Microphase Separation Induced by Hydrogen Bonding in a Poly(1,4-butadiene)-*block*-poly(1,4-isoprene) Diblock Copolymer—An Example of Supramolecular Organization via Tandem Interactions

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Introduction. The design of mesoscopically ordered materials, i.e., materials that self-assemble into mesophase structures on length scales between 10 and 500 nm, has become one of the key issues in polymer material science. Various principles have been used to achieve macromolecular organization on this length scale, like microphase separation in block copolymers or amphiphilic systems, the design of macromolecular objects, layer structures of rodlike polymers, hydrogen bond assemblies, ion cluster formation, etc. As a characteristic feature, the molecular interactions (van der Waals, hydrogen bonding, electrostatic) used in the "construction" of the supramolecular assemblies in most cases are weak compared to covalent bonds. One single building principle has been used in most systems studied so far. Only more recently has research focused on systems where several competing building principles are involved in generating complex mesophase structures. Typical examples would be the combination of microphase separation and liquid crystallinity,[1] microphase separation and semicrystallinity,[2,3] liquid crystallinity and ionic interactions, etc. A summary of these research activities has been given in a recent NATO workshop.[4] In this communication we present a system where the self-assembly process is driven by the combination of microphase separation in a block copolymer and hydrogen bonding between few selectively interacting units attached to one of the blocks. We will focus on a system in which the functional groups (stickers) both induce phase separation of an originally miscible block and additionally cause the formation of a thermoreversible network structure. In previous work we have used hydrogen-bonding systems to generate thermoreversible networks and to manipulate the flow behavior and dynamics of polymer melts. Depending on the structure of the stickers, either binary hydrogen bond complexes or highly ordered aggregates may be formed.[5]

The present work is based on symmetric miscible polyisoprene-*block*-polybutadiene diblock copolymers with predominant 1,4-microstructure in both blocks. While high molecular weight blends of 1,4-PB and 1,4-PI are immiscible, the block copolymer is miscible (i.e. ($\chi N < 10.5$). To introduce the polar stickers, we use the fast ene reaction of 4-phenyl-3,5-dioxo-1,2,4-triazoline (PTD) with allylic systems[6] (Scheme 1). This reaction proceeds quantitatively at room temperature and allows the controlled incorporation of phenylurazole stickers (1-polydienyl-4-phenyl-3,5-dioxo-1,2,4-triazolidine) (PU). The rate of the reaction strongly depends on the nature of the allylic system. For low degrees of substitution the reaction follows pseudo-first-order kinetics. It has been shown that the reaction with 1,4-polyisoprene occurs much faster than with 1,4-polybutadiene (1,2-vinyl units react much slower).[7] The ratio of the rate constants at room temperature is

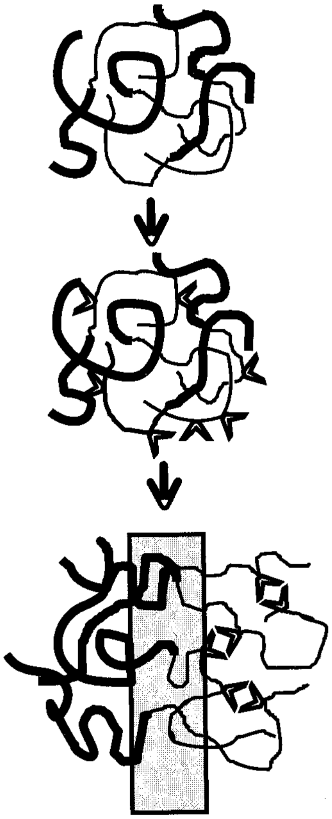

Figure 1. Schematic representation of the regioselective polymer analogous reaction to the originally miscible diblock copolymer and subsequent microphase separation

$$k_{PI}/k_{PB} = 14.6$$

If a compositionally symmetric diblock copolymer is functionalized to a low overall degree of substitution, the functional groups will nearly exclusively add to the 1,4-PI block.[8] It has been shown recently by rheooptical experiments that a nonfunctionalized polybutadiene is not miscible with a polybutadiene containing 1 mol % of PU groups.[9] Thus we expect that selective addition of only small amounts of the polar stickers to the PI block will enhance or induce the thermodynamic contrast. This enhancement will be supplemented by the formation of the binary hydrogen bond complexes: Since the groups are only attached to the PI block, the formation of hydrogen bonds will increase the local segment concentration of PI segments and thus contribute to the microphase separation (Figure 1). This contribution of hydrogen bonding may alter the dynam-

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Scheme 1

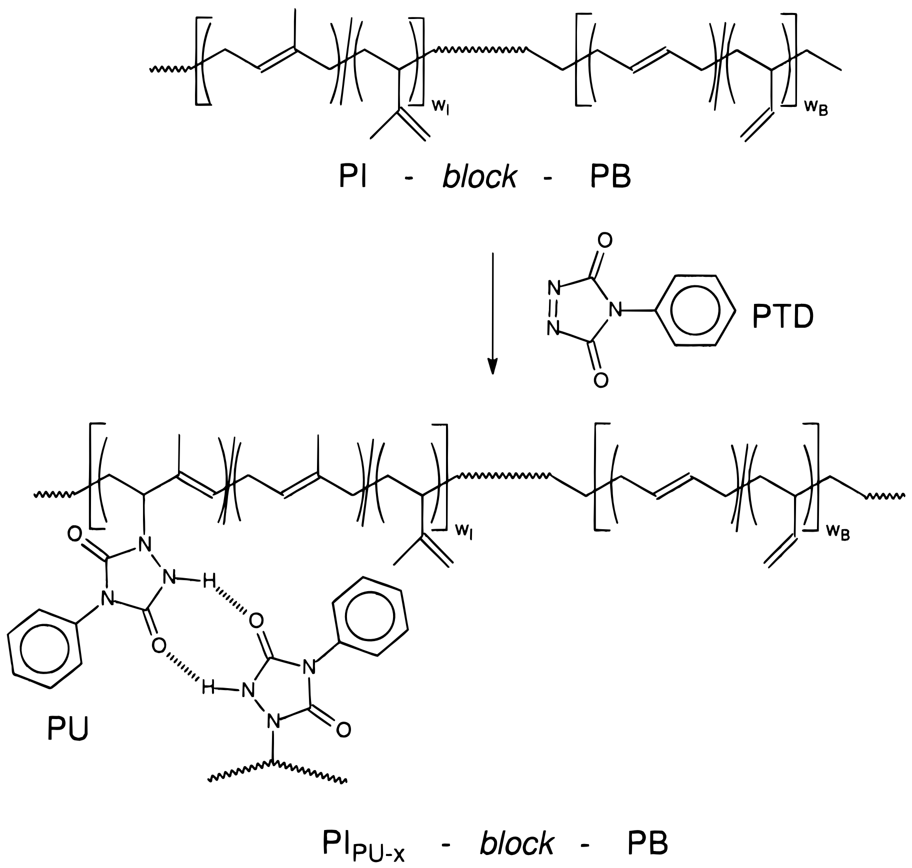

Table 1

sample code	degree of substitution (mol %) total	PI	PB	tan δ^{max}, °C	T_g = E''^{max}, °C	$T_{g(calc)}$,[a] °C	w_{B1}	w_{B2}[b]
IB100-PU-0	0.0	0.0	0.0	−65	−72	−73.5		
IB100-PU-0.5	0.5	1.07	0.074	−60	−70	−71.4		
IB100-PU-1.0	1.0	2.10	0.145	−72, −51	−76, −60	−69.3	0.72	0.14
IB100-PU-2.0	2.0	4.15	0.289	−76, −45	−78, −54	−65.1	0.84	0.14

[a] Calculated on the basis of eqs 1 and 2 assuming no microphase separation. [b] Polybutadiene fractions of the two phases in the microphase-separated regime.

ics and mechanism of microphase separation. However, this problem is beyond the scope of the present work.

Experimental Part. The block copolymer has been prepared by sequential anionic polymerization of isoprene and butadiene using cyclohexane as the solvent and *n*-butyllithium as the initiator, using standard procedures for monomer and solvent purification. The molecular weight of the polymer as determined from GPC using universal calibration is M_n = 98 000, M_w = 118 000; M_w/M_n = 1.20. The composition of the block copolymer, which will be designated as IB100-PU-0, and the polymer microstructure has been determined by ^{1}H NMR spectroscopy ($CDCl_3$, Varian 200 MHz): polyisoprene block, 45 mol % = 51 wt %; PI microstructure, 91% 1,4-units, 9% 3,4 units; polybutadiene block, 55 mol % = 49 wt %; PB microstructure, 81.2% 1,4-units, 18.8% 1,2-units. The polymer analogous introduction of the PU stickers has been performed in THF solution at room temperature according to procedures reported previously:[5] The appropriate amount of freshly prepared PTD was dissolved in THF (10 mL) and added to a THF solution (2 g of the polymer in 20 mL). The addition, which can be monitored by the disappearance of the red color of PTD, was quantitative after about 10 min. After antioxidant (2,6-di-*tert*-butyl-4-methylphenol) was added, the solution was poured into a flat-bottomed Petri dish. Solvent was allowed to evaporate over a period of about 2 days. The films (about 0.5−0.8 mm thick) were subsequently dried in vacuum. Table 1 summarizes the materials used in the present study.

Dynamic mechanical experiments were performed using a Rheometrics dynamic analyzer RDA 2 with parallel plate geometry (8 mm) in the temperature step mode (data points were taken every 1 deg with a waiting time of 1 min upon reaching the desired temperature) at a frequency of 5 rad/s. The glass transition is taken as the maximum G''/T curve.

Results and Discussion. Figure 2 shows the temperature dependence of the storage modulus, G', the loss modulus G'' and the loss tangent (tan δ) of samples IB100-PU-0, IB100-PU-0.5, IB100−PU-1.0, and IB100-PU-2.0. A single quite narrow transition from the glassy to the rubbery region is observed for IB100-PU-0. This indicates a homogeneous mixing of the PI and PB blocks. Already at an overall degree of substitution of 0.5 mol %, a slight broadening of the transition and a shift to higher temperature is observed. At 1 and 2 mol % degrees of substitution, two glass transitions are

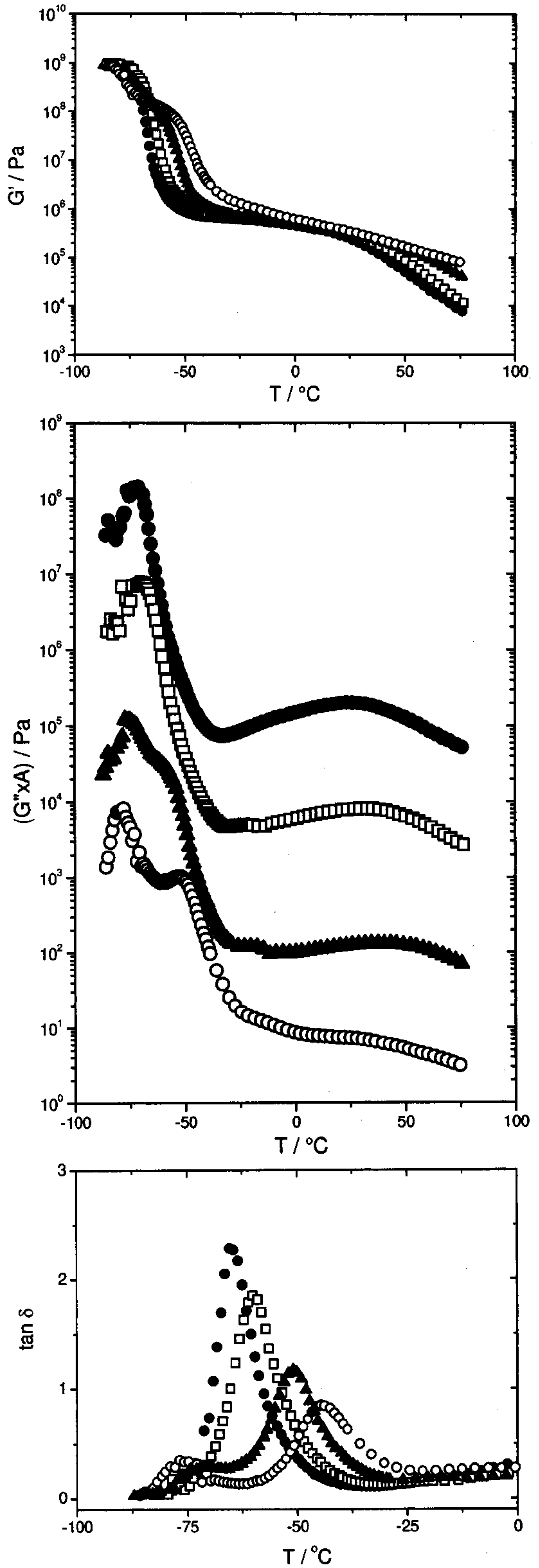

Figure 2. Dynamic mechanical analysis of IB100-PU-0 (●), IB100-PU-0.5 (□), IB100-PU-1.0 (△), and IB100-PU-2.0 (○) obtained at 5 rad/s: (a) *G'/T*; (b) *G"/T*; (c) tan *δ/T*.

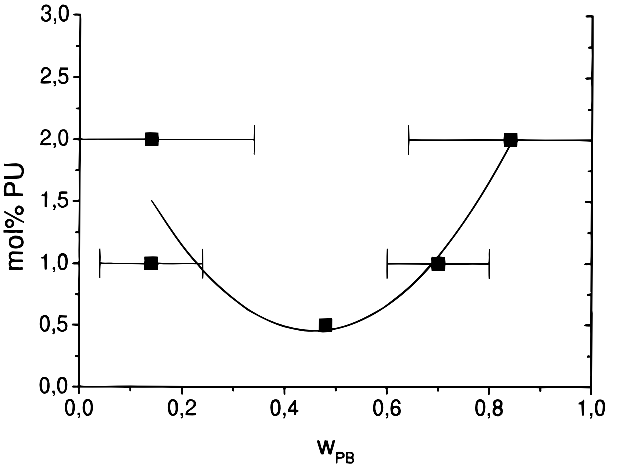

Figure 3. "Phase diagram" describing the microphase separation in IB100-PU-*x*. Microphase compositions are determined by the degree of polar modification (*x*), which corresponds to a variation of χ (Flory–Huggins interaction parameter).

detected (see also Table 1), one shifted to lower and the other to considerably higher temperatures. While the two transition regions still show a considerable overlap in the case of IB100-PU-1, they are well separated in the case of IB100-PU2. The pronounced influence of the polar stickers is also observed at higher temperatures corresponding to the terminal flow region. With increasing degree of substitution, the rubbery plateau is extended to higher temperatures as a result of thermoreversible junctions due to binary hydrogen bond complexes between urazole groups.[5]

The experiments show that the regioselective incorporation of the polar stickers induces microphase separation even at very low degrees of substitution in addition to the formation of the temporary network structure via the hydrogen bond complexes. The analysis of the glass transition temperatures gives a more detailed picture of this chemistry-induced microphase separation. The glass transition in this block copolymer system is influenced by three factors: (i) the microstructure of the polydienes, (ii) the segmental miscibility, and (iii) the presence of the polar stickers. Without the presence of polar stickers, the glass transition of miscible IB diblock copolymers can be described with good accuracy (±1.5 deg) by

$$T_g = T^{o}_{g\,(PB)}w_{PB} + T^{o}_{g\,(PI)}w_{PI} \qquad (1)$$

with $T^{o}_{g\,(PB)}/°C = 5-110\cdot x_{1,4(B)}$ and $T^{o}_{g(PI)}/°C = 35-108\cdot x_{1,4(I)}$, where $x_{1,4(B)}$ and $x_{1,4(I)}$ are the mole fractions of 1,4 units of the PB and PI block respectively and w_{PB} and w_{PI} are the weight fractions of the two components. For low degrees of substitution ([PU] < 10 mol %) the glass transitions of both PB and PI homopolymers increase linearly with the sticker mole fraction according to

$$T_g = T^{o}_g + 3.4\ \text{deg}\ [\text{PU}] \qquad [\text{PU}]\ \text{in mol}\ \% \qquad (2)$$

Substitution of T_g instead of T^{o}_g in eq 1 allows a quite accurate estimate of the glass transition for polar-modified diblocks. For IB100-PU-0.5 the thus calculated T_g is −71.4 °C, which is in quite good agreement with the experimental value (−70 °C). Inversely, we can use eqs 1 and 2 to calculate the compositions of the PB-rich ("PB") and PI-rich ("PI") microphases in the microphase-separated samples, which allows the construction of a crude phase diagram (Figure 3). Despite the relatively large error, we can conclude from these data that phase separation is not complete at a substitution level of 2% and that it is somehow asymmetric. While the "PI" microphase (with stickers) only contains about 14 wt % of PB segments at [PU] = 1%, a considerable fraction of PI segments (28 wt/%) is mixed into the "PB" microphase. The critical concentration of stickers necessary to induce microphase separation seems to be just above 0.5 mol %. This already was indicated by the broadening of the glass transition. We are presently exploring the influence of the block copolymer molecular weight on the critical degree of substitution.[7] This should finally allow us to estimate quantitatively the contribution of a few strongly interacting sites on the microphase separation in a block copolymer. This might be also of theoretical interest because a simple mean field description might be inappropriate for such systems. With respect to mechanical properties, functionalized IBI triblock copolymers offer a unique way to generate thermoplastic elastomers and manipulate the damping properties.[10]

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(8) If a symmetric diblock is considered at an overall degree of substitution of 10 mol % (10 mol % of all double bonds are reacted), the degree of substitution of the PB block will be less than 1 mol % while the degree of substitution of the PI block will be nearly 20 mol %. Only at higher degrees of substitution will the polar groups also become incorporated into the PB block.

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