

Supramolecular association in transiently branched polymer systems

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Abstract In this contribution, an investigation of the hydrogen bonding mechanism in a transiently branched comb – like polymer system is presented. The system under investigation consists of a polybutylene oxide (PBO)- based backbone, randomly functionalized with thymine (Thy) groups, in combination with shorter PBO graft chains, end-functionalized with Diaminotriazine (DAT) groups. The functional groups are able to associate through hydrogen bonds. The hetero-complementary association of these groups leads to the formation of a transiently branched comb-like polymer system and it is known to be dominant in solution, when compared to the weaker self – association (Thy-Thy; DAT-DAT). In the melt state, often polymer systems based on Thy and Dat, can combine the ability to form supramolecular interaction with a tendency for unspecific aggregation and microphase segregation [1,2]. Only recently, virtually exclusive hetero-complementary association could be observed in the supramolecular association of telechelically-modified oligomeric PEG chains [3]. Here, we aim to extend the linear supramolecular assembly mechanism towards branched structures. The interaction of hydrogen bonding groups in the melt state has been studied on the microscopic level by the Small Angle Neutron Scattering technique (SANS), by means of a selective labeling scheme. A peak observed in the scattering function reveals the formation of a block copolymer, due to the complementary association of the hydrogen bonding groups. The scattering profile of a block copolymer is described by means of the Random Phase Approximation (RPA) formalism through which it is possible to obtain the average aggregation number i.e. comb arm functionality and thus, to evaluate very sensitively the association constant directly in the melt state as a function of temperature. On the other hand, rheological measurements in the melt have been performed in order to study the influence of the reversible bonds on the macroscopic dynamics of the polymer system. The rheology data, in good agreement with the SANS results, confirmed the formation of a responsive material of which the structure and dynamics is affected by the rate of the mechanical activation.

References

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