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Towards quantification of butadiene content in styrene–butadiene block copolymers and their blends with general purpose polystyrene (GPPS) and the relation between mechanical properties and NMR relaxation times

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ABSTRACT

The properties of styrene–butadiene–styrene (SBS) block copolymers do not only depend on the butadiene content and the degree of polymerisation but also on their chain architecture. In this contribution we present the results of a low-field time domain (TD) NMR study in which the transverse relaxation behaviour of different SBS block copolymers was analysed and correlated with findings from mechanical testing on pure and blended materials and transmission electron microscopy data which provide information on the microphase separation.

The results indicate that while a straightforward determination of the butadiene content as in blended materials like ABS is not possible for these materials, the TD-NMR results correlate quite well with the mechanical performance of blends from SBS block copolymers with general purpose polystyrene (GPPS), i.e. industrial grade homopolymer polystyrene. Temperature-dependent experiments on pure and blended materials revealed a slight reduction in the softening temperature of the GPPS fraction in the blends.

1. Introduction

Depending on the overall butadiene content, SBS block copolymers can either be used as thermoplastic elastomers [1] or as blend components enhancing the mechanical performance of transparent polystyrene (PS)-based plastics [2,3]. A very similar behaviour is also found for styrene–isoprene (SI) block copolymers. Due to their compatibility with PS and the wide range of possible mechanical properties, these two materials dominate the market for block copolymers in plastics even over 40 years after their discovery [4].

In both cases, the microphase separation due to the miscibility gap of polybutadiene and polystyrene in solid-state is crucial for the properties of the material. Since both the chain architecture of the block copolymer (e.g. the presence of tapered blocks [5,6]) and the microphase separation affect the mobility of the butadiene-rich phase, TD-NMR at low-fields seems to be an appropriate tool for a reasonably fast and low-cost characterization of such polymers. Established methods for the characterization of SBS block copolymers include mechanical testing, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) glass

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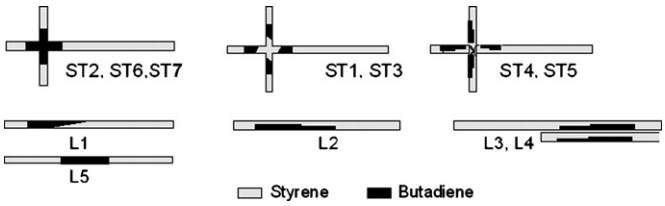

Fig. 1 – (Simplified) chain architectures of the different block copolymers included in the TD-NMR study presented here. The typical length of the long PS blocks is in the range of 80,000 g mol^{-1}. L3 and L4 consist of mixtures of L2-type polymers with and without a long PS "tail".

transition temperature measurements, Fourier-transform infrared (FT-IR), solution NMR, solid-state NMR, small-angle X-ray scattering and microscopy techniques such as transmission electron microscopy (TEM) and scanning force microscopy (SFM) [7–9]. The microscopy investigations of the microphase separation in asymmetric SBS triblock copolymers and star-shaped block copolymers have revealed rich variations of lamellar and bicontinuous phases for the pure block copolymers [8,10] and even further patterns in mixtures with GPPS of different degrees of polymerisation [11]. For thin films of neat SBS cast from solution, the relationship between macroscopic strain response and the geometrical microphase separation patterns was studied by several groups using small-angle scattering, TEM and SFM techniques [12–15].

The data provided by TD-NMR are complementary to the information from other "macroscopic" techniques such as glass temperature measurements and dynamic mechanical analysis (DMA) as they allow the discrimination of components with different dynamic behaviour as a function of temperature. Systematic TD-NMR studies have been reported for high-butadiene SBS block copolymers under tensile stress [16]. Furthermore, transverse relaxation and residual dipolar correlation effects were studied in a sample of a similar material [17].

We have investigated a range of different SBS materials with a butadiene content of 26 and 17 wt.% in the case of ST5, respectively, by means of TD-NMR. Both linear and star-shaped polymers were studied. Fig. 1 provides an overview over the different chain architectures. The molecular weights of the linear block copolymers ranged around M_n values of 130,000 g mol^{-1} and M_w of 160,000 g mol^{-1}. For the star-shaped materials, M_w was around 190,000 g mol^{-1} and M_n 90,000 g mol^{-1}. The large differences between M_w and M_n in the star-shaped materials are due to incomplete coupling (typically 30% of uncoupled molecules). In addition to the neat block copolymers, for some materials blends with GPPS were studied, too. For all materials, the mechanical properties of the neat SB copolymer and its 1:1 blend with GPPS (M_n = 103,000 g mol^{-1}, M_w = 270,000 g mol^{-1}) were investigated, and for some materials also TEM studies of the microphase separation were performed. The examples in Fig. 2 show different topologies and length scales of the microphase separation patterns in the neat materials. The existence of different microphase separation patterns even for materials with the same butadiene content is well known from literature [8,15].

The aim of the experiments was to identify possible correlations between the mechanical behaviour and NMR relaxation parameters. Such correlations can be helpful to support the screening of novel SBS block copolymers with respect to their potential mechanical benefits in blends with GPPS and also in gaining further insights into the relationship between chain topology and molecular dynamics of the "soft" polymer domains.

2. Experimental

The SBS block copolymers were either obtained from commercial sources or produced in house by means of sequential

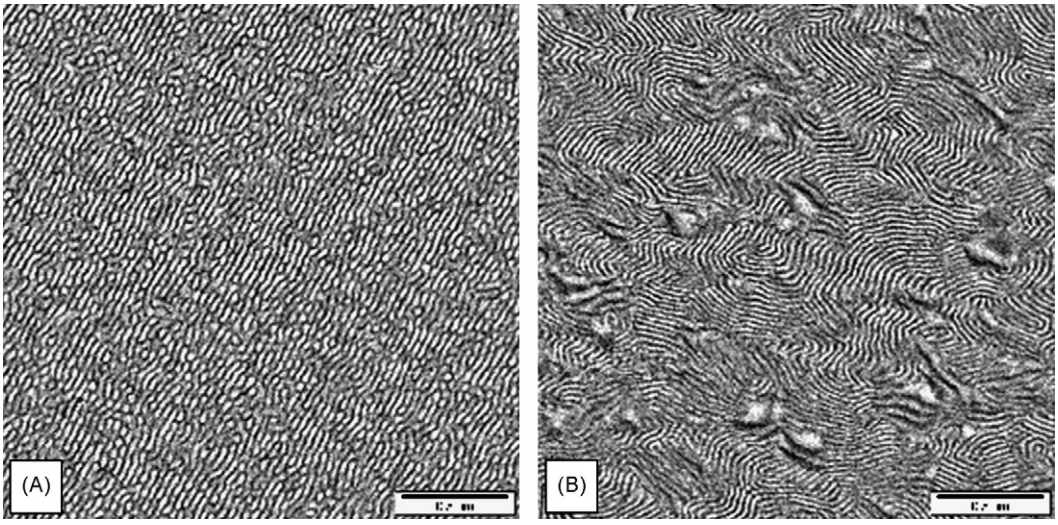

Fig. 2 – TEM micrographs of neat SBS block copolymers ST 4 (A) and L2 (B). Butadiene-rich domains are stained black, polystyrene domains appear bright. The microphase separation pattern in ST4 is bicontinous while the microphase separation of L2 reveals well-ordered crystallites of lammelae with different macroscopic orientation. The apparent variation of the lamellar periods is due to different cutting angles.