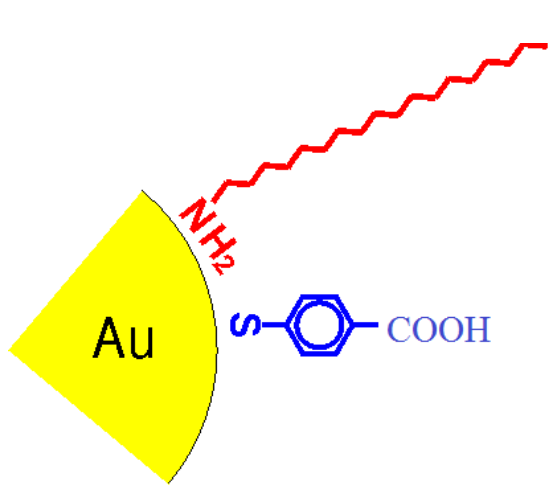
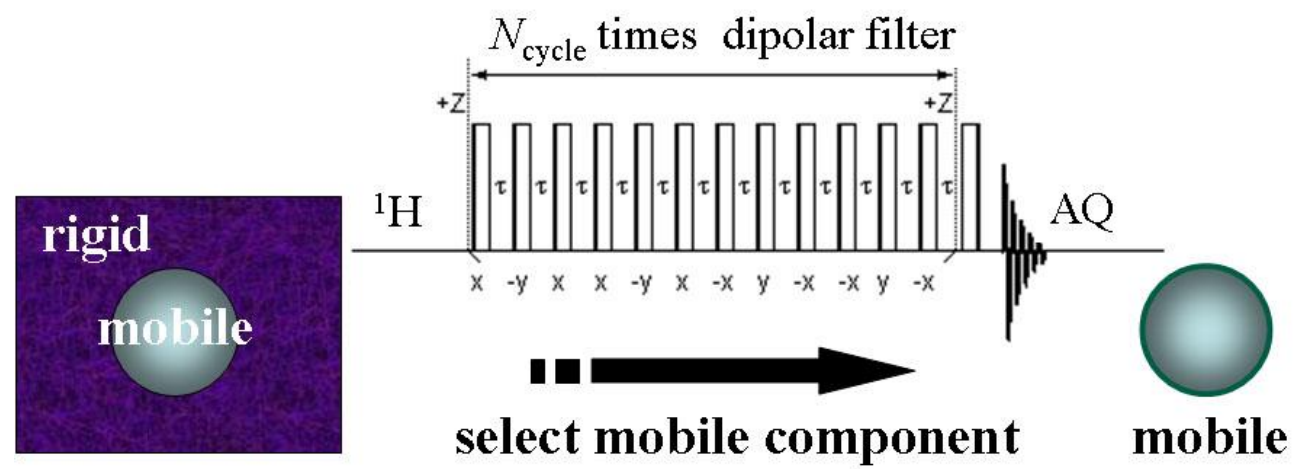
$$H_D^H = -\frac{\mu_0}{4\pi} \hbar \frac{\gamma^2}{r^3} \frac{1}{2} (3 \cos^2 \theta - 1) (3I_Z J_Z - \mathbf{I} \cdot \mathbf{J})$$



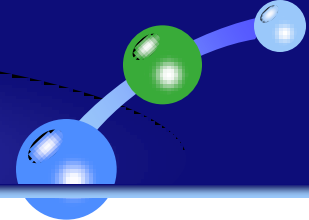
金纳米粒子表面配体受限态与配体反应活性



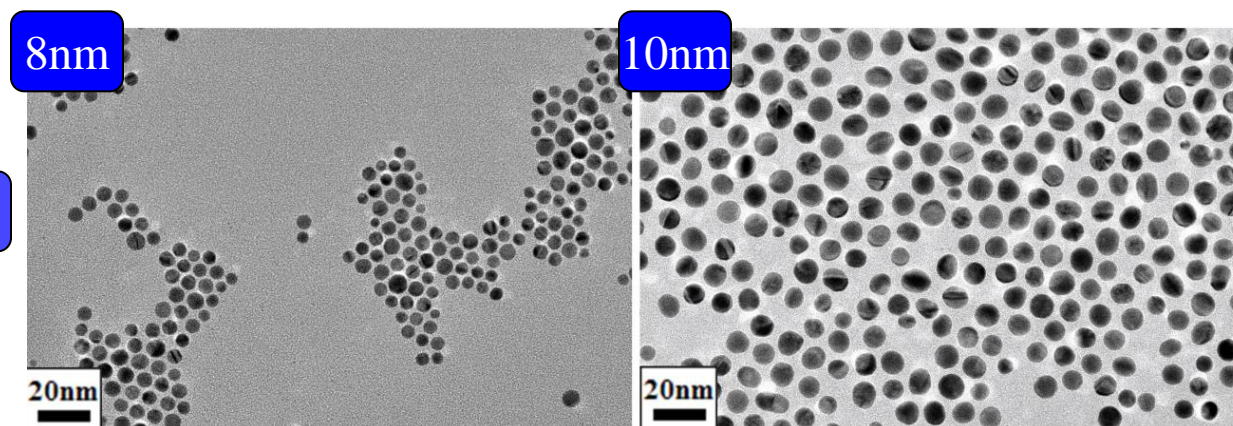
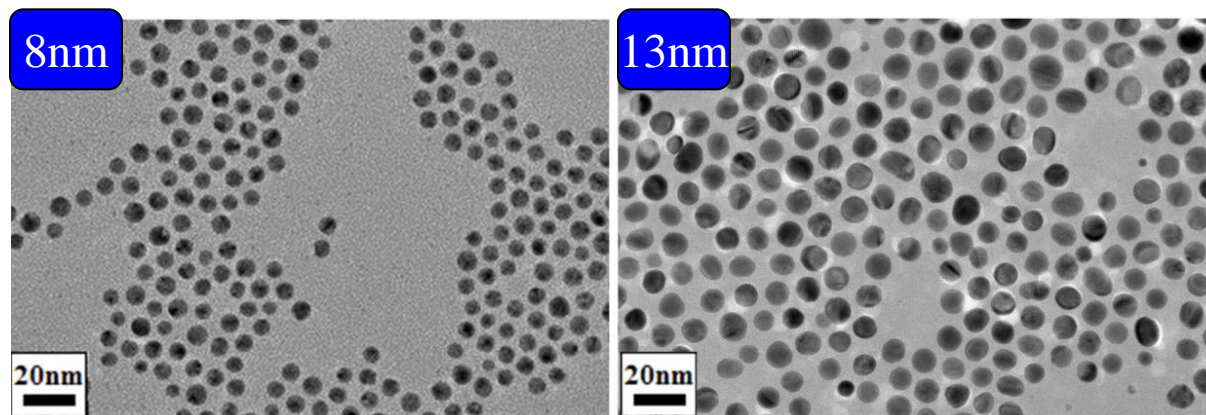
^1H SSNMR 偶极滤波:



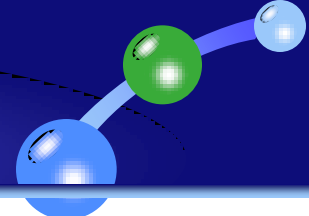
金纳米粒子表面受限的高分子的 玻璃化转变行为



巯基聚苯乙烯保护的金纳米粒子 PS-S-AuNPs:

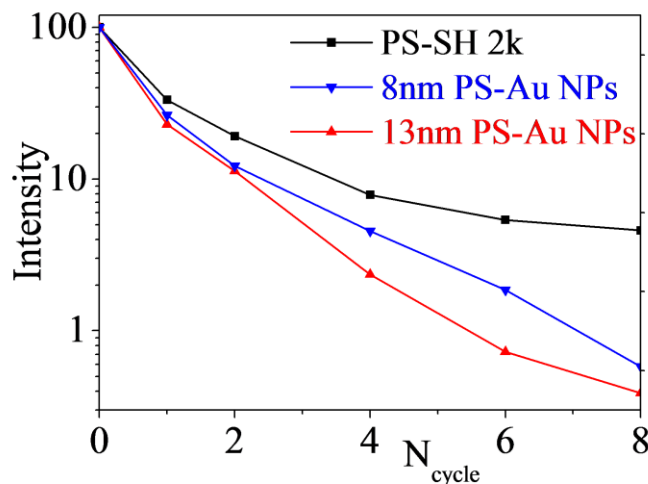


金纳米粒子表面受限的高分子的 玻璃化转变行为

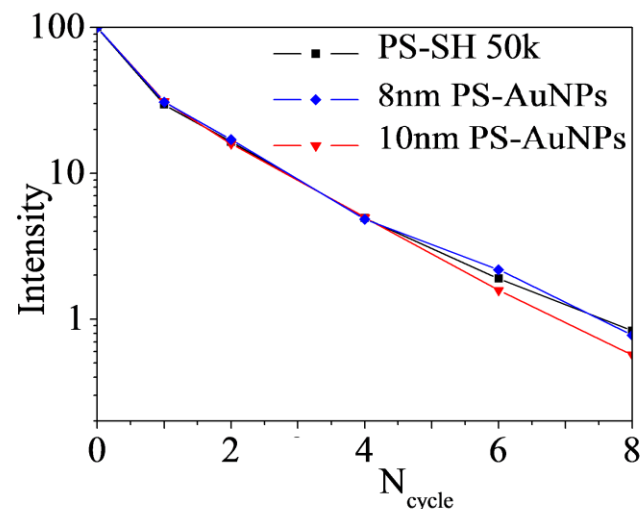


偶极滤波

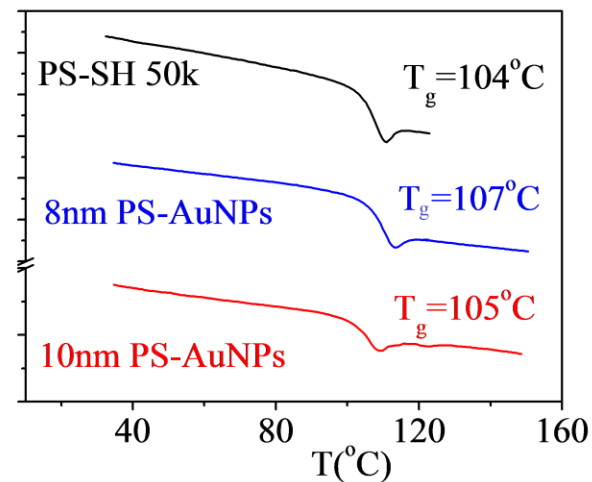
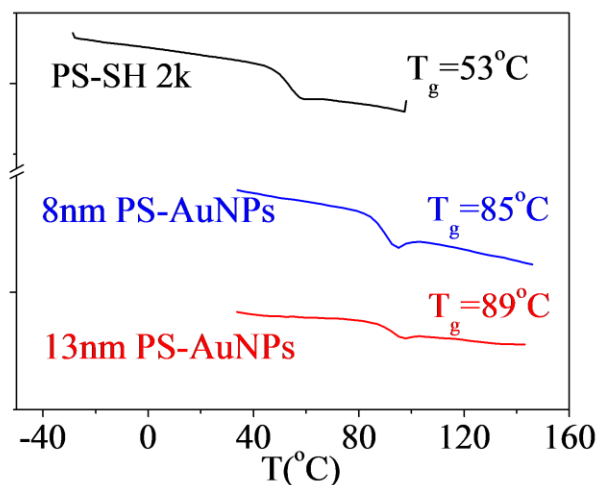
$M_n = 2000 \text{ g/mol}$



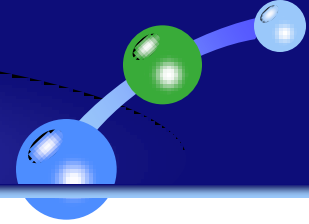
$M_n = 50000 \text{ g/mol}$



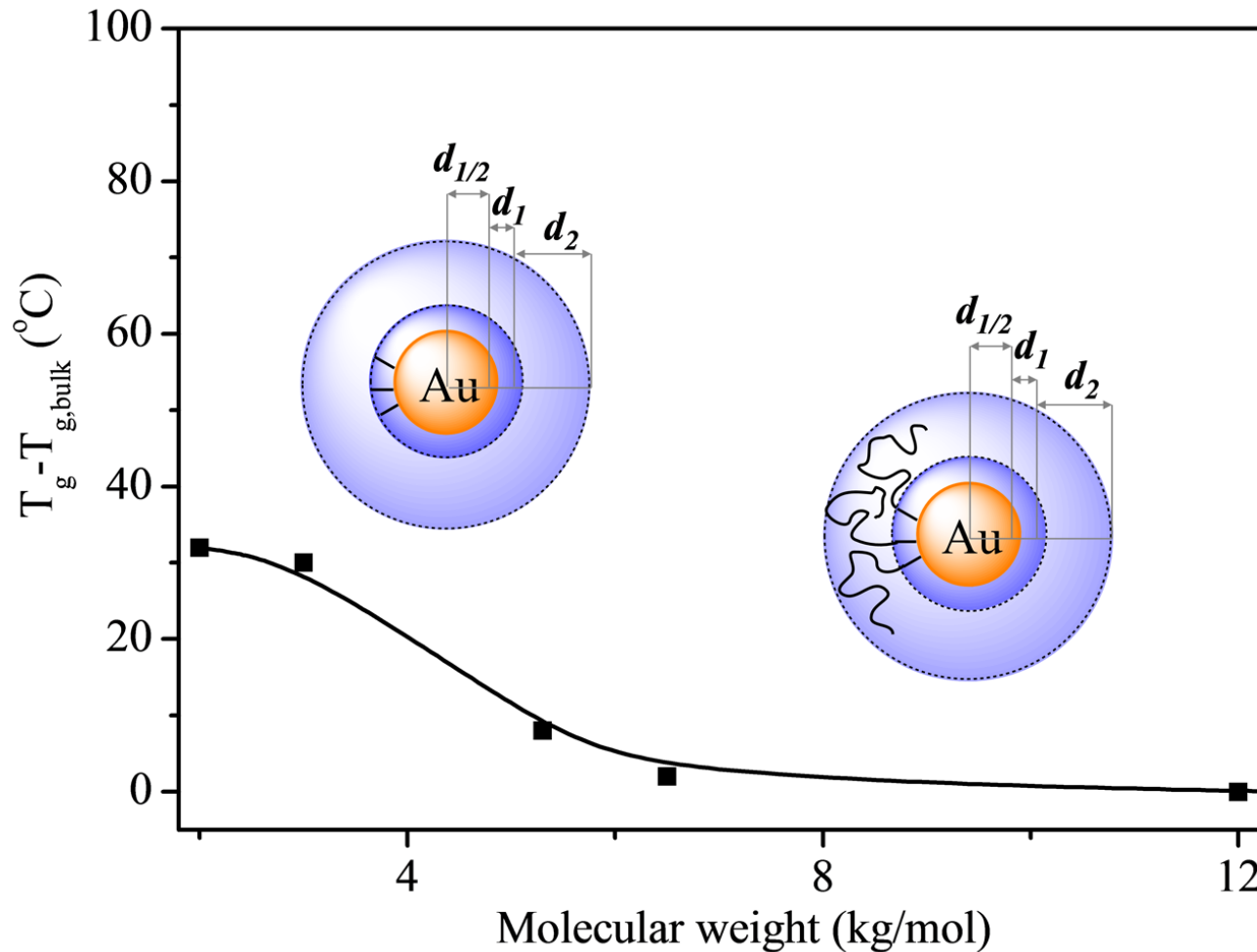
DSC



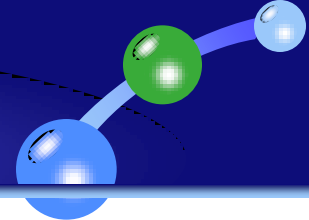
金纳米粒子表面受限的高分子的 玻璃化转变行为



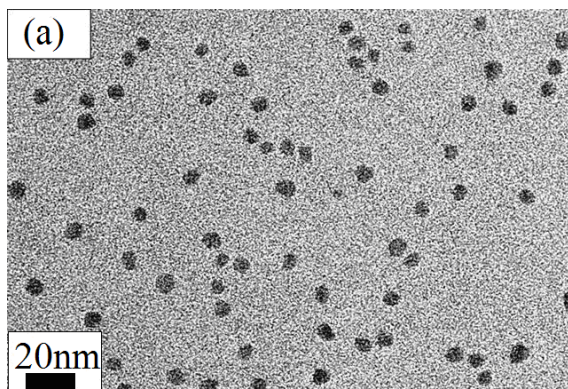
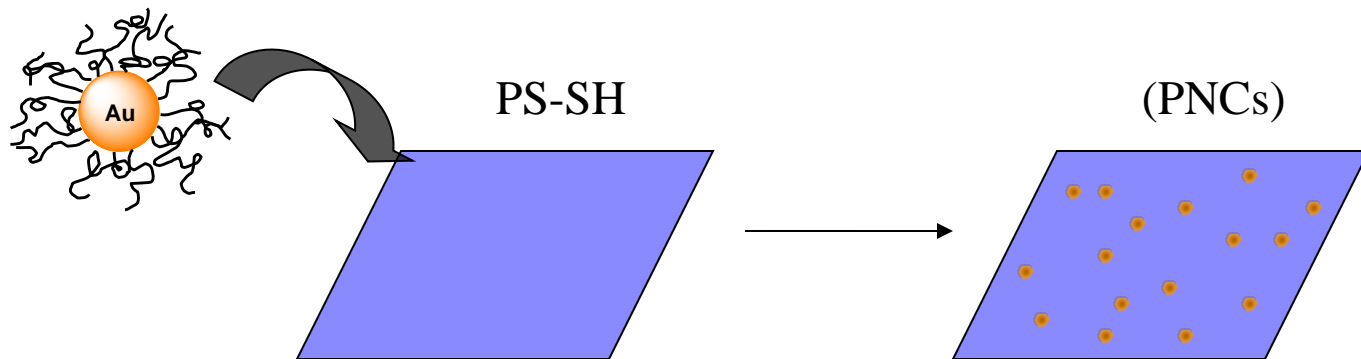
金纳米粒子表面受限态核-壳（两层）模型：



金纳米粒子表面受限的高分子的 玻璃化转变行为

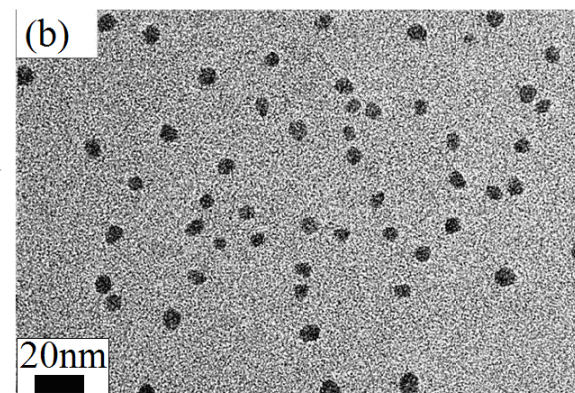


高分子/纳米复合材料 (PNCs)

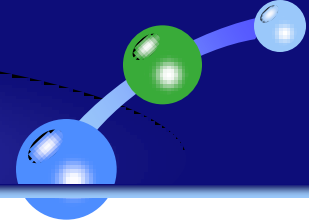


160 °C

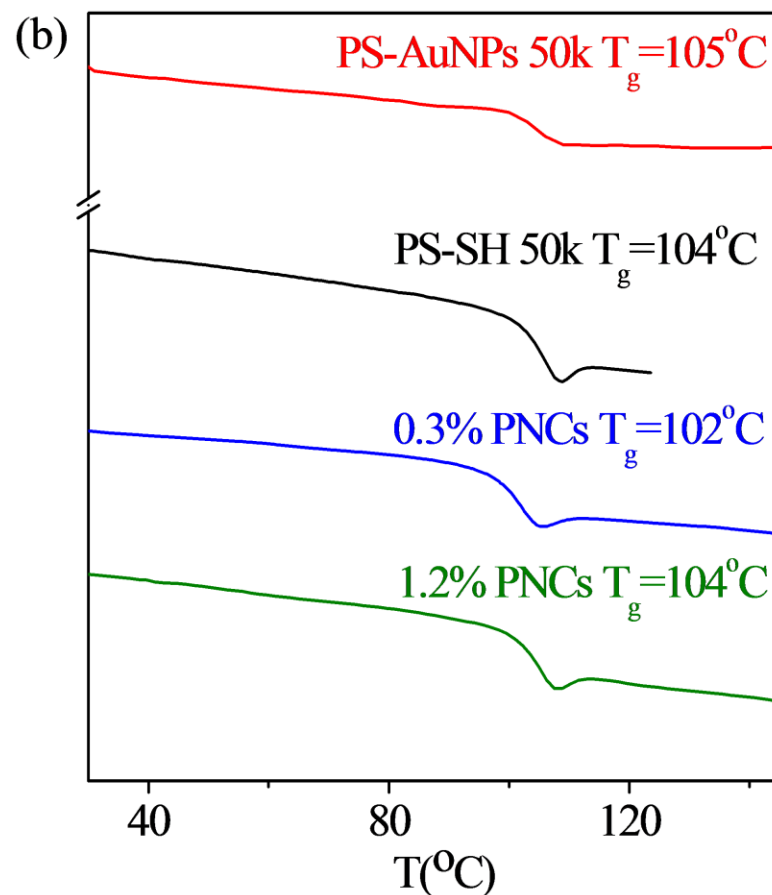
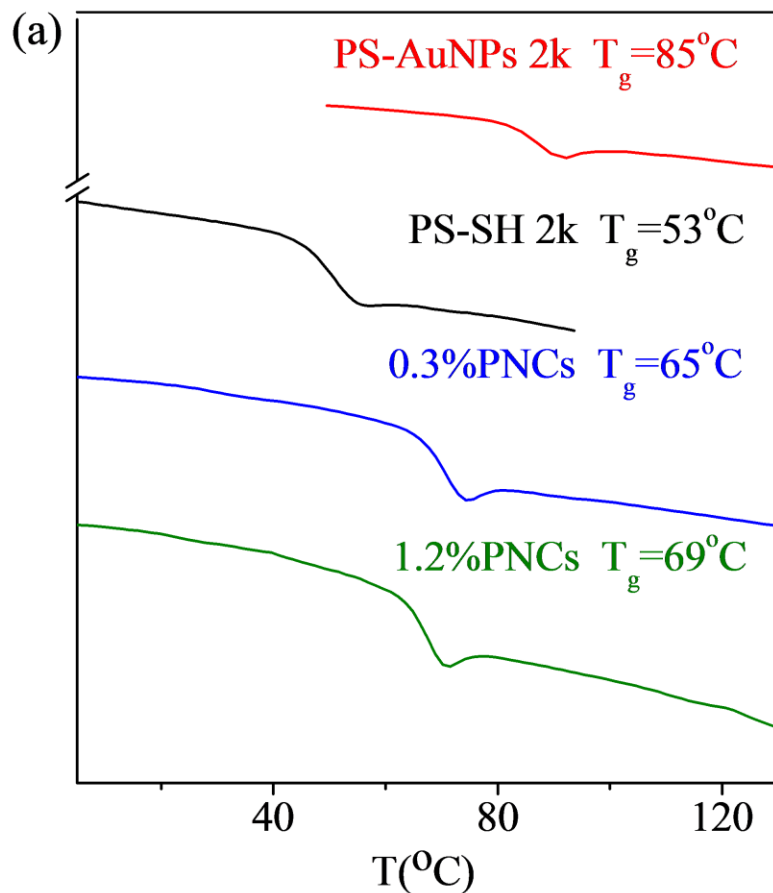
4 h




金纳米粒子表面受限的高分子的 玻璃化转变行为



高分子/纳米复合材料 (**PNCs**) :



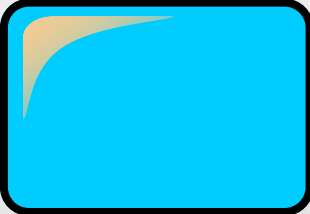
小结



金纳米表面高分子链受限态对玻璃化转变行为的影响



尺寸效应：低分子量PS-S-, 运动性下降, T_g 上升; 粒径越大, ΔT_g 越大; 高分子量PS-S-, T_g 不变

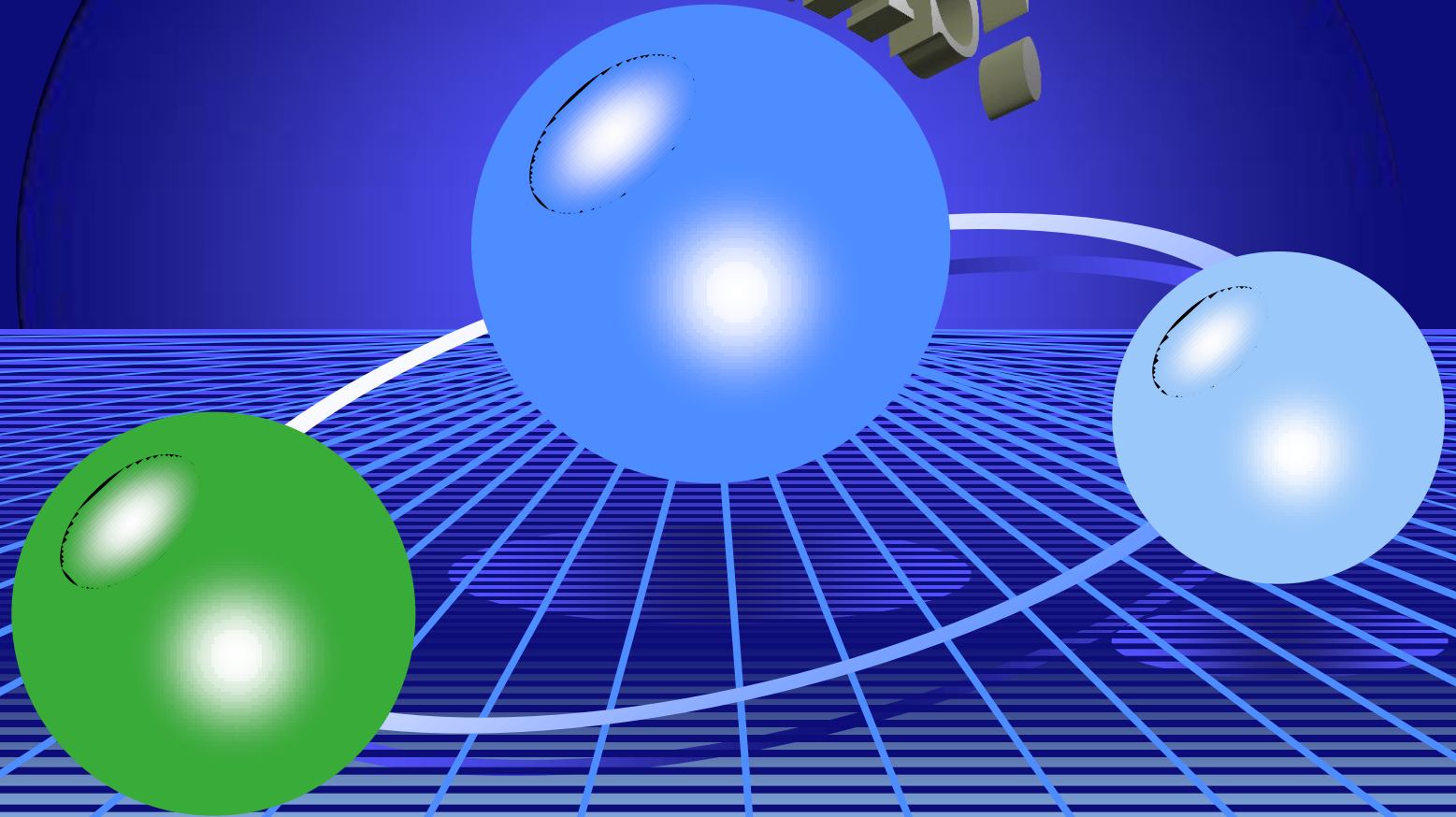


受限态核-壳模型：里层受限强，外层受限弱



高分子纳米复合材料

Thanks!



Further research

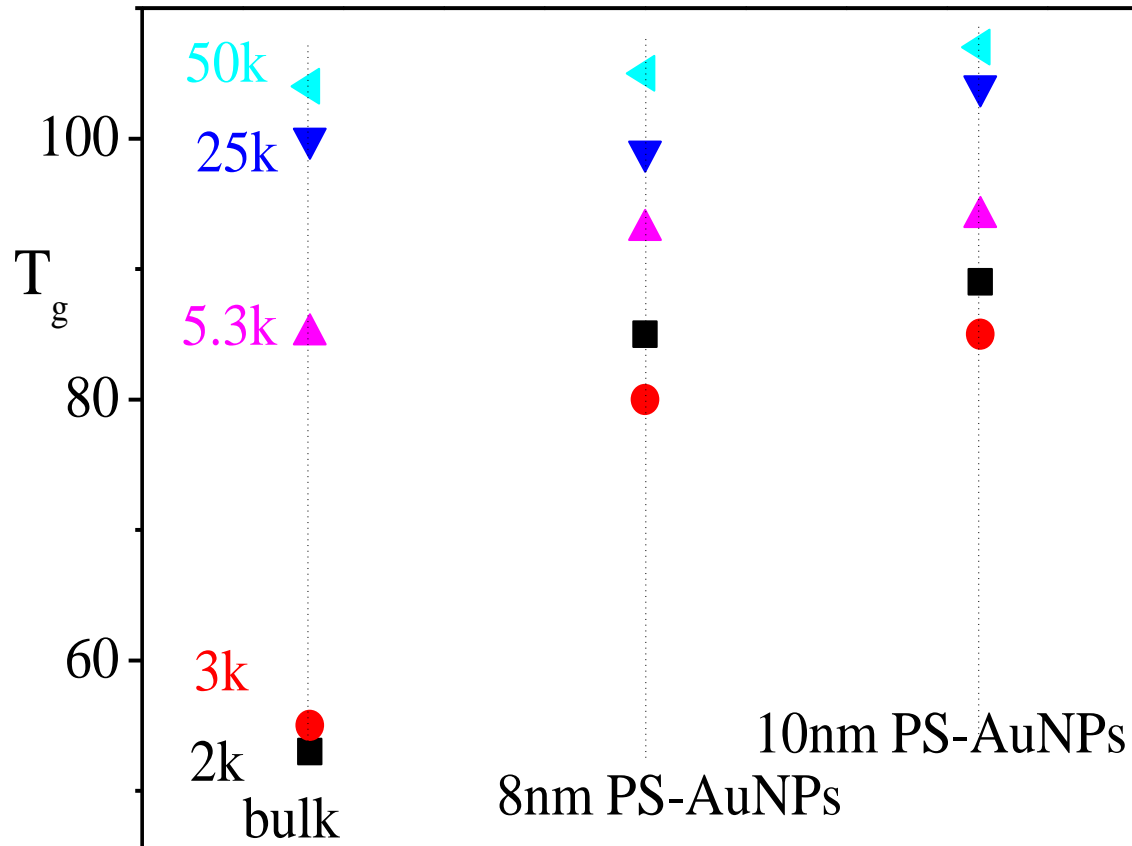
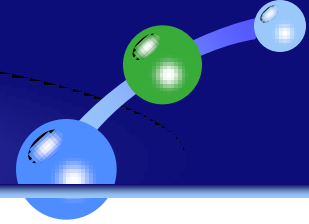
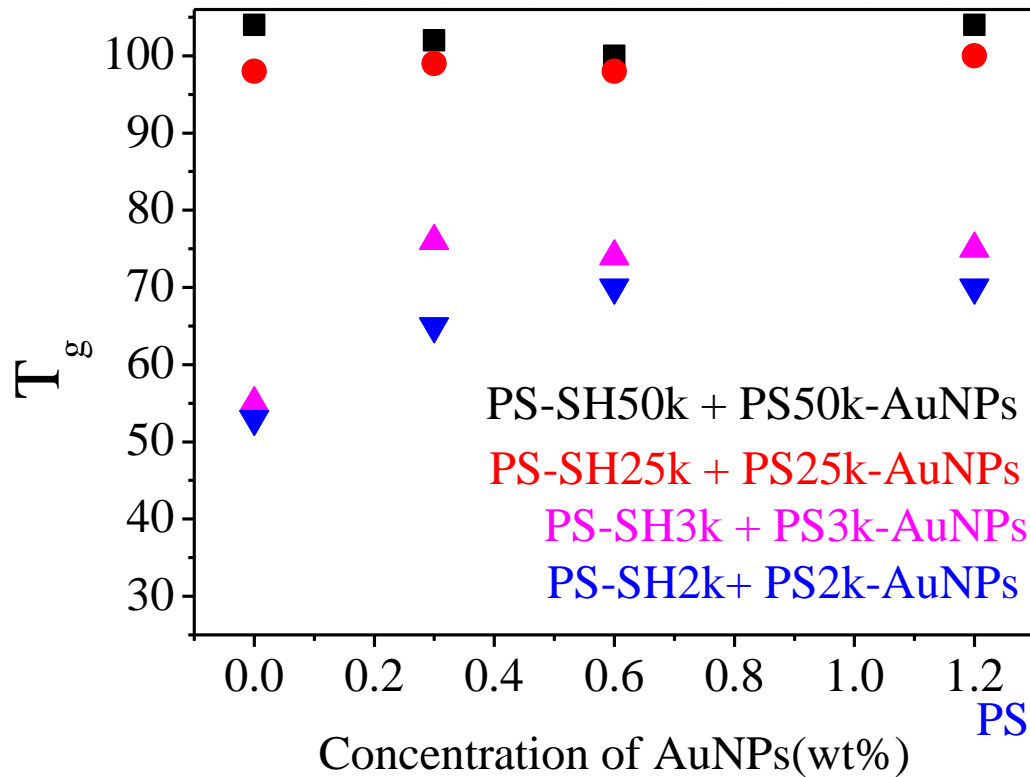
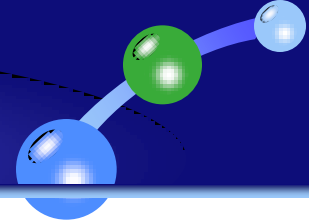


Fig.6 T_g for thiolated PS raw material and PS-AuNPs



PS-SH2k ($T_g=53^\circ\text{C}$)+ PS2k-AuNPs ($T_g=85^\circ\text{C}$)
PS-SH3k ($T_g=55^\circ\text{C}$)+ PS3k-AuNPs($T_g=80^\circ\text{C}$)
PS-SH25k ($T_g=100^\circ\text{C}$)+ PS25k-AuNPs ($T_g=98^\circ\text{C}$)
PS-SH50k ($T_g=104^\circ\text{C}$)+ PS50k-AuNPs ($T_g=105^\circ\text{C}$)

Fig.7 T_g for thiolated PS contain PS-AuNPs (with the same molecular weight) as a function of the concentration of AuNPs

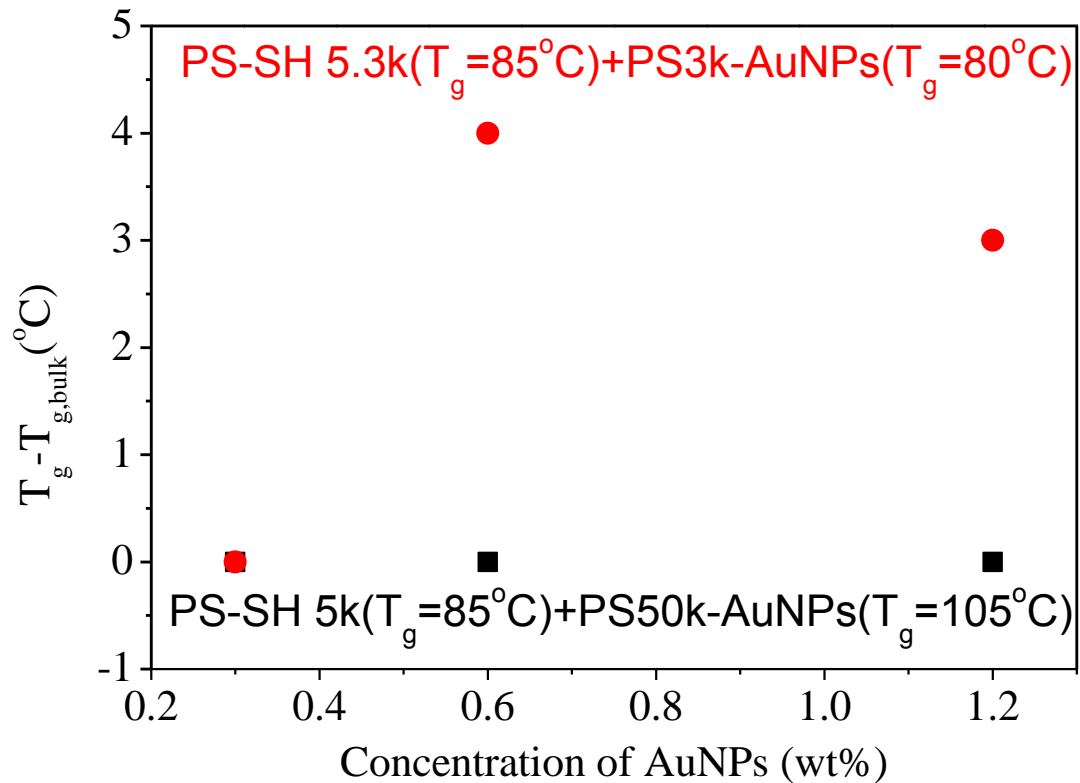


Fig.7 T_g for thiolated PS Mw=5.3k contain PS-AuNPs as a function of the concentration of AuNPs