Preface

This monograph is a follow-up material to the first FRPPP book by Prof. Gerard T. Caneba in 2010. It includes three parts that are related to one another, i.e., they are applicable to emulsion-based systems and they point to the importance of the consideration of the densification phenomenon that occurs in FRRPP systems. In Part I, additional conceptual results, simulation of dynamic thermal behavior, and conventional emulsion polymerization topics are introduced. Conceptual topics include the application of the quantitative analysis presented in the first FRRPP monograph for the occurrence of the FRRPP process to the polystyrene–styrene–ether (PS–S–Ether) and poly(methacrylic acid)–methacrylic acid–water (PMAA–MAA–Water) systems. Also, the generalization of the quantitative analysis is done to consider molecular weight effects, especially based on changes of the phase envelope to an hourglass type. Part I also includes a substantial analysis of the dynamic thermal behavior of reactive domain FRRPP spherical particles, which is a follow-up from the steady-state analysis of quantitative description of FRRPP behavior introduced in Chap. 2 of the first FRRPP monograph. It will be shown that overall composition-based parameters used for steady-state analysis of the PS–S–Ether and PMAA–MAA–Water systems apparently pertain to unstable dynamic behavior in these formulations. This actually agrees with the formation of hot spots in FRRPP systems as introduced in the two cases in Sect. 2.2 of the first FRRPP monograph. However, it has also been established from the first FRRPP monograph that FRRPP reactive sites eventually attain low mobility and possibly vitrified states, which would have to involve much lower monomer concentrations and higher polymer concentrations, due to the inherent tendency of reactive sites toward polymer chain propagation reactions. When lower monomer concentrations are introduced in the analysis of the dynamic thermal behavior of both PS–S–Ether and PMAA–MAA–Water systems, the expected stable FRRPP behavior was obtained from the simulation results.

Part II of this monograph involves implementation of the FRRPP process in emulsion and other dispersed media to produce various polymer products. Topics in implementation of the FRRPP process from pre-emulsions of monomers and the

solvent/precipitant are highlighted, predominantly based on the collaborative efforts with Dr. Yadunandan Dar of Corporate Research, National Starch and Chemical Co. including experimental evidence of the densification phenomenon for the formation of both PS and poly(methyl methacrylate) (PMMA) polymers from emulsion FRRPP. The level of densification has been found to increase as the chain length increases, going through a crossover point compared to densities predicted from polymer physics principles. Quantitatively, the crossover degree of polymerization is found to scale to the particle size and number of chains per particle to the power of 2. Also, the so-called Confinement Index (*CI*) is found to scale with the degree of polymerization (*DP*) by 0.5 and with the particle diameter by 1.5. These results are relatively new, and their polymer physics implications are not yet known.

In Part III of this monograph, additional FRRPP topics are included that pertain to more recent efforts of G. Caneba, such as oil spill control, oil dispersant systems, and caustic sludge remediation from emulsion-based FRRPP materials, hydrolysis of vinyl acetate–acrylic acid-based copolymers, and other polymer modification studies from FRRPP-based emulsions.

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