

SOLID STATE NMR STUDY OF SEGMENTED POLYMER NETWORKS: FINE-TUNING OF PHASE MORPHOLOGY VIA THEIR MOLECULAR DESIGN

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Abstract

Segmented polymer networks (SPNs) based on thermo-sensitive poly(N-isopropyl acryl amide) (PNIPAA) and poly(tetrahydrofuran) (PTHF) have been synthesized by free radical copolymerization of PTHF bis-macromonomers with N-isopropyl acryl amide. The nature of the polymerizable end group on the bis-macromonomer has been varied, respectively from acrylate to acryl amide end groups. The multiphase behaviour of the corresponding SPNs has been examined as a function of the nature of the end group by making use of solid-state ^{13}C CP/MAS NMR relaxometry, ^1H wideline NMR relaxometry and dynamic mechanical analysis (DMA). When PTHF with acrylate end groups was used during the SPN formation, analysis of proton spin-lattice relaxation times ($T_{1\text{H}}$) and proton spin-lattice relaxation times in the rotating frame ($T_{1\rho\text{H}}$) revealed phase separation with domain sizes larger than 5 nm when the PTHF fraction exceeds 10 wt%. Only for lower PTHF-amounts, the SPNs were homogeneous on the nanometer scale. On the other hand, when PTHF with acryl amide end groups was used as macromolecular cross-linker, the NMR results showed the absence of any domain formation for SPNs with PTHF fractions up to 50 wt%. The major impact of the molecular design on the ultimate phase morphology of bicomponent polymer networks has been confirmed in all cases by DMA-analysis.