

Rotaxane Metal Organic Nanocomposites

There are limitless applications for metal organic catenanes and rotaxanes in drug delivery, bactericide containing biomedical devices, electronic assemblies and molecular machines (23-26). Dr. Zaworotko's group (USF Chemistry Department) has been working with us on rotaxane-like polymer assemblies with persistent interactions between the matrix and metal organic moieties. For initial studies (27, 28) we chose the following metal organic, self assembled nanoball with hydroxyl functionality : $[(\text{DMSO})(\text{MeOH})\text{Cu}_2(\text{benzene-1,3-dicarboxylate-5-OH})_2]_{12}$ synthesized earlier by Zaworotko's group (fig. 5) (29).

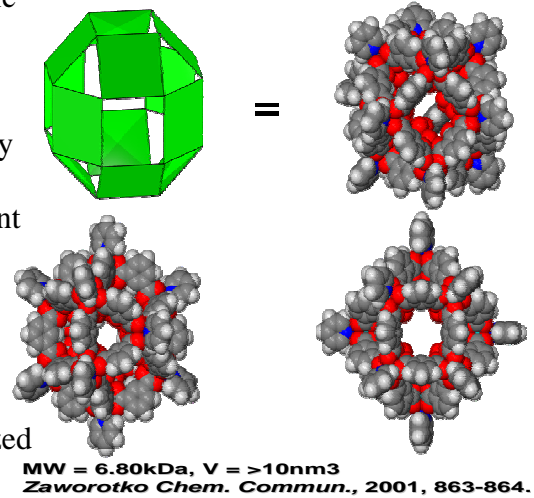


Figure 5

This nanoball is rhombihexahedral with square and triangular secondary building units (SNU). There are 24 -OH groups on the surface and the internal volume is 1nm³. The square SBU window has sides 12.749 Å long and the triangular sides are 12.716 Å long. MeOH ligands actively bind to the interior surface. Hydroxyethyl methacrylate (HEMA) can likewise act as a ligand. It is evident from the size of the open spaces in the structure that when polymerized *in situ*, the HEMA monomer which is approximately 5 Å wide, can find its way into the interior of the nanoball. In this case, the PHEMA-nanoball structure is a type of rotaxane. The PHEMA chains may intertwine amongst the chains and act as "poly-ligands". Fig. 6 is a schematic for possible interactions.

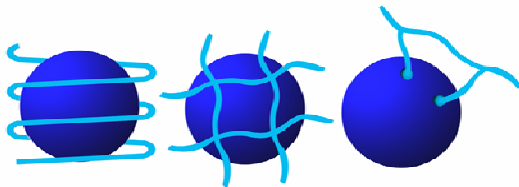


Figure 6

We *in situ* synthesized a series of PHEMA-nanoball, as well as PMMA-nanoball composites for comparison. It was anticipated that the PMMA composites would

have minimal interactions with the nanoballs as compared to PHEMA. Unlike PMMA, both PHEMA and the nanoballs are soluble in methanol. Polyrotaxane synthesis involving hydrogen bonding is thought to enhance self threading yielding branched or cross-linked rotaxanes (23). With this in mind, we probed the effect of nanoballs on the relaxation dynamics. Interestingly, dielectric measurements revealed that the γ transition in PHEMA, assigned to the rotation of the pendant hydroxyl group, broadened and moved to lower temperatures. At 10 Hz, the temperature shifted from -120 °C to -130 °C in neat polymer versus the 1.5 wt % composite. Similarly, the activation energy for the relaxation decreased from 7.8 to 6.6 kcal/mol. This plasticizing effect is in sharp contrast to effects noted on the β relaxation, associated with the motion of the -COOCH₃ side group, and on the glass transition, denoted by α . The activation energy for the beta transition increased from 20.6 to 26.1 kcal/mol upon addition of 1.5 wt % nanoballs. The glass transition temperature, determined via DSC, increased from 99 to 105 °C. We

believe that the restriction of motion induced by cross-linking around and through the nanoballs hindered the cooperative motion associated with the α and β transitions. This indicates the dramatic effect that the nanoball environment has on relaxation dynamics. That is, on the larger segmental- β relaxation scale, the nanoball restricts motion, using its windows to form knots. On a smaller scale, the rotation of the methyl group is facilitated, perhaps by “free volume” inside the nanoball.

Ethylene glycol cross-linker was present in trace amounts in the HEMA monomer. Swelling in methanol followed by Soxhlet extraction for one week in methanol did not remove any nanoballs. Furthermore, the gel fraction increased at the nanoball concentration increased for a series of concentration between 0 and 1.5%. We then further probed the theory that “winding yarn” structures formed via secondary interactions would persist upon swelling. We swelled neat PHEMA in nanoballs dissolved in methanol. The blue nanoballs diffused into the sample. When the sample was placed in pure methanol, the nanoballs diffused out. Thus, we believe that we have produced rotaxane nanocomposites.

The self-threading induced by hydrogen bonding was not noted in linear PMMA. The nanoballs did not dissolve in the monomer and were sonicated to induce dispersion during polymerization. The γ transition is not dielectrically active in PMMA. However, both activation energy for the β transition and the temperature of the α transition decreased; the nanoballs plasticized the matrix. In addition, Soxhlet extraction removed the nanoballs from the matrix. We are currently producing a series of cross-linked PMMA nanocomposites to determine if any nanoballs actually do string on the PMMA.

These exciting results encouraged us to launch a new research effort on metal organic nanoball rotaxanes. We have begun studying model polyurethane systems, where we can control the phase that accommodates the rotaxane. We are also examining nanoballs with controlled solubility for more hydrophobic polymer matrices.

References

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