Towards architecturally designed all-polymer based nanocomposites

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Over the last few decades, advances in nanoparticle synthesis with precisely controlled size and shape have transformed the way we use polymers today. Dispersing these inorganic rigid nanoparticles in soft polymeric matrices resulted in new hybrid materials- *polymer nanocomposites*- with superior properties compared to those of the neat polymers [1]. Likewise, polymer chemists can now synthesize macromolecules with precise length and shape; stars, combs, bottlebrushes, rings, hyper-branched polymers have emerged with exciting new properties that cannot be provided by their linear chain analogs. In particular, the star-shaped polymers in which many linear chains share a common center are interesting as the monomer density changes along the radial direction. Therefore, these polymers can exhibit both soft/penetrable and hard/impenetrable sphere character depending on the length and number of the star arms (see schematic in Figure 1a).

In our work [2], we dispersed high-T_g (≈ 373 K) star-shaped polystyrene (PS) at 20 % by mass in low-T_g (≈ 250 K) linear long poly (vinyl methyl ether) (PVME) matrices to obtain a new kind of nanocomposite in which the interpenetration between the nanofillers and the matrix, and therefore, the bulk rheological properties, can be systematically varied via filler architecture. As the filler structure transitions from flexible linear chains to hard spheres, the resulting nanocomposites reside between the traditional linear polymer blends and conventional polymer nanocomposites- a region that has not been explored before. Our aim was to investigate these nanocomposites using static (SANS) and quasielastic neutron scattering (backscattering and spin-echo) measurements over a wide range of time and length scales in the glassy and melt states of the composites, and relate their bulk flow behavior to the microscopic relaxation mechanisms.

We used deuterated PS (*d*-PS) of various arm number and molecular weights to determine their conformation and dispersion in hydrogenated 20 kg/mol PVME (*h*-PVME) matrix by using small-angle neutron scattering (SANS). The coherent intensity results from the contrast between *d*- and *h*-chains, therefore, the stars are visible to neutrons. Figure 1b shows a peak appearing at intermediate wave-vectors, Q, in the SANS pattern of the 18-arms star shaped *d*-PS filler in *h*-PVME due to intra-chain correlation, confirming their compact particle-like nature. A linear *d*-PS chains of the same total molar mass retains its flexible Gaussian coil structure in the miscible *h*-PVME matrix.

Particularly important for polymers are the localized fast dynamics on sub-monomer level, the segmental dynamics at the monomer level and the entangled/collective dynamics at larger scales. To obtain an overview on the chain motions over a time scale of ≈ 1 ns using the High-Flux Backscattering Spectrometer (HFBS), we first measured the temperature dependence of the elastic scattering intensity (within the 0.8 μeV resolution of the instrument). The incoherent intensity is dominated by the *h*-PVME matrix. The PS fillers are essentially frozen in the time-scale of the neutron experiments, the mobile component is the matrix. Figure 2a compares the normalized elastic intensities, $I_{el}(Q,T)/I_{el}(Q,T = 15\ K)$. Adding linear PS has a minority effect on sub-Tg dynamics of PVME, whereas the segmental dynamics is significantly slowed down above T_g due to increased monomeric friction due to the presence of frozen PS segments, as known from previous linear blend studies [3,4]. What we found different and interesting is that the 18-arms star PS significantly accelerated the localized dynamics of PVME below T_g, possibly due to additional free volume provided to the PVME chains by the free ends of the stars. This brings up exciting new opportunities for tuning glassy dynamics, which is important for high-strength applications.

The segmental dynamics of PVME in presence of PS fillers with different architectures were measured by quasi-elastic neutron scattering (QENS) measurements on HFBS. The quasi-elastic broadening at low-Q is related to thermally driven Rouse motion of the chain segments, which is determined by the local monomeric friction. We found that PS chains slow down the Rouse relaxation of PVME; however, unlike the localized sub-T_g dynamics, the monomeric friction imposed by star-PS chains is the same as their linear counterparts, suggesting that the monomeric friction coefficient is mainly determined by chemistry rather than the shape of the macromolecules.

At larger scales and longer times, the chains feel the presence of other chains in the melt, and their motion is constrained by

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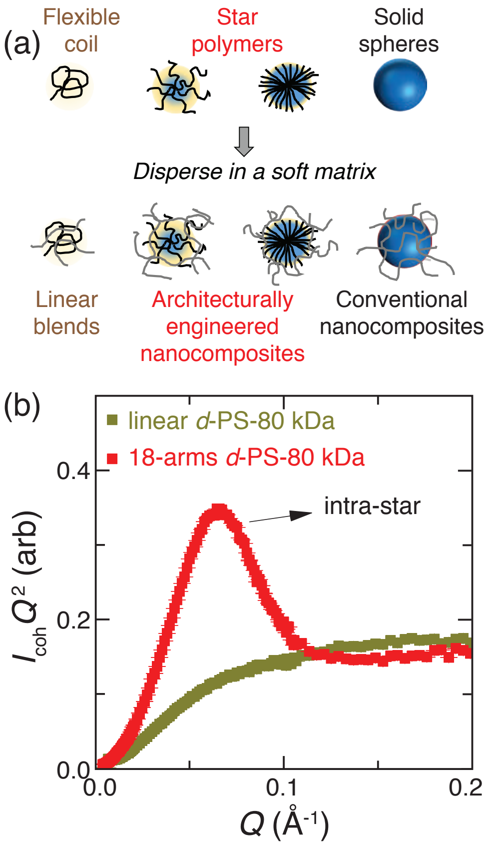

FIGURE 1: (a) Schematic representation of different type of fillers. The glassy star polymers structurally reside in between two hard sphere and flexible coils; dispersing them in soft matrices results in new hybrids between conventional linear blends and nanocomposites. (b) Kratky plot for 80 kDa linear and 18-arms *d*-PS fillers dispersed in *h*-PVME matrix, showing the compact nanoparticle like structure of the high-functionality stars.

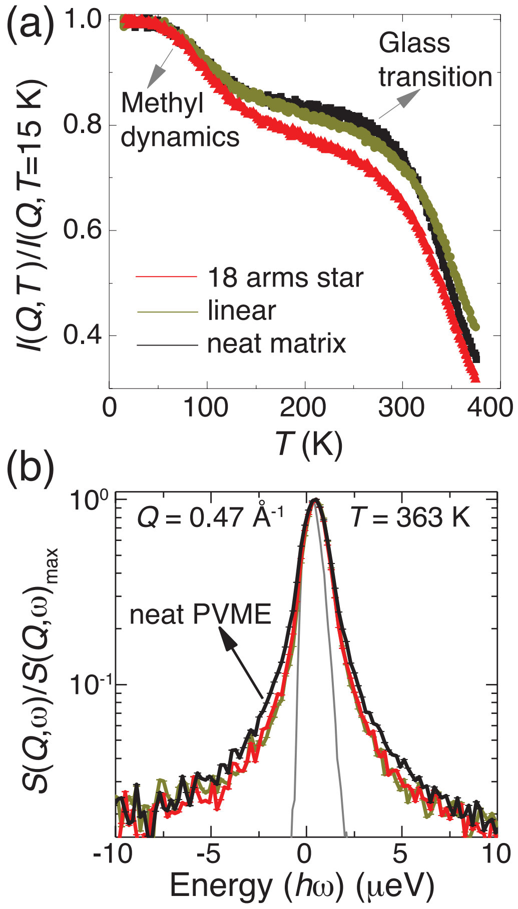

FIGURE 2: (a) Normalized scattered elastic intensities of PVME in neat forms and in composites with 20 % linear (80 kg/mol) and 18-arms (88 kg/mol) deuterated PS. (b) Normalized dynamic structure factors of the same samples at 363 K and at $Q = 4.7\ \mathrm{nm}^{-1}$. The gray line is the resolution.

entanglements (reptation motion). Such confined dynamics of chains is important for bulk rheological behavior of polymers as the rubbery plateau modulus is inversely proportional to the square of the distance between the entanglements, *i.e.* the reptation tube diameter. Using a mixture of *d* and *h* PVME chains, we highlighted the single *h*-PVME chains in the sea of deuterated background. NSE results suggest that star shaped particles do not much alter the apparent tube size of PVME whereas blending with linear chains reduces the tube diameter by ≈ 40 %. This reflects directly on the rheological behavior of the samples. Linear PS chains results in a monotonic and moderate increase of viscosity relative to the neat PVME, as expected from conventional polymer blends. The 13-nm diameter silica nanoparticles, representing the conventional nanocomposites, monotonically reinforce the system orders of magnitude compared to the neat matrix, again as expected. The compact star PS remarkably decreased viscosity at moderate concentrations as they are impenetrable and small, while at higher concentrations percolation of the glassy PS stars causes reinforcement as high as the level that silica can achieve. This dual effect, softening and stiffening, of star macromolecules is novel and brings along a new design parameter- the filler architecture- for all-polymer based nanocomposites.

In conclusion, high-resolution neutron spectroscopy on isotopically labeled components in the resulting '*architecturally engineered*' all-polymer nanocomposites allowed us to directly observe the chain conformation and motions at the nanoscale. The unprecedented bulk rheological behavior was therefore related to very complex microscopic mechanisms at a broad range of time-scale (from sub-nanoseconds to hundred nanoseconds), and length-scales (from monomer size to entanglement mesh sizes).

References

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