LINEAR VISCOELASTIC PROPERTIES OF COMB-SHAPED RING POLYSTYRENES

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Ring polymers with no chain ends and their derivatives (having both ring and linear units in their structures) are known to exhibit characteristic viscoelastic properties.[1] Thus, it is important to correctly understand their properties through experiments using model samples with well-defined structures and analyses based on molecular models. This study examined linear viscoelastic properties in melt of a series of comb-shaped ring (RC) polystyrene samples with different branch chain length, i.e., the molecular weight of the ring backbone M_{bb} ($\simeq 4M_e$ where M_e is the entanglement molecular weight) and linear branch chains M_{br} ($\simeq M_e$, $2M_e$ and $4M_e$), with the average number of branch chains $f \simeq 20$.[2,3] Even for the RC sample with the shortest branch chains, a plateau region of the dynamic modulus $G^*(\omega)$ was observed in the middle angular frequency ω regime. The longer the branch chains of the RC samples, the wider plateau region became, suggesting that intermolecular branch chain entanglement occurs. In the ω region between the plateau and terminal region, $G^*(\omega)$ with a weaker ω dependence than the terminal relaxation was observed. This behavior at low ω was more pronounced for the corresponding linear comb (LC) sample than the RC one. Moreover, the obtained $G^*(\omega)$ data were analyzed by two models: the comb-Rouse in which the structure of the RC/LC molecules is considered by graph theory,[4] and the Milner-McLeish model for entangled star-shaped polymers.[5] The former model qualitatively described the terminal relaxation behavior of $G^*(\omega)$ at low ω, but failed to reproduce the plateau in the middle ω range. In contrast, the latter model described the entanglement plateau in the middle ω, but the difference in the terminal relaxation regime between the RC/LC samples, which was seen in the comb-Rouse model as well as in the data, was disappeared.

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