RHEO-OPTICAL STUDIES ON COOPERATIVE MOTIONS OF HIGHLY BRANCHED CHAIN OF BOTTLE-BRUSH LIKE POLYMACROMONOMERS

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Polymacromonomers have long side chains in every repeating units of their main chain and form various types of highly branched structures. Dynamics of polymacromonomers would differ from that of linear polymers or scarcely branched polymers because of the strong repulsive interaction between the densely branched side chains. In this study, we conducted dynamic birefringence and viscoelastic measurements on bottle-brush like polystyrene polymacromonomers to examine the effect of highly branched structure on polymer chain dynamics. Various polymacromonomers having uniform branched chain length were synthesized by the living anionic polymerization. Polymerization index of the branched chains, N_b, was varied from15 to 110.

The sign of birefringence was found to be negative in the transition zone and positive in the flow region, contrasting to that the sign of the ordinary linear polystyrene is negative in these regions. By using the modified stress-optical rule (MSOR), the complex modulus was separated into two components, associating with the main chain and branched chain motions. The result is shown in Fig. 1. The frequency dependence of the separated viscoelastic spectrum corresponding to the branched chain motions was similar to that of the Rouse model for linear polymers. However, the value of the steady state compliance (J_e) of the branched chain was about fifty times larger than that of linear polymers or star polymers having the same arm length of the branched chain. This large J_e value strongly suggests that dozens of branched-chain in the same main chain segment would move cooperatively. On the other hand, the frequency dependence of the modulus for main chain also showed Rouse like behavior, indicating that dynamics of main chain can be treated as linear chain after adequate coarse graining.

With increasing N_b, the stress-optical coefficient for main chain (C_{Tr}) changed from negative to positive, and the stiffness of main chain defined as M_{Tr}/M_{Br} (polymerization index for main chain segments) first increased and then leveled off.(See Fig. 2) This result suggests that the effect of repulsive interaction between branched chains, increasing the main chain stiffness, would saturate at long side chains.
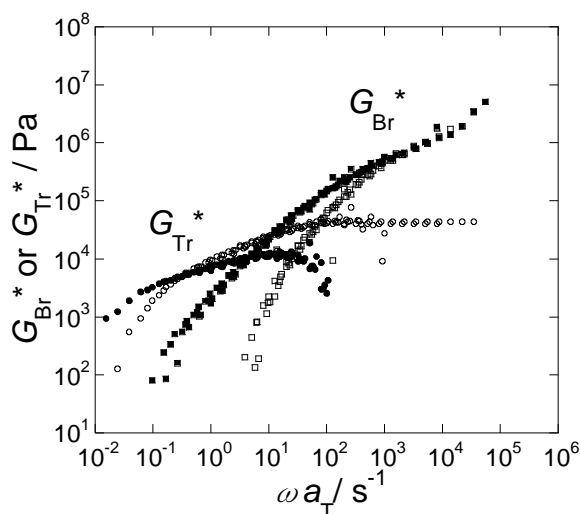

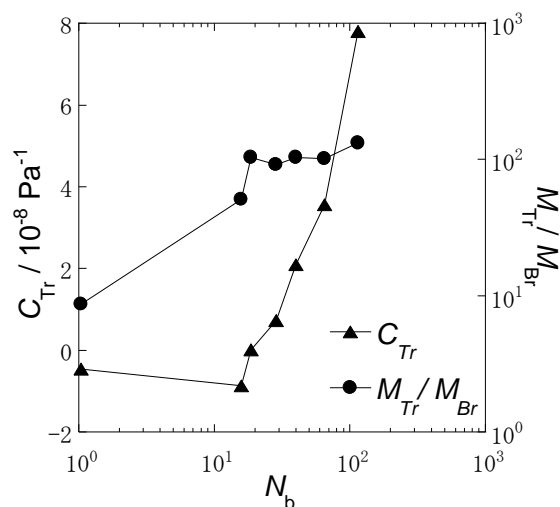Figure. 1. Frequency dependence of G_{Br}^* and G_{Tr}^* for F65 at 420.7K.

Figure. 2. N_b dependence of C_{Tr} and M_{Tr}/M_{Br} for polymacromonomers.