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Thermodynamics of Random Copolymers in Solution

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Abstract : The thermodynamic behavior for solutions of poly (methyl methacrylate-ran-t-butyl methacrylate) of variable composition as compared with the corresponding homopolymers was investigated by light scattering measurements carried out for dilute solutions and vapor pressure measurements of concentrated solutions. The complex dependencies of the Flory Huggins interaction parameter on concentration and copolymer composition in solvents of different polarity (toluene and chloroform) can be understood by taking into account the ability of the polymers to rearrange in a response to changes in their molecular surrounding. A recent unified thermodynamic approach was used for modeling the experimental data, being able to describe the behavior of the different solutions by means of two adjustable parameters, one representing the effective number of solvent segments and another one accounting for the interactions between the components. Thus, it was investigated how the solvent quality changes with the composition of the copolymers through the Gibbs energy of mixing as a function of polymer concentration. The largest reduction of the Gibbs energy at a given composition of the system was observed for the best solvent. The present investigation proves that the new unified thermodynamic approach is a general concept applicable to homo- and copolymers, independent of the chain conformation or shape, molecular and chemical architecture of the components and of other dissimilarities, such as electrical charges.

Keywords : random copolymers, Flory Huggins interaction parameter, Gibbs energy of mixing, chemical architecture
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