

Relaxation and Motion of Hyperbranched Poly(ether ketone)s in Comparison with Their Linear Analogue

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Three different fluoro-terminated hyperbranched poly(ether ketone)s (HPEKs) with controlled degrees of branching and their linear analogous poly(ether ketone) (LPEK) whose chemical structure and molecular weight were similar to those of the HPEKs were synthesized. Depending on the use of amount of the core molecules, degrees of branching of 0.49 (designated as HPEK49), 0.62 (HPEK(CM)62), and 0.67 (HPEK(CM)67) could be obtained with slight variation in the number-average molecular weights among the three HPEKs. From the measurements of the dynamic mechanical properties, it was investigated that the crossover of the storage shear modulus, $G'(\omega)$ and the loss shear modulus, $G''(\omega)$ started to disappear at a critical value ($> 0.62 \sim 0.67$) of the degree of branching, indicating a nearly Newtonian or little entanglement flow. The viscoelastic relaxation and collective motion of the HPEKs and LPEK above their respective glass transition temperatures (T_g 's) were characterized from the treatment of the $G'(\omega)$ data with the empirical Cole-Davidson fitting functions. Then, the single average relaxation time and hence the correlation time, τ_c , were determined, which provided a unique means to evaluate the melt processability on the basis of the molecular mobility. Highly branched structure of HPEKs predominantly increased the molecular mobility and enhanced the melt processability, realizing the optimum processing temperature lowered by $52 \sim 72^\circ\text{C}$ depending on the degree of branching, compared to the LPEK. Further insights into the correlation times with the Vogel-Tamman-Fulcher (VTF) equation and the Arrhenius equation provided some novel information about temperature dependence of the molecular mobility and the activation energy, with respect to the processability and the fragility of the HPEKs in comparison to the LPEK.

The local relaxation and motion of the three HPEKs below their T_g 's were characterized by the solid-state ^1H pulsed wideline NMR spectroscopy and compared to that of the linear counterpart, LPEK. From the measurements of the spin-lattice relaxation times in the rotating frame, $T_{1\rho}$'s, over the temperature range of $140 \sim 400$ K, the correlation times, τ_c 's, and the corresponding activation energies, E_a 's, were determined. They provided information on structural homogeneity/heterogeneity and a direct evaluation for the local molecular motion. HPEKs were found to be structurally heterogeneous because they had two different motional regions (i.e., the linear and the terminal/branched portion, respectively) throughout the system. In contrast, LPEK exhibited the single relaxational and motional behavior, indicating that it was structurally homogeneous. The molecular mobility of the linear portion of HPEKs was higher than that of LPEK and enhanced with increasing degree of branching in the entire range of experimental temperatures. For the terminal/branched portion of the HPEKs, the local mobility was little affected by the degree of branching especially at the temperature range from 140K to the room temperature, but became increased afterward as was for the linear portion.

References

1. C. J. Hawker and F. Chu, *Macromolecules* **29**, 4370 (1996).
2. N. G. McCrum *et al.*, *Anelastic and Dielectric Effects in Polymer Solids*, Wiley, NY, 1967.
3. F. A. Bovey and P. A. Mirau, *NMR of Polymers*, Academic Press, NY, 1996.
4. S.-Y. Kwak and D. U. Ahn, *Macromolecules* **33**, 7557 (2000).
5. S.-Y. Kwak and H. Y. Lee, *Macromolecules* **33**, 5536 (2000).