The non-Innocence of Solvents in Nanocrystal Synthesis

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1-Octadecene (ODE) and tri-n-octylphosphine oxide (TOPO) are two popular, widely used solvents for high temperature nanocrystal synthesis (120 – 320 °C). But they are not innocent.

We show that ODE polymerizes at temperatures relevant for nanocrystal synthesis.[1] Using nuclear magnetic resonance (NMR) spectroscopy, we detect its presence in five different nanocrystal syntheses: ZnS:Mn, $CuInS_2$, CdS, TiO_2, and Fe_3O_4 (see Figure 1). The resulting poly(ODE) has a comparable solubility and size to nanocrystals stabilized by hydrophobic ligands, thus hampering typical purification procedures. To avoid formation of poly(ODE), we replaced 1-octadecene with saturated, aliphatic solvents. Alternatively, the native ligands are exchanged for polar ligands, leading to significant solubility differences between nanocrystals and poly(ODE), therefore allowing isolation of pure nanocrystals, free from polymer impurities.

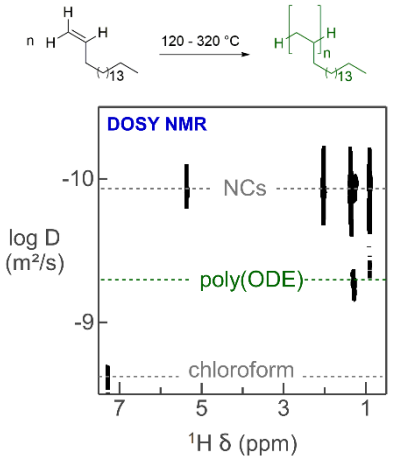

Figure 1 – Contamination of nanocrystals by poly(ODE).

On the other hand, TOPO was shown to decompose into di-n-octylphosphinate and P,P′-(di-n-octyl) pyrophosphonate, during the synthesis of ZrO_2 nanocrystals.[2] These decomposition products have a high binding affinity for the nanocrystal surface and thus contaminate the nanocrystals. Finally, we provided ligand exchange strategies to remove these impurities.

In conclusion, the inertia of solvents should not be taken for granted. Side reactions can seriously compromise the purity of the nanocrystal product, with consequences for ensuing applications.

References

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[2] K. De Keukeleere, S. Coucke, E. De Canck, P. Van Der Voort, F. Delpech, Y. Coppel, Z. Hens, I. Van Driessche, J. Owen, J. De Roo, *Stabilization of Colloidal Ti, Zr, and Hf Oxide Nanocrystals by Protonated Tri-n-octylphosphine Oxide (TOPO) and Its Decomposition Products*. *Chem Mater* **29**, 10233-10242 (2017).