

Viscoelastic Properties of Symmetric Poly(styrene-*b*-2-vinylpyridine)s in the Disordered and Ordered States

方, 龍

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氏名・(本籍・国籍)	フェン ロン 方 龍 (中 国)
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論 文 調 査 委 員	(主 査) 准教授 高 橋 良 彰 (副 査) 准教授 東 藤 貢 教 授 菊 池 裕 嗣

論 文 内 容 の 要 旨

It is well known that block copolymers possess order-disorder transition (ODT) at a certain condition determined by Flory-Huggins interaction parameter χ , degree of polymerization N , and composition ϕ , which can be basically explained by Leibler's theory. The most simple and well studied block copolymer is symmetric diblock copolymers ($\phi \sim 0.5$), which form lamellar structure. Though the diblock copolymer chains in the ordered state can reach thermodynamic equilibrium, the ordered structure is in frozen states of multi-grain structure containing many defects. Because of these structural characters and viscoelastic heterogeneity of components, viscoelastic properties of block copolymers become very complicated so that the relaxation mechanism is not well elucidated yet.

Polystyrene (PS) and poly(2-vinylpyridine) (P2VP) have the same Kuhn segment length, the same glass transition temperature and almost the same viscoelastic properties so that poly(styrene-*b*-2-vinylpyridine)s (SP) is a suitable model diblock copolymer to overcome the above difficulties and progress the study for viscoelastic properties of diblocks. In this study, viscoelastic properties of SPs having a wide range of molecular weights (M_w) are investigated in comparison with corresponding PS and P2VP homopolymers in the disordered and ordered states. The main results of this study can be summarized as follows.

For SP with low M_w in the disordered state, fluctuation effects are examined by combination of dynamic and steady shear flow measurements based on the temperature dependence of χ . The fluctuation effects start to affect on the viscoelastic properties at around $\chi N < 2 \sim 3$ but can be suppressed by high shear rate, which was more apparent for the viscous property than for the elastic property. At $\chi N < 2 \sim 3$ an averaged relaxation time, $\langle \tau \rangle_w$, defined as product of viscosity and compliance, steeply increased with increase of M_w for SP due to the fluctuation effects. The details are published in Nihon Reoroji Gakkaishi (Journal of the Society of Rheology, Japan), vol.41(2), pp83-91 (2013).

The responses from large scale motions of lamellar grains/defects, $\Delta G^*_{\text{grain}}$, at low frequency ω in dynamic moduli data G^*_{SP} became more apparent after appropriate pre-shear and/or annealing for SP with relatively lower M_w in the ordered state. When asymptotic $\omega^{0.5}$ dependence of $\Delta G^*_{\text{grain}}$ (power law behavior) with appropriately lower magnitude than G^*_{SP} are observed at low ω end, the responses of components $\Delta G^*_{\text{chain}}$ having terminal region behavior can be successfully separated by subtracting $\Delta G^*_{\text{grain}}$ from G^*_{SP} . $\langle \tau \rangle_w$ obtained from chain relaxation data can be smoothly connected with the data in the disordered state, however, the relaxation process changes from relaxation of whole chain in the disordered state to independent relaxation of components for ordered state. The M_w dependence of $\langle \tau \rangle_w$ in non-entangled region was the same as homopolymers but the value was much larger than corresponding ones (about 40 times larger at around ODT), since the junction point of components is confined in the interface of domain and the movement is restricted along the interface. The details are published in Nihon Reoroji Gakkaishi (Journal of the Society of Rheology, Japan), vol.41(2), pp93-99 (2013).

With increase of M_w , entangled plateau is developed. The value of plateau modulus was the same as those of homopolymers, implying that the entanglement density of SP is practically the same as that of PS and P2VP. When the number of entanglements is low, the entanglements between the chains from opposite interface may be rare so that liquid like behaviour is still observed in G^*_{SP} and the chain relaxation can be obtained. With increase of number of entanglements, $\langle \tau \rangle_w$ increased exponentially. With further increase of M_w , power law behavior was approached without showing liquid-like behavior in G^*_{SP} . Thus, it is concluded that chain relaxation mechanism of diblock copolymers in the ordered state change from sliding motions to chain retraction motions, which is qualitatively consistent with the theoretical predictions. The details will be submitted soon and expected to be published at around September, 2013.

論文審査の結果の要旨

本論文は、ジブロック共重合体について、粘弾性の分子量依存性を詳細に検討し、相溶状態における密度揺らぎの効果を定量的に明らかにするとともに、ナノ相分離構造中の高分子鎖の分子運動と絡み合いの関係をはじめて明確にしたものであり、高分子科学の発展に寄与するところが大きい。よって、博士(工学)の学位に値するものと認める。