Temperature Coefficients of Unperturbed Chain Dimensions for Flexible Polymers

MASASHI OSA, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, HIDETSUGU KANDA, TAKENAO YOSHIZAKI, HIROMI YAMAKAWA, Department of Polymer Chemistry, Kyoto University, Japan — Until now, we have made a series of experimental studies of dilute solution behavior of typical flexible polymers on the basis of the helical wormlike (HW) chain model. From an analysis of experimental data obtained for the polymers including their oligomers in their respective Θ states, we have shown that atactic poly(α-methylstyrene) (a-PαMS) with the fraction of racemic diads $f_r=0.72$ tends to retain large and clearly distinguishable helical portions in dilute solution while atactic polyetyrene (a-PS) with $f_r=0.59$ does not. In this study, we determined the temperature coefficient $d \ln <R^2>_0 / d T$ of the unperturbed mean-square end-to-end distance $<R^2>_0$ with $T$ the absolute temperature from light scattering measurements for a-PS and a-PαMS. It has then been found that $d \ln <R^2>_0 / d T$ is definitely negative for a-PS but almost vanishes for a-PαMS. The results are consistent with the HW theory prediction.

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