

**Chain arrangement and glass transition temperature variations in polymer nanoparticles under 3D-confinement**

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Polymer nanospheres with different size distributions are prepared by two different methods: with and without the aid of an anionic surfactant. Calorimetric traces of these nanospheres show a different glass transition temperature, with respect to that of the bulk, which has been discussed in terms of an entropy model. The total confinement, imposed by the spherical geometry, leads to a limiting number of repeating polymer units in the sphere and thus to a reduction of the possible configuration states of the polymer chains. This is ultimately related to variations in the bulk value of the glass transition temperature. The model is evaluated against our calorimetric measurements as well as with the data available in the literature. Good agreement between data and model is found for many cases, proving that confinement can be related to reductions in the entropy of these nanosystems.