

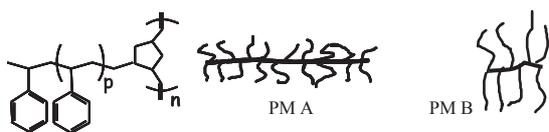
BOTTLE-BRUSH SHAPE POLYMACROMONOMERS: CONFORMATION AND DYNAMICS IN SOLUTIONS AND MELTS

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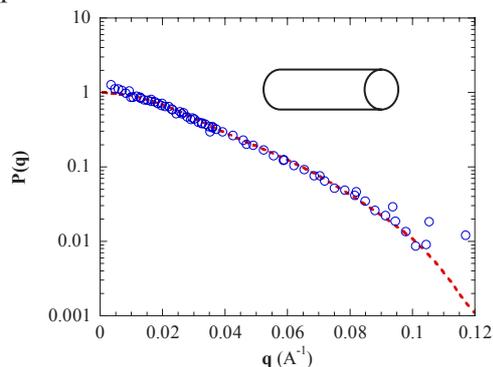
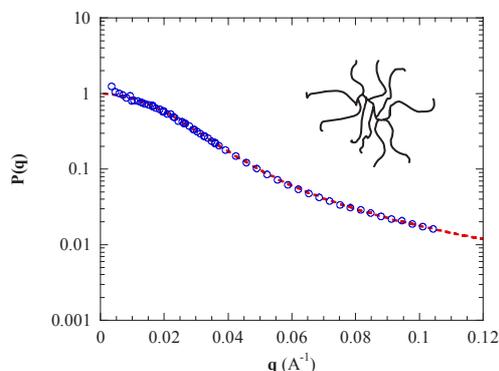
Branched macromolecules exhibit specific solution and melt properties due to a higher segment density compared to linear chains of equivalent molar mass and same chemical composition. Polymacromonomers (PM) are characterized by a regular branching interval and exhibit narrowly distributed molar masses when polymerized under “living” conditions. They can thus be considered as model compounds. Our aim is to describe in a quantitative way the PM conformation using Small Angle Neutron Scattering (SANS) and deuteration, a technique that has been already used to measure the extension of the backbone due to side chains [1].

In order to control the final PM (Fig.1) and allow precise SANS experiments, ring-opening metathesis polymerization has been successfully performed on both labeled and unlabeled PS macromonomers fitted with norbornenyl unsaturation [2]. In order to investigate the influence of the side chain length on the PM conformation as well as on its dynamic behavior. PM with different branch lengths have been prepared, such as PM A or PM B (-H or -D) (Fig.1).


 Figure 1. Poly(ω -norbornenyl polystyrene) PM

The structure of labeled PM has been investigated as a function of its environment: good or Θ solvent of polystyrene PS branches (98 % PM weight) and melts of PM in PM or in linear PS. The SANS measurements evidence that our PM adopt different conformations. The latter roughly varies from a spherical distribution to a tubular symmetry, depending upon the lengths of the side chain and of the backbone, as well as upon the solvent or the matrix used. Different geometric models have been applied to fit experimental form factors $P(q)$, measured by SANS, such as cylinder or star models [3, 4]. At small scale (large q), experimental curves are well fitted, for Θ solvent

(Fig. 2) as well as for molten state (Fig. 3). However, in both cases, the model does not provide the exact description of the conformation. Suitable models should be more complex than a tube or a sphere and should involve the degree of interpenetration of branches.


 Figure 2. $P(q)$ as a function of q for solution 1% PM A-D / cyclohexane \circ , non-oriented cylinder model with $R = 3.1$ nm and $L = 17.3$ nm ---

 Figure 3. $P(q)$ as a function of q for blend 2% PM A-D / linear PS 700k : extrapolation to 0% \square , non-oriented cylinder model with $R = 3.1$ nm and $L = 19.2$ nm ---

Comparison between different blends (PM in linear PS) demonstrates that the matrix affects the conformation. Blends of a labeled PM (A-D or B-D) with unlabeled linear PS ($M_w = 700000$ g.mol⁻¹) have been investigated for different volume fractions. For blends with short branches PM A-D, a clear increase in intensity at low q values is visible in the $q^2I=f(q)$ plot (Fig.3). Note that in such plot, the presence of a peak that is indicative of a high internal density of branched polymers

unlike the case of linear polymers. The low q intensity increase may result from partial immiscibility between labeled and unlabeled macromolecules. However, blends of the same linear PS with long branches B-D show no increase in their low q intensity. This suggests that the specific architecture of short branches PM affects the free energy of mixing. Further experiments have been performed to demonstrate the temperature parameter does not affect the phase separation.

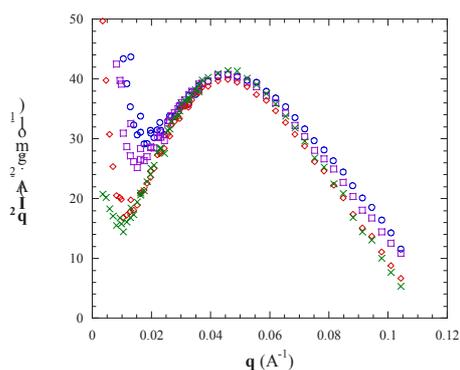


Figure 4. $q^2 I$ as a function of the scattering vector q for blends PM A-D / linear PS 700k: $\phi = 10\%$ \circ , 7% \square , 5% \diamond , 2% \times

Besides, rheological investigation has been performed to define dynamics of the PM relaxation, which strongly differs from that of linear polymers. The latter exhibit for large chain (more than 180 units in PS, i.e. a mass $>M_e = 18000 \text{ g}\cdot\text{mol}^{-1}$) a characteristic time much longer than the maximum time of the free chain. In oscillatory mechanical measurements, the decrease of the storage modulus to zero at low frequencies is shifted to lower frequencies, and a flat region called entanglement plateau appears. This plateau is visible on the curves of storage modulus versus the frequency ($G'(\omega)$) for the *linear* PS of large mass. For PMs, since all PS branches have molar masses below or equal to the entanglement molar mass M_e , no plateau region was really expected. However, a weak shoulder is observed for PM with the longest side chains (namely PM B-H and PM B-D). This indicates some interpenetration between adjacent macromolecules.

References

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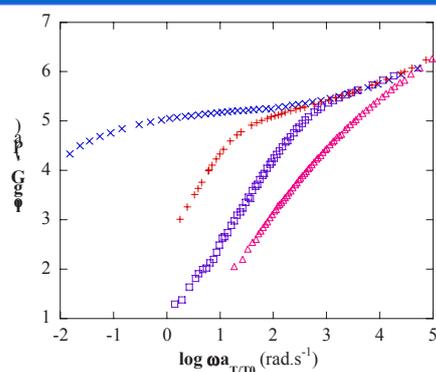


Figure 5. Master curves of G' linear PS 700k \times , PS 70k $+$, PM B-H \square and PM A-H \triangle

This is confirmed by the fact that, the shorter the side chains, the smaller the rubbery plateau. Thus branches seem responsible for the specific response of our PM. These findings are in good agreement with previous studies in literature. They are also consistent with the film-forming property: films of PM with short branches are too brittle to handle, whereas those with long branches enabled to obtain films of thickness around 0.5 mm. Furthermore, blends of 50% PM / 50% linear PS 70k exhibited an intermediate viscoelastic behavior between those of linear polymers and PM. To understand better these rheological behaviors, we are currently investigating the relaxation of the chain conformation after a quick elongation step of PM/linear blends films (Fig. 5).

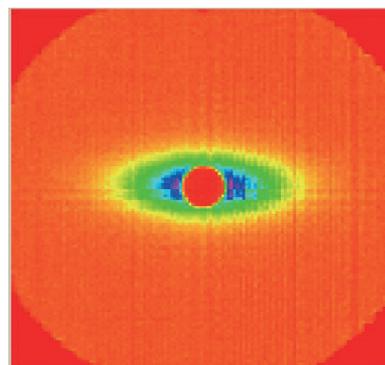


Figure 5. Intensity map of scattering of a sample (Blend 2% PM B-D / linear PS 700k elongated by a facteur 2.5, after a relaxation time = 0s)