UNIAXIAL EXTENSIONAL BEHAVIOR OF (SIS)P-TYPE BLOCK COPOLYMER SYSTEM

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A series of symmetric styrene (S) - isoprene (I) - styrene (S) multiblock copolymers of $(SIS)_p$-type (p = 0.5, 1, 2, 3, and 5 corresponds to di-, tri-, penta-, hepta-, and undecablock) was synthesized [1] and their rheological behavior was examined in n-tetradecane (C14), a solvent dissolving the I block and precipitating the S block. The molecular weights of the constituent blocks were almost identical for these copolymers. At 20°C, the $(SIS)_p$/C14 systems with copolymer concentration of 20wt% and 30wt% formed a bcc lattice of glassy, spherical S domains and exhibited the gel-like elasticity. This elasticity was sustained mainly by the bridge-type I blocks connecting the S domains and partly by the loop-type I blocks. In uniaxial extensional test, $(SIS)_p$/C14 systems exhibited *p*-dependent stretch ratio at rupture λ_{max}. The longest $(SIS)_5$ undecablock system was extensible to the upper limit of the apparatus, Hencky strain of $\varepsilon = 4.5$, corresponding stretch ratio of λ (= exp ε) = 90. Reverse flow measurements up to $\varepsilon = 4$ were also conducted on $(SIS)_5$ system. Almost reversible behavior was observed for the case of $\varepsilon < 3$ ($\lambda < 20$), while significant hysteresis loop, similar to that for ordinary physical gel, was observed for the case of $\varepsilon \geq 3$. These nonlinear extensional features of $(SIS)_5$ system can be related to stretch behavior of the constituent I and S blocks; the full stretch ratio $\lambda_{max,I}$ of single I block (M_I = 40000) is 18 ($\varepsilon_{max,I} = 2.9$), and the full stretch ratio $\lambda_{max,(SIS)5}$ of single $(SIS)_5$ undecablock chain is estimated to be 48 ($\varepsilon_{max,I} = 3.9$) under assumpti1n of full stretch of all constituent I and S blocks. Reversible flow behavior observed at lower strain is due to stretch of individual I block, without any change in the microdomain structure. Hysteresis behavior observed at larger strain is attributed to stretch of S block in addition to full stretch of I block, which would be accompanied by partial rupture of S domain. Inter-chain interaction among $(SIS)_5$ chains (connection of more than two $(SIS)_5$ chains through S domains) may play an important role to stretch the $(SIS)_5$ system more than $\lambda_{max,(SIS)5}$ of single $(SIS)_5$ undecablock chain.

Reference

[1] Watanabe et al., *Macromolecules,* **2007,** *40,* 6885-6897.